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ACETAL RESINS

Introduction

Acetal resins are the family of polymers derived primarily from formaldehyde and therefore have a repeat unit, $(\text{CH}_2-\text{O})_n$. The homopolymers are completely characterized by this repeat unit and the name polyoxymethylene is more structurally descriptive. Acetal copolymers have the oxymethylene structure occasionally interrupted by the comonomer unit. The designation aldehyde polymers generally refers to polymers of aldehydes larger than formaldehyde. The term polyacetal should be reserved for polymeric products of the reactions of aldehydes and polyhydric alcohols.

Commercialization of formaldehyde polymers did not occur until some 100 years after the first reported observation of them (1). Research during the 1920s contributed much of the background on linear formaldehyde polymers, on which today's acetal resins are based (2); in 1922 the formation of a white polymer from the sublimation of trioxane was observed (3). However, formaldehyde polymers of sufficient molecular weight to be commercially significant were not prepared until the late 1950s (4). DuPont developed this technology and the end-capping reaction that imparts stability, and launched a new plastic in the family of engineering resins. In 1959 DuPont's commercial plant went into operation, producing an acetate end-capped homopolymer called Delrin. Shortly thereafter, Celanese researchers developed an acetal resin based on the copolymerization of trioxane and cyclic ethers, such as ethylene oxide (5). In 1962 a commercial plant began producing this acetal copolymer, designated Celcon. Today both homopolymers and copolymers are commercially available. DuPont and Ticona are the largest producers (6).

The successful development of these engineering resins is better appreciated if one considers the modes of degradation that had to be overcome. These have been summarized and include unzipping from the chain ends to yield monomeric formaldehyde, oxidation and chain scission followed by depolymerization, acidic attack on the acetal chain, and thermal scission which occurs above 270°C (7). Stabilization to prevent or limit these modes of degradation was

Table 1. Properties of Formaldehyde and Trioxane

Property	Formaldehyde	Trioxane	Refs.
molecular weight	30.03	90.08	
formula	CH ₂ O	C ₃ H ₆ O ₃	
density, g/cm ³			
−20°C	0.815		8
10°C		1.17	9
normal boiling point, °C	−19	114.4	10,11
melting point, °C	−118	62	9,10
vapor pressure, Antoine constants, Pa ^a			
<i>A</i>	9.28176	10.040	12,13
<i>B</i>	959.43	1849.920	
<i>C</i>	243.392	253.270	
heat of vaporization at normal			
boiling point, kJ/mol ^b	23.3	42.0	9,10
heat of combustion, kJ/mol ^b	561	1488	9,14
critical constants ^c			
temperature, °C	137.2	331.4	
pressure, MPa ^d	6.784	5.797	
flammability in air			
lower/upper limit, vol%	7.0/73	3.6/29.0	17
ignition temperature, °C	430	413.9	17

^a $\text{Log}_{10}P = A - B/(C + T)$; where $T = ^\circ\text{C}$; To convert Pa (kPa) to mm Hg, multiply by 0.0075 (7.5).

^bTo convert J to cal, divide by 4.184.

^cEstimated by methods in refs. 15 and 16.

^dTo convert MPa to psi, multiply by 145.

essential to the commercial development of acetal resins. Throughout this discussion, the homopolymers and copolymers referred to are generally DuPont's Delrin and Ticona's Celcon, respectively.

Physical Properties of Monomer

Acetal resins are produced from either formaldehyde or its cyclic trimer, trioxane. Formaldehyde is a well-known, widely used commodity chemical. At room temperature, it is a colorless, pungent gas that is highly irritating to the mucous membranes of the eyes, nose, and throat. Formaldehyde is not commercially available in the anhydrous monomeric form, and is usually sold in aqueous solution, with methanol added as an inhibitor. Trioxane is the anhydrous trimer of formaldehyde. It is a white, crystalline solid with a pleasant etherlike aroma unlike that of formaldehyde. Trioxane is soluble in alcohols and ethers and will also dissolve in water without depolymerization to formaldehyde. Both formaldehyde and trioxane are flammable. Table 1 lists the physical properties of each.

Chemical Properties of Monomer

Formaldehyde is extremely reactive with itself and with other chemicals. It is readily soluble in water, with which it immediately reacts to form methylene glycol, $\text{CH}_2(\text{OH})_2$, and poly(oxymethylene) glycol, $\text{HO}(\text{—CH}_2\text{O—})_n\text{H}$. It can oxidize to formic acid, and in aqueous alkali, the Cannizzaro autooxidation–reduction reaction may produce both formic acid and methanol (18).

At ambient temperatures, pure formaldehyde gas polymerizes slowly, yielding a white solid; traces of water markedly increase the polymerization rate. Polymerization of the dry gas can be avoided by maintaining the temperature above 100°C .

Trioxane is chemically stable; pure material shows little decomposition at 224°C (11). Trioxane readily depolymerizes to monomeric formaldehyde in an acid environment at elevated temperatures.

Manufacture of Monomer

Formaldehyde is manufactured from methanol. In a typical process, methanol and air are passed across a catalyst bed, consisting of a silver or a metal oxide catalyst (19). The reactor product, consisting of formaldehyde, unconverted methanol, and the by-products, carbon monoxide and dioxide, methyl formate, and formic acid, is cooled and then scrubbed with water in an absorption tower. The aqueous product is then purified by distillation.

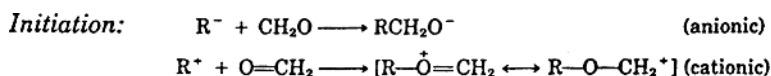
Anhydrous formaldehyde used in the manufacture of acetal homopolymer must be extremely pure. Even very low concentrations of residual formic acid or hydroxy compounds, such as water and methanol, in the monomer can result in unacceptably low molecular weight in the finished product; great care is taken to eliminate these species in monomer production. In order to obtain the necessary purity, the formaldehyde process is modified to scrub the product gases with cyclohexanol in a series of columns. The formaldehyde is absorbed and forms cyclohexyl hemiformal with the cyclohexanol (20). Residual formaldehyde and cyclohexanol carried over from the absorption columns are scrubbed out by water before the remaining gases are discharged. The cyclohexanol from the absorption columns containing the hemiformal, along with some water and methanol, is sent to a distillation column in which the water-cyclohexanol azeotrope and methanol are removed overhead at 95°C . Bottoms from this column are then sent to a pyrolysis column, where they are heated to 160°C in order to decompose the hemiformal; formaldehyde gas goes overhead. Removal of trace cyclohexanol and any remaining water is accomplished by condensation after chilling the formaldehyde gas to 1°C . The purified monomer must then be introduced to the polymerization reactor immediately.

On a laboratory-scale basis, an effective way of generating anhydrous formaldehyde is to depolymerize trioxane in the vapor phase over a supported acidic catalyst, such as phosphoric acid. Using nitrogen as a carrier gas, trioxane vapors are passed over the catalyst at 200°C . The formaldehyde product can then be further purified by passing through a series of U-tubes held at -15°C .

Acetal copolymer is commonly produced from trioxane, which is made from aqueous formaldehyde in the presence of a strong acid catalyst. Dilute formaldehyde solution is concentrated to 60% and introduced into the reactor, which contains 6 wt% sulfuric acid. The product is then distilled; a trioxane-formaldehyde-water azeotrope is taken overhead and the residue returned to the reactor. Extraction of the distillate with solvents, such as benzene or methylene chloride, separates the trioxane from the water and most of the formaldehyde. The dilute formaldehyde solution is sent to recovery; separation of the trioxane from the solvent is accomplished by distillation. If necessary, the trioxane can be further purified by another distillation and treatment with molten sodium (21).

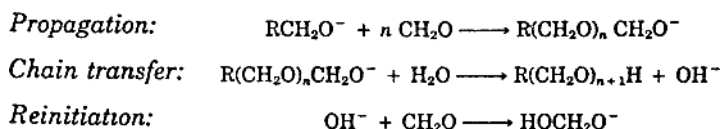
Polymerization

Mechanism. Formaldehyde is very reactive and readily polymerizes with ionic initiation. Either anionic or cationic materials such as amines, phosphines, onium salts, sulfur compounds, mineral acids, halogens, and Lewis acids, etc (22, 23), will initiate the polymerization reaction, as illustrated below:



Ionizing radiation also initiates polymerization (24). However, this method has not been used commercially.

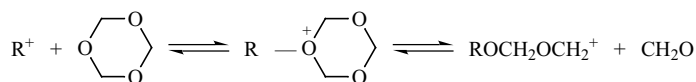
In the case of an anionic initiator, the reaction then proceeds as follows:



The reaction propagates by addition of the monomer to the double bond. The polymer molecule continues to grow until it encounters an impurity capable of undergoing chain transfer. Reaction of the growing chain with the impurity terminates the chain and releases an ionic species, which then initiates another polymer chain. Because of chain transfer, the amounts of impurities present in the monomer must be rigorously controlled in order to obtain products of the desired molecular weight. A detailed review of reaction mechanisms and kinetics has been published (25). In commercial practice, it is believed that anionic initiators are used to produce acetal homopolymers; cationic polymerization is more complex because of the nature of the cation.

Trioxane is also readily polymerized, but a cationic initiator is employed. The polymerization of trioxane also differs from that of formaldehyde in that an induction period is observed during which, although a reaction is occurring, no visible polymer is formed. One explanation is that the cationic catalyst associates with an oxygen atom of the trioxane ring and the complex then undergoes ring opening. The cationic oligomer thus formed reversibly depolymerizes releasing

formaldehyde. An equilibrium concentration is built up, which then remains constant during the polymerization (26,27):



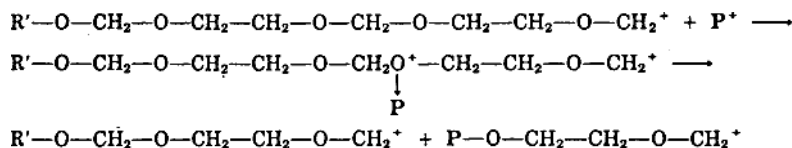
Propagation occurs by the ring opening of the activated species and the addition of trioxane monomer. Chain transfer with impurities can occur. Recent investigations have shown that in the boron trifluoride dibutyl etherate-initiated trioxane polymerization, a cocatalyst such as water is necessary for reaction (28). In this scheme, the BF_3 dibutyl etherate is hydrolyzed to form a protonic acid which then becomes the initiating species:



In the study, no polymer was formed if water was completely absent from the reaction system.

Commercial acetal copolymers are typically produced by the cationic polymerization of trioxane and 0.1 to 15 mol% of a cyclic ether, such as ethylene oxide or 1,3-dioxolane. The presence of the comonomer usually extends the induction period observed for neat trioxane. In the case of the polymerization of trioxane with ethylene oxide, it has been shown that all the ethylene oxide reacts before any trioxane is polymerized (29,30). During this period, the comonomer reacts with formaldehyde generated from the opening of the trioxane ring to form cyclic ethers, predominantly 1,3-dioxolane and 1,3,5-trioxepane. These increase in concentration until the ethylene oxide is consumed and the trioxane polymerization begins. A detailed reaction mechanism for the copolymerization of trioxane and ethylene oxide initiated with BF_3 dibutyl etherate has been proposed (31).

The preferential consumption of the comonomer, ethylene oxide, in the very early stages of the polymerization reaction implies that the comonomer would appear as blocks in the final polymer. This, however, is not the case and the final distribution is found to be arbitrary. The growing polymer chain undergoes a transacetalization reaction and the result is the redistribution of single comonomer units randomly along the chain (32). In transacetalization, the growing end of a polymer chain (**P**) attacks the acetal linkage of a portion of a completed chain. As a result of this attack, one chain is terminated and a new growing chain is formed by the following scheme:



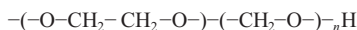
This reaction is thought to occur many times during the course of polymerization and is responsible for the narrow molecular-weight distribution ($\bar{M}_w/\bar{M}_n = 2$) found in acetal polymers formed by cationic catalysis.

Stabilization. High molecular-weight polyoxymethylenes readily depolymerize into monomeric formaldehyde when subjected to increased temperatures. This unzipping begins at the chain ends (33); the activation energy is 109 kJ/mol (26 kcal/mol) at acetal polymer melt temperatures (34). Polymers not end-capped degrade at the rate of 0.4 to 0.8%/min at 222°C. This rate can be reduced to 0.1%/min by end-group stabilization or by comonomer incorporation. For this reason, commercial acetal resin must be stabilized in order for it to be meltprocessed by conventional plastic-processing techniques.

The end-capping reactions commonly used for the prevention of the unzipping mechanisms are reactions of the hemiacetal, ie, $\text{—O—CH}_2\text{—OH}$, chain ends which normally result from the polymerization. At least one commercial end-capping procedure uses esterification to stabilize these chain ends by producing stable acetate end groups, $\text{—O—CH}_2\text{—OCOCH}_3$. To accomplish this, the polymer is allowed to react with acetic anhydride, either in solution or heterogeneously in the presence of a catalyst such as sodium acetate (35). There is a small amount of acetic acid by-product in this reaction. Care must be taken to exclude moisture during this process to prevent the generation of excess acetic acid, which attacks the acetal chain. Also, thorough washing is necessary to remove all traces of anhydride or acid which can promote degradation during subsequent processing.

Alkylation is a second route to the production of stable ends on the acetal polymer chain; this reaction creates ether end groups, $\text{—O—CH}_2\text{—OR}$ (36). Reaction with isocyanates provides a third route to stable end groups (37). If diisocyanates are used, chain extension can result and molecular weights can be readily increased.

All of these end-group reactions can be performed on homopolymers or copolymers. However, copolymers can also be stabilized by other means. For example, the carbon-carbon bonds in copolymers with ethylene oxide or 1,3-dioxolane can appear at the chain ends. A random copolymer with ethylene oxide produces chains with an occasional $(\text{O—CH}_2\text{—CH}_2\text{—O})$ group distributed in its backbone. From that group to the chain end, the molecule appears as follows:



Techniques have been devised to remove the unstable hemiacetal chain ends until the stable carbon-carbon link is reached. This can be achieved by exposing the unstable copolymer to heat, ie, melting the raw copolymer and allowing unzipping to occur with the release of formaldehyde. This unzipping proceeds until the —C—C— bond is reached; the comonomer unit (in this case, ethylene oxide) becomes the end of the chain. Compounding mill rolls (38) and vented extruders (39) have been described as means to carry out this process. During this melt process, stabilization additives should be used to prevent other modes of degradation.

Removal of unstable ends from acetal copolymers can be achieved hydrolytically, by taking advantage of the fact that the hemiacetal unit degrades in the presence of alkaline media; this hydrolysis can be achieved either in solution (40) or heterogeneously (41). This process produces copolymers with —C—C— bonds at the chain ends, just as in the case of the melt process.

Acetal resins are subject to degradation other than unzipping of unstable end groups. Hemiacetal structures are vulnerable to attack by oxygen and peroxy radicals. Commercial polymers contain antioxidants to prevent this mode of degradation. Hindered phenols and aromatic amines are typical of the compounds that successfully prevent chain attack by oxidation (42).

Commercial acetal resins also contain compounds that act as scavengers for any formaldehyde released under abusive processing conditions. Soluble polyamides, amidines, and epoxides are a few examples of such additives. Released formaldehyde must be consumed because it readily oxidizes to formic acid, which promotes acidic degradation even if present in only small amounts at polymer processing temperatures.

Because of the development of these techniques, stable acetal resins have been commercially available since 1960. In general, acetal copolymers have superior thermal stability. This is so because, whereas an occasional chain scission (eg, via oxidative degradation) will completely destroy the homopolymer molecule via chain unzipping, the copolymer will unzip only to the nearest comonomer unit.

Manufacture. Many processes have been proposed for the polymerization of formaldehyde and trioxane, including vapor-phase, bulk, solution, and suspension systems. Although the actual manufacturing processes for acetal resins have never been revealed, the following process descriptions are believed to be representative of those used for homopolymer and copolymer.

In general, monomer is purified on site and fed to a polymerization reactor; the resulting polymer is sent through another reactor, in which end-group stabilization takes place by acetylation for the homopolymer, or hydrolysis for the copolymer. The resin is then washed and dried before a final compounding operation, in which thermal stabilizers, formaldehyde scavengers, and other additives are incorporated in the product.

In the homopolymer manufacturing process, anhydrous formaldehyde is fed into a reactor containing an agitated inert hydrocarbon solvent, such as cyclohexane (43,44). Small amounts of an initiator, such as tri-*n*-butylamine, and a chain-transfer agent for molecular-weight control are also added to the solvent. The kinetics of the reaction system is complicated; formaldehyde gas dissolves in the solvent and then diffuses to an active site on or within the polymer particle. A reaction temperature of approximately 40°C is maintained by evaporation of the solvent. The finely divided polymer is separated by filtration from the reaction medium, and the solvent is returned to the reactor. The polymer is slurried with acetic anhydride and introduced to a series of stirred-tank reactors with sodium acetate catalyst. Acetylation of the polymer end groups is carried out in these reactors at a temperature of 140°C. The polymer is then separated by filtration and subjected to a series of washes, first with acetone, and then with water, to remove the anhydride, catalyst, and any other impurity. The polymer is dried in a rotary steam-tube dryer, prior to the finishing operations of stabilizer incorporation, extrusion, and packaging.

Copolymer production begins with feeding pure molten trioxane to the polymerization reactor along with the comonomer, an initiator, such as boron trifluoride dibutyl etherate, and a chain-transfer agent, if required. Polymerization occurs in bulk; the rapid solidification of the polymer requires a reactor that

provides a shearing action to reduce particle size and permit adequate temperature control (45). Alternatively, the reaction mass is spread in a thin film on a moving belt, thus providing good heat removal (46). After discharge from the reactor, particle size is reduced, if necessary, and the polymer prepared for stabilization. Normally, this consists of washing with an alkaline medium to remove formaldehyde, trioxane and other impurities. Water and an alkaline catalyst, such as ammonia, are added to the polymer, which is then hydrolyzed at 100°C. Material discharged from hydrolysis is filtered from the hydrolysis medium and dried prior to stabilizer incorporation, extrusion and product packaging.

Mitsubishi Gas Chemical Company indicate another hydrolysis procedure. The polymerization reactor product is combined with heat stabilizers and a tertiary phosphine catalyst-deactivating agent, and fed directly to a thermal hydrolysis reactor. Hydrolysis and stabilization take place under vacuum in the melt, with a residence time of no more than an hour. The hydrolysis reactor contains two stirring shafts on which several mixing paddles are mounted to provide constant surface renewal of the polymer melt (39). Product from this reactor is fed to the finishing operations without further processing.

A recent patent describes a process with short induction time, which is tolerant towards impurities and traces of water in formaldehyde. Also the catalyst, containing metals and a cyclooctadine, is light and recyclable (47).

Polymer Properties

Acetal resins are crystalline polymers; the reported crystallinity is between 60 and 77%, measured either by x ray or from density data. The lower values are typical of copolymer materials. Commercially available products have number-average molecular weights ($\bar{M}_n$) in the range, 20,000–90,000. Typical weight-average molecular weights ($\bar{M}_w$) can be calculated from dilute solution viscosities using the relationship:

$$[\eta] = K\bar{M}_w^\alpha \quad (1)$$

The values for K and α have been determined to be 1.33×10^{-4} and 0.81, respectively, for inherent viscosity values of acetal copolymers measured at concentrations of 0.1 g/100 mL in 98% *p*-chlorophenol –2% α -pinene at 60°C (48). In this determination, the $\bar{M}_w$ values were obtained by light-scattering techniques. The same workers measured $\bar{M}_n$ by osmometry and found the molecular-weight distribution ($\bar{M}_w/\bar{M}_n$) to be about two. This agrees well with an estimate of this ratio obtained indirectly from the effect of chain-transfer agent quantitatively incorporated during the polymerization. A useful compilation of references for the determination of molecular weights of acetal resins can be found in ref. 49.

A convenient measure of $\bar{M}_w$ can be provided by the melt index (MI), that is, melt viscosity determination using ASTM D 1238, condition E, at 190°C. The relationship between MI and $\bar{M}_w$ is given by

$$MI = 1.30 \times 10^{18} \bar{M}_w^{-3.55} \quad (2)$$

Table 2. Solvents for Acetal Homopolymer

Solvent	Gel temp, ^a °C	Soln temp, ^b °C
<i>m</i> -chlorophenol	55	89
phenol	58	109
<i>p</i> -chlorophenol	60	98
3,4-xyleneol	88	128
aniline	102	130
γ -butyrolactone	112	134
<i>N,N</i> -dimethylformamide	115	135
pentachloroethane	117	140
ethylene carbonate	117	145
benzyl alcohol	119	132
styrene oxide	125	146
formamide	130	150
nitrobenzene	134	148
cyclohexanol	140	150
propionic anhydride	144	155

^aTemperature below which precipitation occurs.

^bLowest temperature at which a 1% solution can be formed.

The high crystallinity of acetal resins contributes to their lack of solubility in most solvents. Table 2. provides a list of solvents, the lowest temperatures at which a 1% solution of homopolymer is formed (solution temperature), and the lowest temperature at which a solution can be kept without precipitation (gel temperature). Phenolic compounds are the best solvents for acetal polymers. The solubility behavior of commercially available copolymers is quite similar to that observed for homopolymers, because the comonomer content is relatively low.

Mechanical Properties. Mechanical properties of acetal resins are given in Table 3 (50,51). The typical values reported for homopolymers are representative of Delrin and those for copolymer are representative of Celcon. These resins are known for their good balance of strength, stiffness, and toughness. In addition, their lubricity and low coefficient of friction against acetal, metals, and other plastic resins make them desirable in applications where contact between parts is needed.

In addition to these short-term performance characteristics, acetal resins resist dimensional changes that occur under continuous stress after initial deformation. This phenomenon, called creep or cold flow, is an important consideration in the design of parts subjected to a wide range of use conditions over the life of the part. Acetal resins have low and predictable flexural, compressive, and tensile creep over a wide range of conditions.

Another excellent characteristic of these polymers is their fatigue resistance, that is, their ability to survive repeated stress loads without failure. A high degree of fatigue resistance is retained even in the presence of water and some solvents. This behavior can be accurately measured and is valuable in the design of parts which undergo cyclic stresses.

Table 3. Mechanical Properties of Acetal Resin

Property	ASTM test method	Homopolymer	Copolymer
tensile strength, yield, MPa ^a , 23°C	D 638	68.9	60.6
elongation, break, %	D 638	23–75	40–75
tensile modulus, MPa ^a , 23°C	D 638	3100	2825
flexural strength, MPa ^a , 23°C	D 790	97.1	89.6
flexural modulus, MPa ^a , 23°C	D 790	2830	2584
compressive stress, MPa ^a , 23°C	D 695		
1% deflection		35.8	31
10% deflection		124	110
shear strength, MPa ^a , 23°C	D 732	65	53
Izod impact strength,			
notched, 3.175 mm, J/m ^b ,	D 256		
23°C		69–122	53–80
–40°C		53–95	43–64
water absorption, %	D 570		
24-h immersion		0.25	0.22
equilibrium, 50% rh, 23°C		0.22	0.16
equilibrium, immersion		0.9	0.80
Rockwell hardness, M scale	D 785	94	80
coefficient of friction, dynamic	D 1894		
steel		0.1–0.3	0.15
aluminum, brass			0.15
acetal resin			0.35
specific gravity	D 792	1.42	1.41

^aTo convert MPa to psi, multiply by 145.

^bTo convert J/m to (ft·lb/in.), divide by 53.39.

Table 4. Thermal Characteristics of Acetal Resins

Property	ASTM test method	Homopolymer	Copolymer
heat deflection temperature, °C	D 648		
at 1.82 MPa		136	110
at 0.45 MPa		172	158
coefficient of linear thermal			
expansion × 10 ⁶ per °C –40 to 30°C	D 696	75	84
thermal conductivity, W/(m·K)		0.2307	0.2307
specific heat, J/(kg·K)		1465	1465
melting point, °C		175	165
flow temperature, °C	D 569	184	174

Thermal Properties. Thermal properties of acetal resins are given in Table 4 (50,51). The crystalline melting point of the homopolymer is about 10°C higher than the copolymer, and differences of this magnitude are also noted in the flow temperature and heat deflection temperature. The latter property at low stress, 0.45 MPa (65 psi), is very close to the crystalline melting point, indicating that intermittent exposure to high temperatures can be tolerated without deformation.

A further indication of the thermal stability of acetal resins is demonstrated by the retention of mechanical properties upon continuous exposure to air at high temperatures. For example, homopolymer has been shown to retain a tensile strength in excess of 55 MPa (8000 psi) for approximately 5 yr at 60°C, or 1.5 to 2 yr at 82°C. Similar stability is observed in copolymer aging studies.

Chemical Resistance. Acetal resins have excellent resistance to most chemicals, including a wide range of organic solvents, such as those encountered in automotive applications. However, strong mineral acids attack acetals, causing rapid depolymerization and degradation. Contact with acids should generally be avoided. However, a new process to produce acetal resins with improved acid resistance has been reported (52).

The acetal structure is basically stable to alkaline environments. However, ester end groups can undergo hydrolysis in the presence of a base, and chain unzipping follows. Thus, acetylated homopolymer is not recommended in strongly alkaline environments.

Acceptance of acetal resins in plumbing applications is dependent, in part, on their property retention after long-term exposure to hot water. Acetal copolymer properties remain virtually unchanged after immersion in water at 82°C for 1 yr.

A summary of the behavior of acetal resins in various chemicals is given in Table 5 (50,51).

Electrical Properties. The electrical properties summarized in Table 6 (49,50) are fairly typical of thermoplastic resins in general. However, they are important in combination with the other attributes of acetal resins. One significant observation is the relative constancy of dielectric constant and low losses in the useful operating range of -40 to 50°C.

Acetal polymers are rated HB using the Underwriter Laboratories (UL) 94 test; ie, these resins will burn if ignited. UL also assigns a 105°C continuous-use temperature for acetals (electrical properties), and a 75 to 100°C continuous-use temperature (mechanical properties with and without impact), depending on the type and grade.

Processing of Polymers

Injection Molding. Parts from acetal resins are readily fabricated using conventional injection molding techniques, ie, both plunger and reciprocating screw-type machines. The ease of flow of these resins permits the use of multi-cavity molds, and even thin-walled sections can be completely filled. Temperatures should be kept between 182 and 216°C, and never permitted to exceed 249°C, where degradation is probable. Mold temperatures from 66 to 121°C with pressures of 100 to 140 MPa (14,500 to 20,300 psi) are adequate to fill even the most intricate parts. Regrind can be used at moderate levels without adverse effect on physical properties. Cycle times are dependent on part size, thickness, molding conditions, and flow grade of the resin used, but can generally be kept between 20 and 40 s.

Caution must be exercised when changing from another material to an acetal resin in injection molding machines. Direct transfer to acetals from a resin

Table 5. Chemical Resistance of Acetal Resins

Material	Test conditions		% change ^a			
			Tensile strength		Weight	
	Duration, mo	Temp, °C	Homopolymer	Copolymer	Homopolymer	Copolymer
<i>Inorganics</i>						
ammonium hydroxide, 10%	3	23	U		U	
	6	23		NC		0.88
hydrochloric acid, 10%	3	23	U		U	
	6	23		U		U
sodium hydroxide, 10%	12	23	U	-2	U	0.73
<i>Organics</i>						
acetic acid, 5%	12	23	NC	0.6	0.8	1.13
acetone, 100%	12	23	-5	-17	4.9	3.7
benzene, 100%	9	60	-11		4	
	6	49		-17		3.9
carbon tetrachloride, 100%	12	23	-3	2	1.3	1.4
ethyl acetate, 100%	12	23	-7	-17	2.7	4.2
ethyl alcohol, 100% (95%)	12	23	-5	(-6)	2.2	(2.2)
<i>Others</i>						
brake fluid, Super 9	10	70	-6		1.6	
	12	23		3		0.53
motor oil, 10W 30	12	70(23)	3	(5)	-0.2	(0.04)
Igepal, 50%	12	23	2		-0.2	
	6	70(82)	U	(NC)	U	(1.62)
unleaded gasoline	8	23(40)		-2(-2)		0.33(0.69)

^aU = unsatisfactory; NC = no change.

Table 6. Electrical Properties of Acetal Resins

Property	ASTM test method	Homopolymer	Copolymer
dielectric constant, 10^2 – 10^6 Hz	D 150	3.7	3.7
dissipation factor,	D 150		
10^2 Hz			0.0010
10^3 Hz			0.0010
10^4 Hz			0.0015
10^6 Hz		0.0048	0.006
dielectric strength, kV/mm,			
short time, 2.29-mm sheet	D 149	20	20
surface resistivity, ohm	D 257	1×10^{15}	1.3×10^{16}
volume resistivity, ohm. cm	D 257	1×10^{15}	1×10^{14}

such as nylon, which melts at temperatures above the acetal processing temperature range, from a resin such as cellulose acetate, which has poor heat stability at acetal processing temperatures, or from a resin such as poly(vinyl chloride), which can generate acids on processing, should be avoided. In these instances, the old material should be thoroughly purged from the cylinder with polyethylene or polystyrene, and the cylinder temperatures reset and stabilized at 185–193°C before the acetal resin is fed into the machine. This precaution applies not only to injection molding, but also to the other common processing techniques. Other information on injection molding can be found in refs. 53 and 54.

Other Processing Techniques. Acetal resins can be fabricated into rod, tubing, sheet, and slab stock by extrusion (55). Resin manufacturers recommend the use of extruders with barrel length–diameter ratios of at least 20. These ratios give the material adequate residence time to reach the processing temperature and achieve a uniform melt. To prevent surging, a metering-type screw is recommended with a uniform square pitch, followed by a gradual compression section. As a rule of thumb, 20–25% of the total screw length should be taken by the metering zone, a similar proportion by the feed zone, and the balance in a constant-taper transition zone. Normally, barrel and die extrusion temperatures between 175 and 180°C are required. The zone nearest the hopper is kept at a lower temperature to prevent premature melting of the pellets, which can plug the throat of the machine.

The rod, tubing, sheet, and slab stock of acetal resins can be further fabricated into finished parts using conventional metalworking equipment. The techniques are useful for preparing prototypes, for manufacture of precision parts, or for the economical production of a small number of parts.

Conventional grades of acetal resin do not have the proper melt characteristics to enable processing by extrusion blow-molding techniques. A ter-polymer grade, Celcon U10, has melt-viscosity behavior which allows it to be fabricated into containers in rapid cycles by extrusion blow-molding equipment. This same grade is used in injection blow-molding fabrication processes as well (56).

Although it is less commonly used for crystalline thermoplastics than for amorphous resins, the foam-molding process can be adapted to acetal resins. Structural foam consists of a rigid, closed cellular core surrounded by a solid skin;

Table 7. General Purpose Acetal Resins

Grade designations		General description	Recommended uses
Celcon	Delrin		
M25	100	high viscosity	extrusion, rod, sheet, slab, etc
M90	500	low to medium viscosity	general purpose, injection molding
M270	900	lowest viscosity	fast cycling injection molding
U10		high melt strength	blow molding, extrusion

the foam is strong and stiff. Foam usually offers a 20–40% density reduction over the solid with little sacrifice in mechanical properties and thus offers potential cost savings. Foaming can be achieved by the introduction of an inert gas into the melt which expands in the mold. Alternatively, a chemical foaming agent can be added to the resin prior to processing; it decomposes at the resin’s processing temperature and releases an inert gas. Foam-molding processing is more suitable for fabrication of large parts.

Another processing technique available to acetal resin users is rotational molding. This is primarily utilized for limited-volume runs of extremely large, complex shapes in hollow or partially hollow forms, where part size and volume usually would not justify manufacture by injection molding.

Resin Grades

The general-purpose grades of acetal resins are characterized by differences in melt flow properties as is shown in Table 7 (50–54). These grades are available with or without lubricants and in a wide variety of colors. In addition to the general-purpose resins, specialty grades have also emerged, such as Celcon GC-25A, a glass fiber-reinforced copolymer which provides higher strength and stiffness, and the chemical resistance of acetals. The significance of this development is that the glass fibers are chemically coupled with the acetal through the sizing agent. Without this feature, the high tensile strength, 7.7 MPa (1117 psi), and flexural modulus, 510 MPa (73,950 psi), of this specialty resin could not be achieved.

Both the homopolymer and copolymer are also available in grades specially formulated to reduce wear and are, therefore, particularly suitable for bearing applications. These grades are Delrin AF, which contains fibers of Teflon, and Celcon LW90-SC, a silicone concentrate which is mixed with unmodified Celcon to suit the requirements of the specific applications.

Developmental grades of mineral-filled resins (to minimize warpage in large parts), plateable acetals (suitable for decorative and functional automotive applications), antistatic acetals, and impact-modified variants are being introduced to fill specific use requirements. The most recent specialty acetal introduced is a super-tough grade, Delrin 100ST, which boasts a notched-Izod impact strength of 900 J/m (16.9 (ft. lbf)/in.) at 23°C. This is seven times greater than the general-purpose resin, and the specialty polymer retains a modulus of 1380 MPa (200,000

Table 8. Consumption of Polyacetal Resins by End Use, % of Regional Total, 2004^a

Sector	United States	Western Europe	Japan	China
automotive	25	40	50	10
plumbing	15	5	10	—
industrial	25	12	10	10
consumer	20	10	—	30
electrical	5	18	25	30
appliances	5	—	—	—
other	5	15	5	20

^aRef. 6.

psi). Retention of good solvent resistance is also claimed by DuPont. These new developments indicate the high level of research activity in the field and a healthy business outlook in the future.

New Delrin resins reported by DuPont in 2007 include: three new homopolymers with extremely low volatile release (Delrin 100PE, 500PE, and 527 UVE); Delrin 100T1 is a new acetal with 1.5% Teflon to give a resin with low wear and low coefficient of friction against a variety of counter surfaces combined with high impact strength; Delrin 500MP with Teflon and an advanced lubricant gives good wear performance and processing flow; Delrin 100T is a toughened grade of high viscosity acetal homopolymer with optimized toughness and good flow; Delrin 327 UV has a combination of enhanced weathering, such as for interior uv resistance and molding productivity, and processing ease.

Economic Aspects

Polyacetal resins are important engineering resins. They have replaced metals and other plastics in many applications.

Production of polyacetal resins is a highly concentrated business. There are only a few producers. In 2005, Ticona (Germany) and DuPont (U.S.) were the largest producers. They were followed by Mitsubishi Gas Chemical Company of Japan. Ticona accounts for 41% of world capacity; DuPont, 25%; and Mitsubishi, 15%.

Consumption of polyacetal resins in the U.S., Western Europe, and Asia was 668×10^3 metric tons in 2004. Consumption in the U.S. and Western Europe is expected to grow at an average rate of 3–4% per year. Japanese consumption is forecast as flat.

Table 8 gives the consumption of polyacetal resins by end use.

Specifications and Standards

Acetal resins have temperature index ratings assigned by Underwriters Laboratories (UL), which indicates the expected continuous-use performance in terms of mechanical and electrical properties. UL also measures and publishes specific

electrical properties and flammability characteristics. Both homopolymers and copolymers are rated 94HB in the flammability test.

The Food and Drug Administration regulates acetals intended for repeated contact with food. These regulations are the result of extensive extraction tests in food-simulating solvents and animal-feeding studies. The FDA regulation for homopolymer is 21 CFR 177.2480, and that for copolymer is 21 CFR 177.2470. Similarly, the United States Department of Agriculture regulates the use of acetal polymers in contact with meat and poultry.

The National Sanitation Foundation publishes a list of acetal resins which it finds acceptable for use in potable water applications (nonpressure pipes, fittings, and appurtenances). The Plastic Pipe Institute of the Society of the Plastics Industry has rated acetal resins as fittings, with a recommended hydrostatic design stress (RHDS) of 6.89 MPa (1000 psi) at 23°C.

In addition to these important standards, acetals are covered by several local plumbing codes, by ASTM D 2133 and by Federal Specification LP-392-a.

Acetal resins are normally shipped in 25 kg multi-wall bags and 500 kg Gaylords (rigid containers). Special packaging, such as drums, is also available at an extra charge. Manufacturers also supply custom colors, usually in minimum orders of 1000 kg. Color concentrates, available in 2.5 kg and 25 kg bags, allow fabricators to color compound in their own molding or extrusion processes by letting down with the natural resin. The advantage of this technique is the reduced stock of standard colors.

Health and Safety Factors

If acetal resins are processed at temperatures substantially above their melting points or otherwise abusively treated, small amounts of monomeric formaldehyde may be released. Continued exposure to formaldehyde over a prolonged period of time is harmful. It is important, therefore, to locate processing operations in well-ventilated areas.

The human nose is sensitive to concentrations of 0.1 to 0.5 ppm of formaldehyde. As little as 3 to 5 ppm can cause lacrimation, coughing, nasal irritation, and possibly nausea. It is unlikely that a person would remain in areas at these concentrations for more than a few minutes. The current threshold limit value (TLV) for formaldehyde is 1 ppm.

Under proper recommended processing conditions, formaldehyde concentrations around the equipment typically measure about 0.1 ppm. Several commercially available sensing devices detect formaldehyde concentrations as low as 0.1 ppm in air. These instruments monitor air quality in the processing area. One device marketed by CEA Instruments, Inc. in Westwood, N.J., provides a recorded readout which compares the color change of a reagent against a standard as an air sample is passed through. A second instrument manufactured by MDA Scientific, Inc. in Glenview, Ill., uses an electrochemical fuel cell measurement and is a compact hand-held unit. Finally, the 3M Formaldehyde Monitor 3750 is a badge-style detector which can be worn by a machine operator to monitor the exposure to formaldehyde over a specific time period. At the end of that period, the badge is sealed and submitted for analysis.

Table 9. Typical Acetal Resin Use

Application area	Use	Attributes needed for use
transportation	fuel pump housing cooling fan parts fuel caps window regulators	solvent resistance dimensional stability, heat resistance solvent resistance strength, flexibility
plumbing and hardware	fittings and valves water softener components ballcock valves filter housings	hot-water resistance, fatigue resistance stiffness, dimensional stability, chemical resistance wear resistance, low friction dimensional stability
machinery	conveyor parts gears, bearings air-flow valves	wear resistance, low friction fatigue and wear resistance creep and chemical resistance dimensional stability
appliances	can opener drive train food mixer parts electric kettle body sprayer body	wear resistance, toughness wear and creep resistance, low friction hot-water resistance, heat resistance chemical resistance, creep resistance
consumer goods	disposable lighter body water sprinkler parts	toughness, chemical resistance wear resistance, low friction

Trioxane has a low degree of toxicity; however, it can decompose to formaldehyde under certain conditions and present the same hazards already mentioned. Ingestion of trioxane can result in the release of formaldehyde and irritation of the gastrointestinal tract. Trioxane is irritating to the eyes; repeated and prolonged skin contact may result in skin irritation as well. Certain individuals may become sensitized to trioxane. Delrin PEh OSHA is 15 mg/m³ δ -h TWA for total dust, 5 mg/m³ δ -h TWA for respiratee dust (57).

Uses

Acetal resins have proved successful in applications traditionally confined to metals because of their predictable mechanical properties, low friction and wear resistance, and long-term characteristics, such as chemical and hot-water resistance. In addition, the ease of molding, adherence to close tolerances, and dimensional stability contribute to replacement of metals in many areas. Often the use of engineering resins such as acetals results in reduced fabrication costs through elimination of costly finishing steps associated with metal-parts fabrication. Not to be overlooked are the appealing aesthetics of acetals: choice of color, glossy finish, and pleasant tactility, etc. A polymeric acetal resin used in lithographic printing has been reported (58).

Examples of more specific applications in each market area are given in Table 9 along with the specific attributes of the resins which contribute to their selection.

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ACETYLENIC POLYMERS

Introduction

The term “acetylenic polymers” used here does not only refer to “polyacetylenes” but also to all the polymers that are synthesized from acetylenic monomers containing single or multiple carbon–carbon triple bonds. In the past decades, research on polymer chemistry of carbon–carbon acetylenic triple bonds has grown enormously. From the viewpoint of bond structure, the step polymerization of the difunctional monomer and the chain polymerization of the vinyl monomer sketched in Figure 1 are single- and double-bond reactions, respectively. When the single and double bonds of the monomeric species are opened and reacted, new species with higher molecular weights are formed. The final destinies of these chemical reactions are the formation of polymeric products, whose monomer repeat units are connected by single bonds. Since the single bonds are electronically saturated, these polymers are generally electronically inactive. As a result, traditional polymers are commonly used as commodity materials, such as plastics, fibers, rubbers, and elastomers (1).

When a triple bond is opened, however, it yields a double bond. Multiple linkages of these double-bonded active species can furnish a polyene or polyarylene. The triple bonds can also be coupled in the unbroken or “intact” form, giving a polyyne with multiple triple-bonds. Thus, polymerizations of triple-bonded monomers can produce polymers with repeat units knitted together by electronically unsaturated double and triple bonds, as diagrammatically delineated in Figure 1. Such polymers are expected to be electronically active. The triple-bonded molecules, however, had been much less explored as potential monomers in the formative years of polymer science, partially due to the fewer varieties of acetylenic compounds available in the early time and partially due to the higher tendency for acetylenic polymers to become insoluble, in comparison to the vast varieties of the difunctional and vinyl monomers and the excellent processability of their polymers. For example, Natta and co-workers polymerized acetylene in 1958 but the obtained polyacetylene (PA) powder was completely intractable (2).

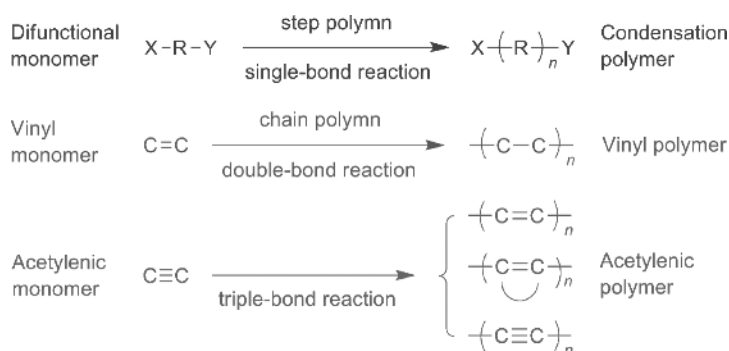


Fig. 1. Examples of polymerization reactions.

With the rapid advances in acetylene chemistry in the last century, many more acetylenic compounds have become synthetically accessible or even commercially available (3–5). The pioneer work on the discovery of the metallic conductivity of the doped PA films by Shirakawa and co-workers in the late 1970s verified the long anticipated electronic activity of π -conjugated polymers and lent a strong impetus to research on acetylenic polymers (6–9).

As can be seen from Figure 1, the backbones of the acetylenic polymers are π -conjugated due to the electronic communications between their electronically unsaturated repeat units. This unique electronic structure has the potential to endow the polymers with novel properties that are very difficult, if not impossible, to access by their congeners of condensation and vinyl polymers with electronic saturation. The prerequisite to realize this attractive potential is to establish versatile processes for synthesizing the polymers. This has motivated many research groups all over the world to work on the exploration of acetylene-based polymerization reactions (10–41). As a result, a large variety of acetylenic polymerization reactions have been developed, especially after the ground-breaking work of Shirakawa and co-workers (6).

For example, effective polymerization processes of terminal and internal alkynes with one triple-bond (monoynes) and two triple-bonds (diynes) based on the reaction mechanisms of metathesis, insertion, cyclization, coupling, and addition have been well established, affording acetylenic polymers with linear and cyclic molecular structures such as PA, polydiacetylene (PDA), poly(aryleneethynylene) (PAE), and poly(1,2,3-triazole) (PTA) as well as their substituted derivatives (Figure 2). In the past decades, polymer scientists have been working on the expansion of their research territories from linear system to nonlinear, especially hyperbranched, system (42–48). Along this line, a dozen of research groups have embarked on the research programs on the development of effective polymerization processes for the syntheses of hyperbranched macromolecules from acetylenic monomers. As exemplified in Figure 3, cyclotrimerizations of A_2 -type diynes, cycloadditions of AB_2 -type carbonyldiynes, and homocouplings of A_3 -type triynes have been found useful for the syntheses of hyperbranched polyphenylene (*hb*-PP), polydiyne (*hb*-PDY), and their derivatives. Cross-couplings of $A_2 + B_3$ monomers such as diynes and trihalides have been utilized to synthesize hyperbranched polyyne (*hb*-PY) and derivatives, whereas 1,3-dipolar cycloadditions or “click” reactions of $A_3 + B_2$ monomers such as triynes and diazides have been developed into versatile polymerization techniques for the preparations of hyperbranched PTAs.

In the linear and nonlinear polymerization reactions discussed above, the acetylenic triple bonds are transformed into polyene chains in PAs, ene-yne chains in PDAs, benzene rings in PPs, triazole rings in PTAs, diyne rods in PDYs, etc. The structural issues unique to the linear and hyperbranched acetylenic polymers include steric conformation (e.g., *cis* and *trans* polyene chains) and topological pattern (e.g., 1,2,4- or 1,3,5-trisubstituted benzene and 1,4- or 1,5-disubstituted triazole rings), which determine the stereo- and regioregularities and the degrees of branching (DBs) of the polymers. Much work has been done to understand the structural issues and various approaches have been taken to control or modulate the macromolecular structures, such as the design of molecular structures of alkyne monomers, the search for stereospecific or regioselective

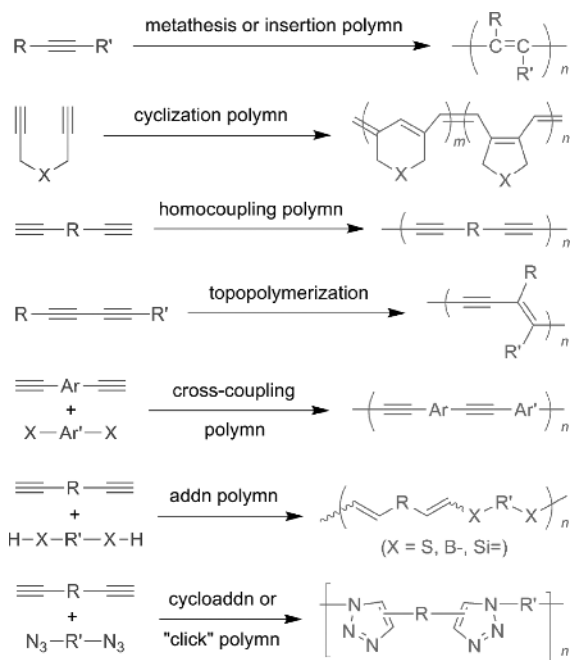


Fig. 2. Examples of linear alkyne polymerizations.

catalyst systems, and the optimization of polymerization conditions or parameters. An appreciable portion of these structural investigations has been carried out in combination with the studies of materials properties of the polymers, in an effort to collect information on and gain insights into the structure–property relationships involved in the acetylenic polymer systems (Figure 4) (10–41).

As the traditional driving force for acetylenic polymer research was to generate π -conjugated polymers with electronic activity, much of the early work had been devoted to the development of highly conductive materials. As the ene, yne, enyne, diyne, phenyl, and triazole units in the acetylenic polymers are rich in π -electrons, the electronic communications between these units governed by the effective conjugation lengths in the polymer chains or spheres result in the formation of “dynamic” chromophores with varied optical and photonic responses. The recognition that the segments or branches of conjugated polymers are chromophoric units has triggered a surge of interest in the development of optically and photonic active polymers. As a result, a diversity of acetylenic polymers with photoconductivity, luminescence, chromatism, refractivity, optical nonlinearity, and photochemical patternability have been developed. Introductions of mesogens, chiral groups, metal ligands, and functional moieties of biological origin as pendants to the polymer chains or spheres have led to the generation of novel acetylenic polymers with liquid crystallinity, chiroptical activity, magnetic susceptibility, and biological compatibility.

It has been shown that the polymer chemistry of the carbon–carbon acetylenic triple bond has expanded very fast in the past decades. A lot of acetylenic reactions (azide-alkyne and thiol-yne click reactions,

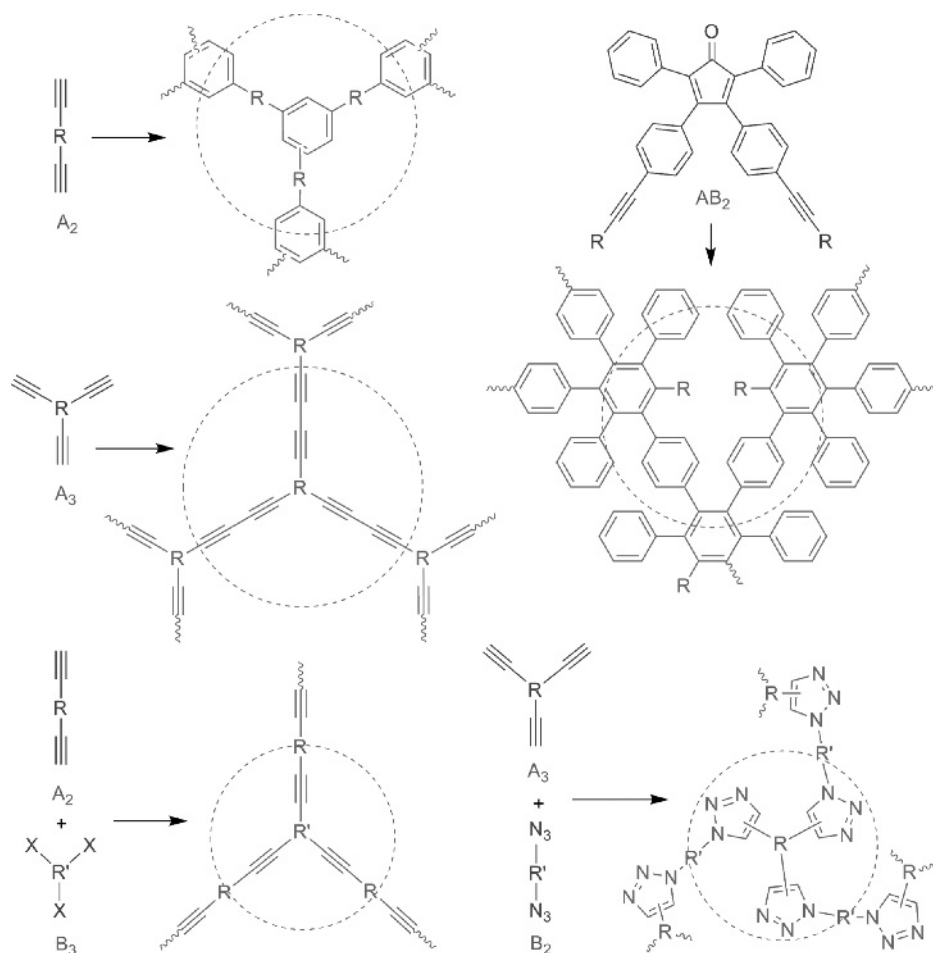


Fig. 3. Examples of nonlinear alkyne polymerizations.

cyclotrimerization, coupling, etc.) have been utilized to construct various functional polymers. In this review, we will focus on introducing the development of fundamental synthetic chemistry of acetylenic polymers, with the purpose of inspiring research enthusiasm in this area.

Polymer Chemistry of the Acetylenic Carbon–Carbon Triple Bond

Although polymer syntheses based on triple-bonded acetylenic monomers have traditionally lagged behind those based on double-bonded vinyl monomers, remarkable advances have been made in the area in recent decades. Successes in the exploration of effective catalytic systems, the development of versatile polymerization reactions, and control over polymerization processes have resulted in the generation of a wide variety of acetylenic polymers. Acetylenic building blocks can now be readily connected together through various construction strategies to

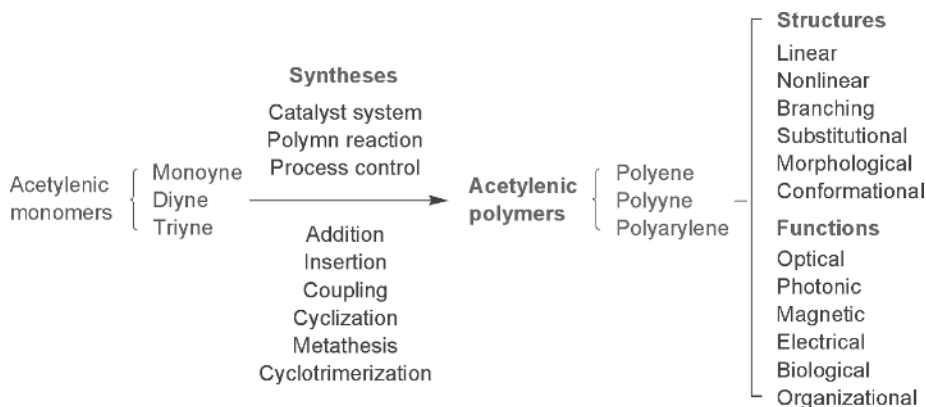


Fig. 4. Research on syntheses, structures, and functions of acetylenic polymers.

furnish linear and hyperbranched polymers. The combined use of direct polymerizations of monomers and postpolymerization reactions of polymers (or polymer reactions in short) offers a molecular engineering means for tuning the structures and modulating the functions of the polymers at molecular level. Here, an account of the syntheses of various acetylenic polymers by polymerization reactions of acetylenic monomers with one, two, and three triple-bonds, that is, monoynes, diynes, and triynes, respectively, is given.

Polymers from Monoynes

The monoyne polymerizations, especially the effectiveness of the catalyst systems based on various transition metals and the polymerizability of the acetylene monomers containing different numbers and kinds of substituents will be discussed in this part. The most noteworthy advancement in the area is the exploration of functionality-tolerant and living-polymerization catalysts, which have enabled the syntheses of highly functionalized substituted PAs with well-defined conformational structures and molecular weights. Furthermore, the successful development of effective postpolymerization reactions has allowed the preparations of functionalized PAs that are inaccessible by the direct polymerizations of their corresponding monomers.

Catalyst Systems. Typical examples of effective catalyst systems based on various transition-metal species for monoyne polymerizations are diagrammatically shown in Figure 5. In 1958, Natta's group synthesized PA by using a Ti-based Ziegler catalyst (2). Polymer scientists at that time envisioned that PA might exhibit semiconductivity. The theoretical calculations carried out in the late 1960s and early 1970s suggested that PA might show even high-temperature superconductivity (49,50). These intriguing predictions had attracted several research groups to investigate acetylene polymerization by Ti- and Fe-based Ziegler–Natta catalysts (51,52). The acetylene polymerization proceeded via an insertion mechanism, yielding a polymer with alternative single and double bonds. Unfortunately, however, the black powdery polymer was

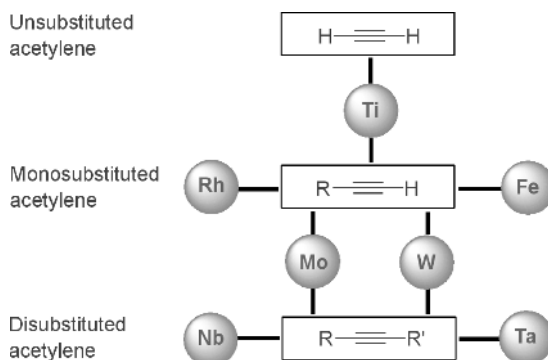


Fig. 5. Monomer-catalyst matching map for monoyne polymerizations.

difficult to process into a sample suitable for the measurements of its physical properties due to its insolubility, infusibility, and instability. There was thus no significant progress in these early studies. In 1974, Shirakawa and co-workers reported that the PA films with metallic lusters could be prepared over a wide temperature range by using highly concentrated Ziegler-Natta catalyst of $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$ (53). The PA films were later found by Shirakawa and co-workers to exhibit very high electrical conductivity upon doping (6,54).

In an effort to confer processability, stability, and functionality on PA, several research groups tried to polymerize substituted acetylenes. This task critically depended on the exploration of effective catalyst systems. In the early stage, the acetylene polymerizations were studied by using conventional Ziegler-Natta catalysts. However, the catalysts could only polymerize sterically unhindered monosubstituted acetylenes into insoluble polymers and/or soluble oligomers. Examples include the polymerizations of phenylacetylene (**1**) by Berlin and Cerdashin (55), Percec and co-workers (56–59), Kern (60), and Ehrlich and co-workers (61). Efficient polymerization of **1** was achieved by Masuda and co-workers in 1974: WCl_6 and MoCl_5 catalyzed the polymerization of **1** to give poly(phenylacetylene) (PPA) with molecular weights over 10,000 (62). Some co-catalysts such as Ph_4Sn and $n\text{-Bu}_4\text{Sn}$ were found to accelerate the polymerization reactions of phenylacetylene.

The WCl_6 and MoCl_5 catalyst systems, however, are sensitive to air and moisture and intolerant of polar functional groups in the monomers, especially those monomers containing active hydrogen atoms, such as amino and amido groups (63). Metal-carbonyl complexes are more stable than the metal halides but need to be preactivated by chlorine-containing additives and/or UV photoirradiation in halogenated solvents (64–66). In 1989, Tang discovered that several stable metal-carbonyl complexes could catalyze polymerizations of 1-alkynes (67). Tang's group extended their efforts in the area and prepared a series of transition metal-carbonyl complexes with a general formula of $\text{M}(\text{CO})_x\text{L}_y$ with M being Mo and W (68). Delightfully, these complexes were found to polymerize various functionalized acetylene monomers in normal, nonhalogenated solvents without UV irradiation. The metathesis mechanism of the Mo- and W-catalyzed polymerization was proposed by Masuda and co-workers (69) and verified by Katz and Lee

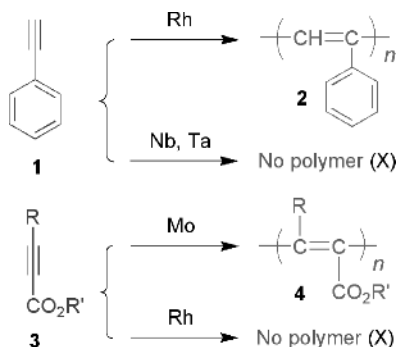


Fig. 6. Examples of substrate–catalyst matching.

(70,71). In addition to the commercially available metal-halide salts, well-defined Mo-carbene complexes have been developed by Schrock and co-workers (72–74). These salts and complexes have proven to be effective catalysts for the polymerizations of a variety of mono- and disubstituted acetylenes, including those sterically demanding monomers.

In parallel to the progressive developments of the metathesis catalysts, the Rh-based complexes were found to polymerize acetylenes to yield stereoregular PAs in an insertion mechanism. Although Kern found that **1** was polymerized in the presence of $RhCl_3-LiBH_4$ and $Rh(PPh_3)_3Cl$ in 1969 (75), the real interest in the Rh-based catalysts was stimulated by the work of Furlani and co-workers in 1989 and Tabata and co-workers in 1991, who found that a series of Rh complexes, such as $[Rh(diene)Cl]_2$ [diene = 2,5-norbornadiene (nbd), 1,5-cyclooctadiene (cod)], could effectively polymerize monosubstituted acetylenes such as **1**, especially in the presence of additives of inorganic and organic bases (76,77). Masuda found that some organometallic additives such as $PhLi$, Et_2Zn , Et_3B , and Et_3Al served as effective cocatalysts (78). Noyori and co-workers developed a zwitterionic Rh complex of $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$ that could polymerize acetylenes to polymers of moderate molecular weights in the absence of added cocatalysts (79). Tang and co-workers developed water-soluble Rh-based catalysts such as $Rh(diene)(tos)(H_2O)$ ($tos = p$ -toluenesulfonate) that could catalyze acetylene polymerization even in tap water and open air, giving stereoregular polymers of high molecular weights in high yields (80). All the Rh-based catalysts are tolerant to polar functional groups in the monomers and solvents and produce polymers with high *cis* contents but generally only work well for the polymerizations of monosubstituted acetylenes. For example, **3** cannot be polymerized by the Rh-based complexes, though it can be effectively polymerized by the Mo-based catalysts (Figure 6) (33).

Halides of group 5 transition metals (NbX_5 , TaX_5 ; $X = Cl, Br, F$) catalyzed the cyclotrimerization of **1**, giving no polymeric products (Figure 6) (81). Cotton and co-workers synthesized dinuclear complexes of Nb and Ta with six chlorides and three tetrahydrothiophenes as ligands and demonstrated their catalytic activity in polymerizing 1-phenyl-1-propyne (82). Stimulated by the work of Cotton, Masuda tried to polymerize 1-phenyl-1-alkynes in the presence of pentahalides of Nb and Ta (83). Completely soluble polymers with very high weight-average

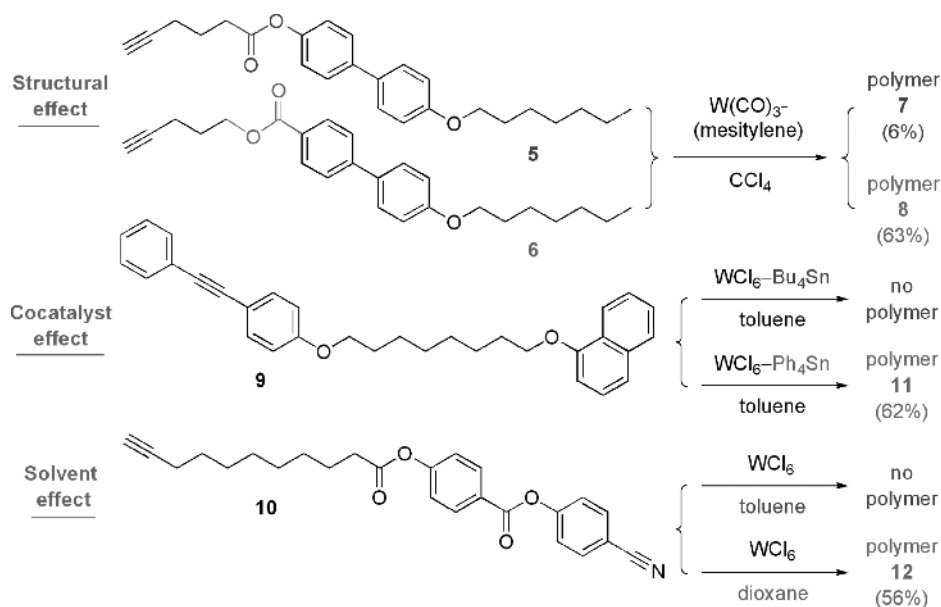


Fig. 7. Effects of substrate, cocatalyst, and solvent on monoyne polymerizations.

molecular weights (M_w 5×10^5 – 1×10^6) were obtained from the polymerizations catalyzed by $TaCl_5$ and $TaBr_5$. All the polymers are white-colored, air-stable, and electrically-insulating solids because the steric crowdedness caused by the presence of two substituents in one repeat unit has significantly twisted the conformation of the polyene backbone. Generally, use of cocatalysts such as $n\text{-Bu}_4\text{Sn}$ and Et_3SiH accelerates the polymerization and increases the molecular weights of resultant polymers (84). Similar to the Mo- and W-based catalysts, the Ta and Nb halides and the Schrock's Ta-alkylidene complexes catalyze the polymerizations of disubstituted acetylenes in a metathesis mechanism. The catalysts are ineffective in polymerizing disubstituted functional acetylenes containing polar groups due to the poisoning effects of the functional groups on the metathesis catalysts.

Polymerization Behaviors. The molecular structures of the acetylenic monomers greatly affect their polymerization behaviors. For example, the substrate–catalyst matching discussed above is structurally susceptible: a seemingly subtle variation in the functional group can greatly influence the polymerizability of a monomer by a given catalyst. As can be seen from the examples shown in Figure 7, monomers **5** and **6** differ only in the orientation of the ester unit but show distinct polymerization behaviors in the presence of metal carbonyl complex of $W(CO)_3(\text{mesitylene})$: **6** can be effectively polymerized but **5** cannot (68). The polymerization conditions, such as cocatalyst and solvent, can affect the fate of a specific substrate–catalyst pair. For instance, **9**– WCl_6 can be a “bad” or “good” combination, depending on whether $n\text{-Bu}_4\text{Sn}$ or Ph_4Sn is used as a cocatalyst (23). Polymerization of **10** does not occur at all in toluene but proceeds well in dioxane (85).

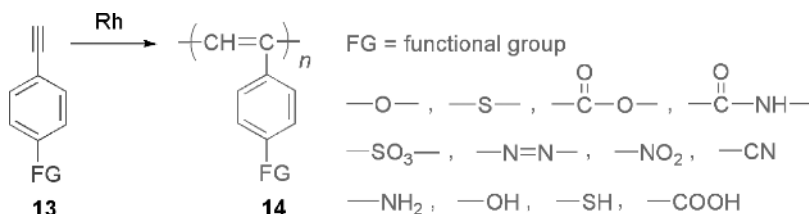


Fig. 8. Polymerizations of functionalized acetylene monomers.

The syntheses of PAs carrying functional pendants have attracted much attention. The main obstacle to the polymerizations of functionalized acetylenes had been the incompatibility of the polar groups in the monomers with the early transition metals in the metathesis catalyst systems. Even by using the Rh-based catalysts, the polymerizations of highly polar monomers, especially those with acidic protons, had been a difficult proposition: for example, the direct polymerization of 4-ethynylbenzoic acid was very challenging (86). As a result, its polymer was prepared indirectly by hydrolysis of preformed polymer of its protected monomer. Tang and co-workers tackled this difficult issue and succeeded in the direct polymerizations of a series of highly polar phenylacetylene derivatives (87–95). Under optimized reaction conditions, the functionalized phenylacetylene derivatives (13) with various polar groups, such as oxy, carboxy, hydroxy, azo, cyano, thiol, amino and nitro, have been directly polymerized in the presence of Rh complexes of $[\text{Rh}(\text{cod})\text{Cl}]_2$, $[\text{Rh}(\text{nbd})\text{Cl}]_2$, and $\text{Rh}^+(\text{nbd})[\text{C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ to afford corresponding polymers (14) with high molecular weights (M_w up to $\sim 5 \times 10^5$) and low polydispersity indexes (PDI down to 1.03) in good yields (Figure 8).

Living Polymerization. Living polymerizations have made a revolutionary impact on polymer science and have opened a new avenue for the syntheses of macromolecules with uniform molecular weights, precise architectures, and nanostructured morphologies (96–99). In a living polymerization, the propagating chains undergo neither transfer nor termination. The number-average degree of polymerization (DP_n) of a living polymer is thus determined by the ratio of the concentration of consumed monomer ($[\text{M}]_0 - [\text{M}]_t$) to the initiator concentration ($[\text{I}]_0$). The molecular weight distribution of a living polymer is normally very narrow (often close to unity). Most of the living polymerizations studied so far have been on vinyl monomers. Living polymerizations of acetylenic monomers may enable the syntheses of electronically conjugated polymers with well-defined structures and desired materials properties (100). This intriguing possibility has prompted several research groups to explore the possibility of developing living polymerization systems of substituted acetylenes.

To date, transition-metal halides **15–20** (101–104), transition metal-alkylidene complexes **21** and **22** (72–74), and rhodium complexes **23–28** (105–107) have been found capable of initiating the living polymerizations of acetylenes (Figure 9). In the late 1980s, Percec and Kunzler and Masuda and co-workers reported on the living polymerizations of several substituted acetylenes catalyzed by TaCl_5 (**15**) (108) and MoCl_5 – and MoOCl_4 – $n\text{-Bu}_4\text{Sn}$ – EtOH mixtures (**17** and

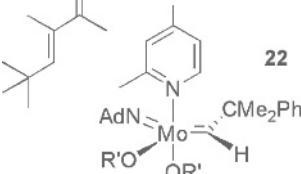
TaCl ₅	15	Rh(C≡CPh)(nbd)(PPh ₃) ₂ -DMAP	23
MoCl ₅	16	[Rh(nbd)OCH ₃] ₂ -PPh ₃ -DMAP	24
MoCl ₅ - <i>n</i> -Bu ₄ Sn-EtOH	17	[Rh(nbd)Cl] ₂ -NaOCH ₃ -PPh ₃ -DMAP	25
MoOCl ₄ - <i>n</i> -Bu ₄ Sn-EtOH	18	[Rh(nbd)Cl] ₂ -Ph ₂ C=C(Ph)Li-PPh ₃	26
MoOCl ₄ - <i>n</i> -BuLi	19	Rh(PhC=CPh ₂)(nbd)(PAR ₃)-PAR ₃	27
WOCl ₄ - <i>n</i> -Bu ₄ Sn- <i>t</i> -BuOH	20	Rh(PhC=CPh ₂)(tfb)(PPh ₃)-PPh ₃	28
Ta(Py)(DIPP) ₃	21	Abbreviations:	
		Py = pyridine, nbd = 2,5-norbornadiene	
		DMAP = 4-(dimethylamino)pyridine	
		Ad = 1-adamantyl, R' = -CH(CF ₃) ₂	
		DIPP = 2,6-diisopropylphenoxide	
		tfb = tetrafluorobenzobarrelene	
		PAR ₃ = P(4-X-Ph) ₃ , X = F, Cl	
	22		

Fig. 9. Examples of Catalyst Systems for Living Acetylene Polymerizations.

18) (101,102). It was hypothesized that the alkynes with bulky substituents would suppress the back-biting and inter-chain reactions due to the steric hindrance and thus promote living polymerizations. In the MoCl₅-initiated polymerization of *t*-butylacetylene, the plots of molecular weight versus monomer conversion and $\ln([M]_0/[M]_t)$ versus time (*t*) gave linear lines, indicating the living nature of the acetylene polymerization, although the PDIs of the resulting polymers (>1.9) were higher than those expected for a classical living polymer (100,108). Masuda succeeded in the preparation of triblock PA copolymers of A-B-A and B-A-B types through the successive polymerizations of 1-chloro-1-hexane (A) and 1-chloro-1-hexadecyne (B) initiated by Mo-based ternary mixture **18**, although the initiation efficiency was very low (~2.5%) (102).

In 1989, Wallace and co-workers reported the living polymerization of 2-butyne using a single-component, well-defined, and Ta-based initiator (**21**) (72). The resultant poly(2-butyne) had DP_n's up to 200 and PDIs down to 1.03. Remarkably, the initiation efficiency was virtually quantitative and the living chain ends could be functionalized conveniently by an appropriate aldehyde via a Wittig-like capping reaction. However, **21** worked for living polymerization of 2-butyne only. Schrock's group further developed well-defined Mo-based alkylidene complexes, for example, **22**, that were able to efficiently polymerize in a living manner a variety of acetylene monomers, such as *o*-substituted phenylacetylenes and metallocenyl-substituted 1-alkynes (73,74). The activity and selectivity of the Mo-based alkylidene complexes could be tuned by the steric and electronic effects of the ligand peripheries surrounding the metal center.

The early transition metal-based living polymerization catalysts generally work for the disubstituted or sterically crowded monosubstituted acetylenes with no polar functional groups but are ineffective for the acetylenes with low steric effects such as **1**. Steric hindrance seems to have prevented the formation of *cis-cisoidal* backbone conformation and the occurrence of back-biting reaction. Furthermore, intra- and interchain reactions are presumably eliminated because of the protection of the polyene backbone by the bulky substituents. Different from these early transition-metal catalysts, the late transition-metal Rh-based

catalysts can initiate the living polymerizations of sterically less demanding phenylacetylene derivatives. The living polymerization of **1** was first accomplished by Noyori and co-workers in 1994 by using mixture **23** as initiator, affording PPAs with PDI of ~ 1.1 in quantitative yields (109). The initiation efficiencies of the living polymerization reactions were ~ 33 – 56% . The living polymerization catalyst systems generated in situ, for example, **24** and **25**, also enabled the controlled stereoregular polymerization of **1** (105,106).

As the propagating species derived from the Rh catalysts was proposed to be vinylrhodium, Masuda designed a living polymerization system of **1** mediated by a ternary catalyst **26** (110). In a typical run, the PDI of the resultant PPA was ~ 1.1 and the initiation efficiency was virtually quantitative. A successive addition polymerization experiment revealed that the DP_n value of the polymer increased in proportion to the polymer yield, whereas its PDI remained to be as small as ~ 1.1 . This indicates that the propagating species remained active even after the consumptions of the early added batches of monomers. Soluble star polymers and star block co-polymers were synthesized from the living linear PPA and poly(*p*-methylphenyl)acetylene] by employing 1,4-diethynylbenzene and 1,4-diethynyl-2,5-dimethylbenzene as linking agents. Furthermore, use of the (triphenylvinyl)lithium reagents containing functional groups led to the formation of functionalized PPA with the functional groups located at the initiating chain end. Thereafter, well-defined Rh complexes **27** and **28** were developed for the living polymerizations of **1**, yielding PPAs with PDIs as low as 1.04 in virtually quantitative initiation efficiency (107).

Polymer Reactions. Postpolymerization reactions can be used to further functionalize the preformed acetylenic polymers, to prepare the functional polymers that are inaccessible by direct polymerizations of their corresponding monomers, and to modulate the properties of the acetylenic polymers by structural modifications (111–113). Tang and co-workers have developed a series of facile polymer reactions for the functionalizations of acetylenic polymers. For example, **29** consists of hydrophobic PPA skeleton and hydrophilic amine pendant (Figure 10). Because of this unique structural feature, the polymer is insoluble in either organic solvents or aqueous media. Ionization of **29** by hydrochloric acid gives rise to polyelectrolyte salt **30** and makes the polymer readily soluble in water (87). Although macromolecular reactions normally do not proceed to 100%, remarkably the deprotection reaction of **31** beautifully proceeds to completion: the cleavage of its ether protection groups by acid-catalyzed hydrolysis furnishes **32** with cytocompatible sugar pendants that do not contain any ether residues (114).

Whereas the studies on the polymerizations of acetylenic monomers have made impressive progresses in the past decades, it is still very difficult to access to functionalized disubstituted PAs through the direct polymerizations of their corresponding monomers, owing to the thorny problems associated with the intrinsic intolerance of the early transition metal-based metathesis catalyst systems to the polar functional groups. Polymer-reaction approaches can help solve this problem. For example, using the azide-alkyne click reactions, Tang and co-workers succeeded in attaching a number of polar functional groups to the pendants of disubstituted PA **34** (113). Nucleophilic substitutions (114) and hydrolysis reactions (115) of polymers **36** and **38** resulted in the formation of

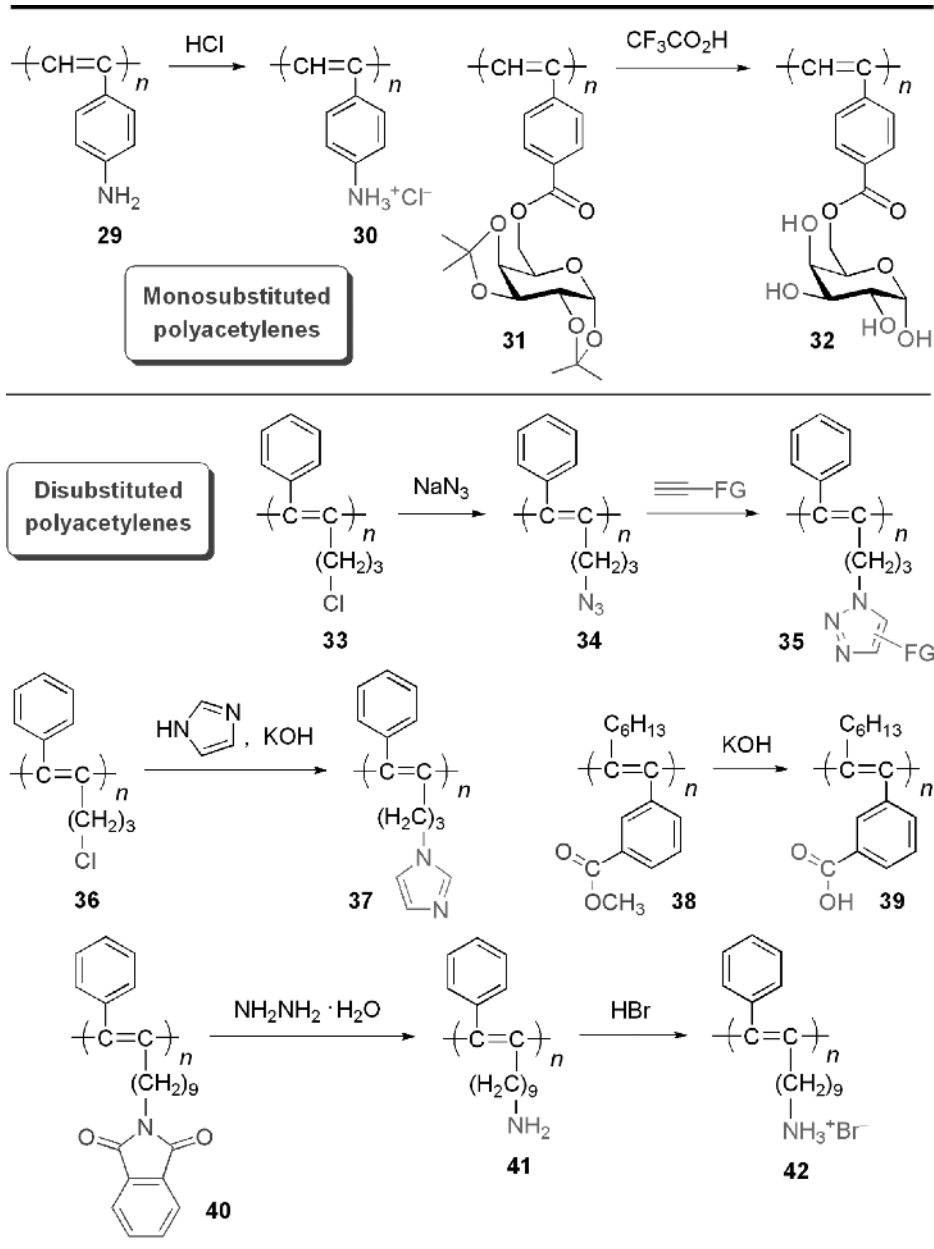


Fig. 10. Syntheses of highly functionalized polyacetylenes through polymer reactions.

imidazole- and carboxy-functionalized disubstituted PAs **37** and **39**, respectively. Hydrazine-catalyzed deprotection of polyimide **40** brought about polyamine **41**, which could be further ionized by hydrobromic acid to give polyelectrolyte salt **42** (94,95).

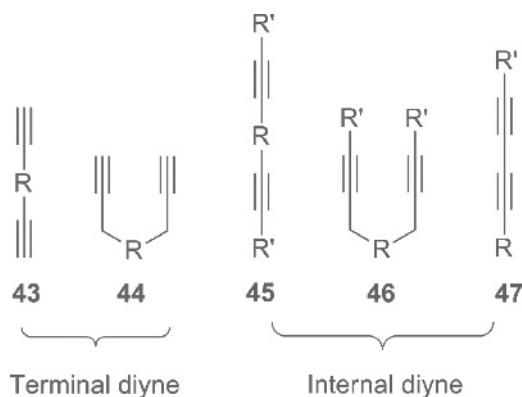


Fig. 11. General Structures of Terminal and Internal Diyne Monomers.

Polymers from Diynes

Monomer Structures. Diynes are a group of acetylene derivatives with two triple-bonds in a single molecule that have been extensively studied as potential monomers for acetylenic polymerizations. Terminal and internal diyne monomers **43–47** (Figure 11) have been utilized as building blocks to construct polymers with different molecular conformations and topological structures. Different from the monoyne monomers discussed above, the diyne monomers can be polymerized not only by linear but also by nonlinear polymerization reactions. Typical examples of the linear polymerization reactions include cyclopolymerization of 1,6-heptadiynes, metathesis polymerization of internal diynes, cross-coupling polymerization of diynes with dihalides, photoinduced solid-state topopolymerization of diacetylenes, polyhydrosilylation of diynes with (di)silanes, polyhydroboration of diynes with boranes, polyhydrothiolation of diynes with dithiols, Diels–Alder polycycloaddition of diynes with dicyclopentadienones, and click polymerization of diynes with diazides. The nonlinear polymerization reactions include polycoupling of diynes with triiodides, polyhydrosilylation of diethynylsilanes, polybisthiolation of diethynyl disulfides, polycycloaddition of cyclopentadienonyldiynes, polycyclotrimerizations of diynes, and click polymerization of azidodiyne.

Linear Polymerizations. It is already known that monoynes undergo metathesis polymerization in the presence of Mo- and W-based catalysts. Theoretically, polymerization of diyne monomers generally gives highly cross-linking polymers. However, owing to their special geometrical arrangements, 1,6-heptadiynes **44** and **46** can be polymerized into linear polyenes with cyclic structures recurring along the backbone (11,116). The advances in the area of research on poly(1,6-heptadiyne)s have been thoroughly reviewed by Kim and co-workers (11) and recently by Buchmeiser (116) and we thus will not repeat what have been summarized in those reviews. Typical examples of 1,6-heptadiyne monomers are given in Figure 12 [48(a–f)]. A mixture of five- and six-membered alkenyl rings are usually formed in the cyclopolymerizations of 1,6-heptadiynes. Schrock-type metathesis complexes, however, can cyclopolymerize diethyl dipropargylmalonate

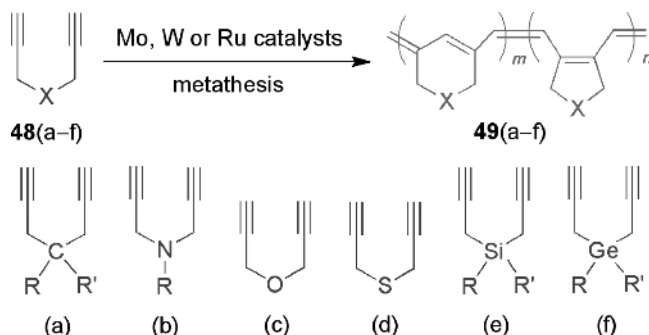


Fig. 12. Cyclopolymerization of 1,6-heptadiyne derivatives.

(48a, $\text{R} = \text{R}' = -\text{CO}_2\text{C}_2\text{H}_5$) in a regioselective manner, giving polymers with either five- or six-membered repeat units (117,118). A series of trifluoroacetate- and pentafluorobenzoate-modified Grubbs–Hoveyda catalysts were found to polymerize sterically demanding 1,6-heptadiyne esters, dipropargylamines, dipropargylammonium salts, and an alkyl-substituted dipropargyl ether into cyclic polyenes (49) with repeat units of predominate (>95%) five-membered rings (119).

In sharp contrast to the active research on the polymerizations of terminal 1,6-heptadiynes, little work has been done on internal 1,6-heptadiynes, mainly due to the involved synthetic difficulty. Tang and co-workers designed and synthesized a group of α,ω -disubstituted alkadiynes containing different aryl rings (120). The terminally disubstituted 1,6-heptadiynes [50(a–d)], whose structures are given in Figure 13, show polymerization behaviors distinctly different from those of their unsubstituted parents: the former cannot be effectively polymerized by the binary $\text{MoCl}_5\text{--Ph}_4\text{Sn}$ mixture, which is a good catalyst for the polymerization of the latter. Delightfully, however, Tang and co-workers found that the binary $\text{WCl}_6\text{--Ph}_4\text{Sn}$ mixture could effectively transform the aryl-disubstituted 1,6-heptadiyne derivatives into high molecular weight cyclic polyenes (51) consisting of exclusively six-membered rings. The polyenes with their labile olefinic hydrogen atoms replaced by the stable aromatic rings are, as anticipated, very stable and readily processable.

Schrock tungsten-carbyne complex $(t\text{-BuO})_3\text{W}\equiv\text{C-}t\text{Bu}$ can catalyze alkyne metathesis (121). Schrock and Bazan have shown that the complex is capable of initiating ring-opening metathesis polymerization of cyclic alkynes (122,123). In 1997, Bunz and Müllen reported the synthesis of poly(phenyleneethynylene)s (PPEs) by alkyne metathesis: $(t\text{-BuO})_3\text{W}\equiv\text{C-}t\text{Bu}$ was used to initiate acyclic metathesis polymerization of 2,5-dihexyl-1,4-dipropynylbenzene, producing defect-free polymers with $\text{DP}_n \sim 100$ in high yields (124). The Schrock catalyst, however, is difficult to prepare and sensitive to air and moisture and must be used in carefully dried solvents in a glovebox or Schlenk line. On the other hand, the Mortreux–Mori–Bunz catalyst generated in situ from commercially available reagents of Mo(CO)_6 and phenols could work in unpurified solvents (125). A series of dipropynylated benzenes (52) was metathesis polymerized to furnish PPEs 53 in quantitative yields and high purity (Figure 14). The DP_n 's of the PPEs can reach very high values (up to 2000) when long side chains (R) are

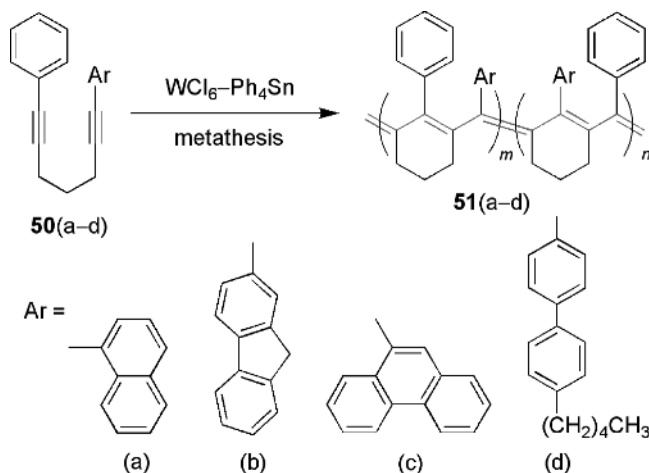


Fig. 13. Cyclopolymerization of internal diynes.

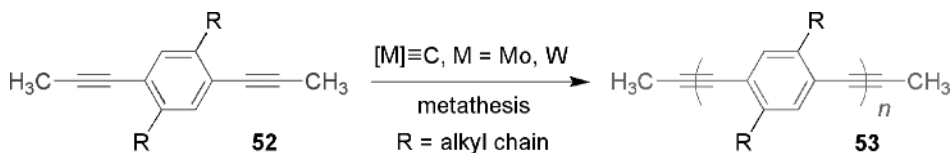


Fig. 14. Metathesis polymerization of internal diynes.

used as solubilizing groups in **53**. The metathesis polymerizations carried out at elevated temperatures produced high molecular weight polymers.

One of the characteristic reactions of alkynes is the coupling reaction: under appropriate conditions, alkynes can undergo homo- and cross-coupling reactions to yield molecules with newly formed carbon-carbon bonds (3–5). The first oxidative polycoupling of terminal diynes was investigated by Hay (126), from which a new class of PDYs was generated, which could be solution cast into films or spun into fibers. Polymer **55a** from *m*-diethynylbenzene **54a** has exceptionally high carbon content (~97%) and forms transparent, flexible films (Figure 15). Carbon fibers with high mechanical strengths and moduli were fabricated from these carbon-rich polymers. The conversions from the polymers to the graphite fibers were fast and could be completed in a few minutes. The polymers containing the diyne moieties were photo-sensitive and could be cross-linked by photoirradiation (127).

Diederich and co-workers have designed and synthesized a large variety of acetylenic all-carbon or carbon-rich polymers, using Glaser-Hay coupling reactions between the carbon-carbon triple bonds. Diederich has comprehensively reviewed the progresses in this area and interested readers are referred to the review articles (22,39,128). The constructions of these carbon-rich acetylenic scaffolds and nanometer-sized structures have opened up new avenues for basic research and technological innovation at the interface between chemistry and material sciences. For example, stable and soluble conjugated molecular wires with

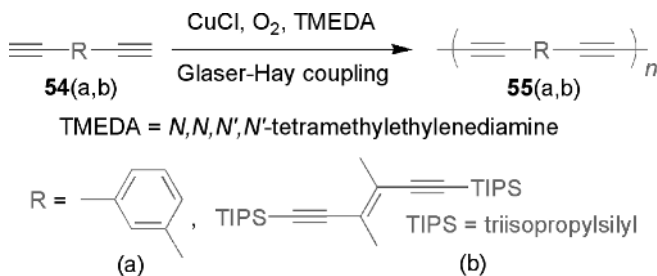


Fig. 15. Polycoupling of terminal diynes.

persilylethynylated poly(triacetylene) **55b** and its derivatives modified by different peripheral groups have been found to exhibit useful electronic and optical properties (129).

In addition to the alkyne metathesis approach, Sonogashira coupling between diynes and dihalides (130) is another powerful tool for the syntheses of conjugated PAEs (Figure 16). It should be noted that in this $A_2 + B_2$ -construction strategy, stoichiometric balance of the mutually reactive A and B groups must be ensured in order to obtain high molecular weight PAEs. Bunz has reviewed on the synthesis of PAEs including the influence of substrate structures and reaction conditions (12,125). This Pd-catalyzed cross-coupling polymerization is highly tolerant of substrate variations. Through direct polymerizations and polymer reactions, a wide variety of functionalized PAEs have been prepared. Selected examples include the PAEs containing bulky pentiptycene group (**59**) (131), crown ether chelator (**60**) (132), electrolyte ions (**61–63**) (133,134), hydrophilic sugar moiety (**64**) (135), and transition metals (**65** and **66**) (21,136). A number of research groups, including those led by Swager and co-workers (137,138), Müllen and co-workers (139), Weder and co-workers (140,141), Bunz (12,125), Pinto and Schanze (142), Whitten (133,143), Huang and co-workers (144) and Wong (21,136), have demonstrated that the functionalized PAEs can find practical applications in explosive detectors, biological sensors, organic light-emitting diodes (OLEDs), liquid crystal displays (LCDs), photovoltaic cells (PVCs), etc.

Wegner and Naturforsch discovered a unique diyne polymerization reaction, namely solid-state polymerization of 1,4-diacetylenes (Figure 17) (145). When the reactive diyne monomers are preorganized at a distance commensurate with the distance between the repeat units in the final PDAs, application of thermal or photochemical energy can initiate the topopolymerization reaction. This preorganization is satisfied in some diacetylene crystals and some diacetylene amphiphiles in monolayers, LB-multilayers, bilayer vesicles and tubules (146–150). For example, closely packed and properly ordered diacetylene lipids readily undergo polymerization through 1,4-addition to give alternative ene-yne polymer chains, for example, **68**, upon irradiation with UV light (in the case of thin films and vesicle solutions) or with γ -ray irradiation (in the case of solid powders). As no chemical initiators or catalysts are used in the polymerization process, the PDAs are not contaminated with impurities and consequently the purification steps are not required. The PDAs possess novel structures and exhibit unique properties, such as large quasi-one-dimensional structure of their single crystals,

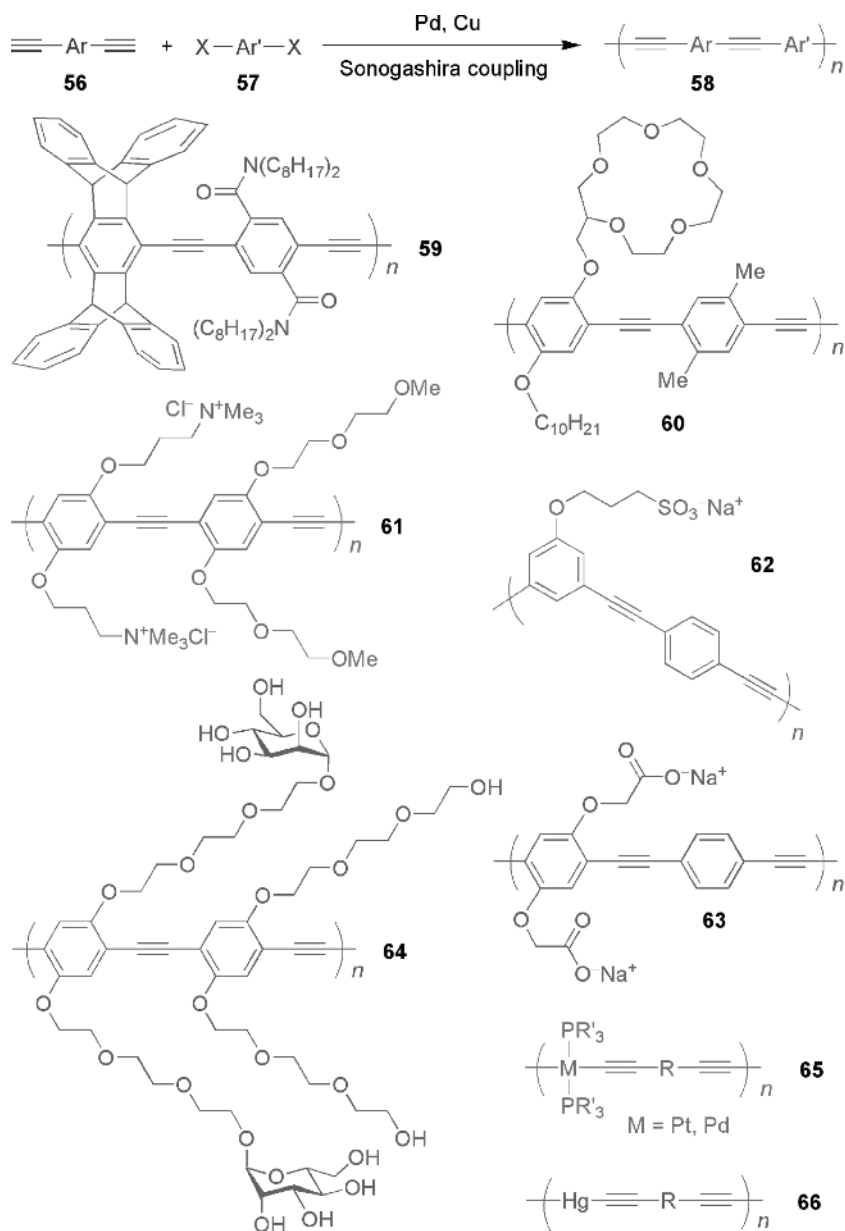


Fig. 16. Cross-coupling polymerization of arylenediynes with arylenedihalides.

large optical nonlinearity (especially high third-order susceptibility), and high photoconductivity (151,152). The most characteristic and attractive property of the PDAs is their dramatic chromic transitions. Normally, the PDAs generated by photoinduced topopolymerization have a blue color. The PDAs undergo a blue-to-red color change in response to thermal agitation, solvent fumigation, mechanical stress, or ligand-receptor interactive perturbation (149,150,153).

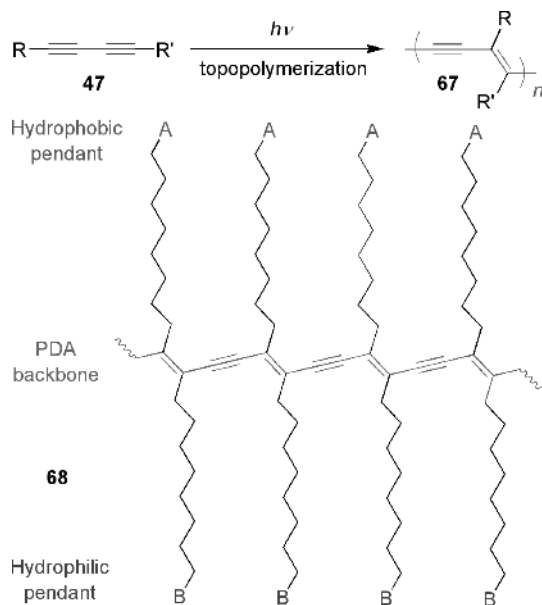


Fig. 17. Topopolymerization of diacetylenes.

Acetylene derivatives readily undergo addition reactions with heteroatom-containing compounds, such as silane (hydrosilylation), borane (hydroboration) and thiol (hydrothiolation) (3–5). Many research groups have worked on the utilization of these reactions for the syntheses of heteroatom-containing acetylenic polymers. Polyhydrosilylation of diynes leads to the formation of poly(silylenevinylene)s, which possess excellent processability and stability and have found applications as ceramic precursors, cross-linkable prepolymers, electron-transport media, and luminescent materials (27,37,154), thanks to the unique $\sigma^*-\pi^*$ conjugation along the polymer backbone (37,155). The alkyne hydrosilylation is realized by the oxidative addition of the Si–H bond across the $C\equiv C$ bond, which yields the silylenevinylene unit. The reaction is tolerant of various functional groups, such as ester, nitrile, amine, amide, nitro, ketone, ether, phosphate, sulfide, and sulfone. Structurally, alkyne hydrosilylation can produce several isomers, including *trans* (*E*), *cis* (*Z*), and geminal products that result from the β -1,2 (*syn* and *anti*) and α -2,1 additions. The regio- and stereoselectivities depend on the steric effect, kinetic control, and the catalyst used. Over the past decades, many metal complexes have been investigated as potential hydrosilylation catalysts. Among the most popular are platinum, palladium, rhodium, and ruthenium complexes. The Speier hexachloroplatinic acid has become the catalyst of choice for most hydrosilylation reactions (156).

By increasing the steric hindrance of substrates and exercising kinetic control (e.g., high temperature), Keller (157), Luneva (158), Shim (159) and Trogler (154,160) have prepared various poly(silylenevinylene)s with *trans*-rich stereoregularity by using the Speier's catalyst (e.g., Figure 18). In some cases, geminal linkage and chain branching have occurred as a result of further hydrosilylation

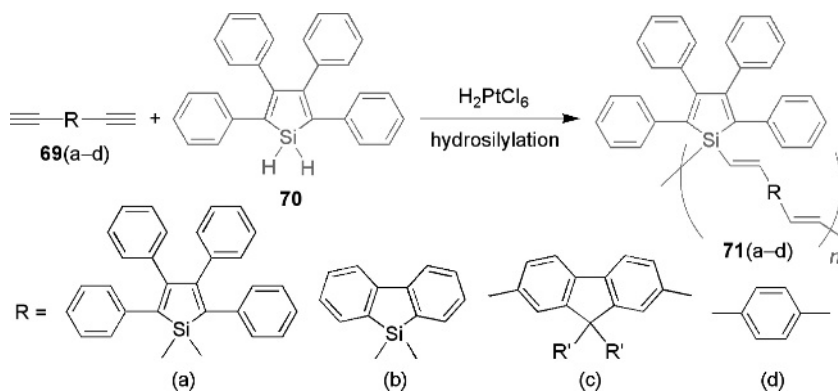


Fig. 18. Polyhydrosilylation of diynes with silanes.

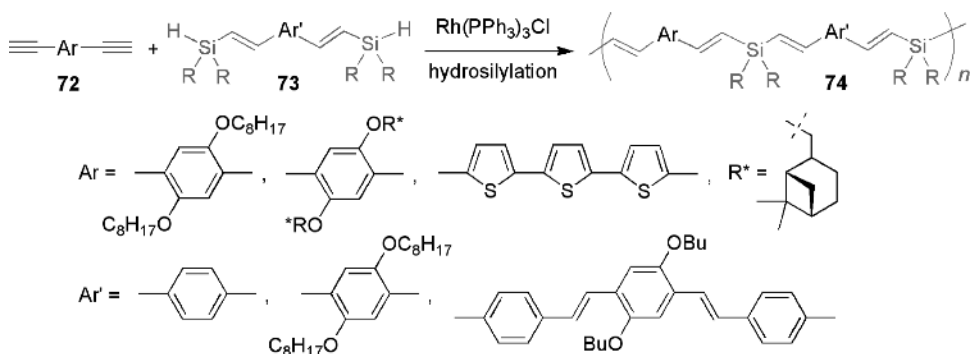


Fig. 19. Polyhydrosilylation of diynes with disilanes.

of the Si–H bond to the vinylene unit formed during the polymerization process (161). The palladium complexes are not as reactive as their platinum counterparts. The rhodium catalysts can control the ratio of the regio- and stereoisomers formed. Using Wilkinson's catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, Luh and co-workers have developed very useful hydrosilylation protocols for the synthesis of polymers carrying more than two different chromophores in a regio- and stereoregular manner (Figure 19) (27,162). The optical properties of the polymers with all *trans* vinylene structures have been actively investigated. Mori found that $\text{Rh}(\text{PPh}_3)_3\text{I}$ could be used to prepare polymers with *trans*- or *cis*-rich conformation, depending on the sequence of monomer addition and the polymerization temperature (163). Using the bisilylarylene and bisethynylarylene monomer pairs, high molecular weight polymers with *trans*- or *cis*-rich structures were prepared. The fluorescence quantum yield (Φ_F) of the *trans* polymer is much higher than that of its *cis* counterpart. This is because the *trans* isomer is electronically more delocalized, which enables more extensive orbital overlapping between the monomer units as compared to the *cis* isomer. Upon UV irradiation, *cis* structure is isomerized to all-*trans* structure, which shows the expected increase in Φ_F as well as the high stability of the Si–C bond (164).

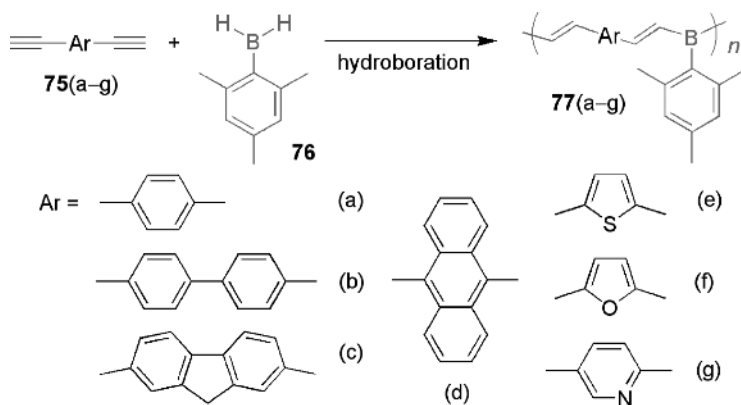


Fig. 20. Polyhydroboration of diynes with boranes.

Although alkyne hydroboration is well-known in organic chemistry, examples of using this reaction to synthesize polymers are rare. Chujo and co-workers synthesized organoboron polymers **77** with moderate molecular weights by polyhydroboration of aromatic diynes **75** with mesitylborane **76** in THF at room temperature, utilizing the highly regioselective nature of the reaction of borane with alkyne (Figure 20) (165). The polymers showed high solubility but relatively low stability to air and heat. Corriu and co-workers found that 2,5-dialkynylthiophenes $(\text{RC}\equiv\text{C})_2\text{C}_4\text{H}_2\text{S}$ ($\text{R} = \text{Ph}, \text{Me}_3\text{Si}, t\text{-Bu}$) treated with HBCl_2 and Et_3SiH in dichloromethane (DCM) underwent hydroboration polymerization to give highly colored polymers, which were extremely sensitive to oxygen and water (166). In the polymers prepared by Chujo, the extension of π -conjugation through the boron atom was observed (167). Further studies revealed that the polymers belonged to typical electron-deficient n-type conjugated polymer. Incorporation of donor (D) chromophores is expected to modulate the optical properties of the polymers. Indeed, while polymers **77(a-d)** emit blue light, the polymers containing electron-donating units of thiophene, furan, and pyridine, that is, **77(e,f)** and **77g**, emit green and white lights, respectively, due to the donor-acceptor (D-A) interactions in the polymers.

Similar to hydrosilylation and hydroboration, hydrothiolation is a potentially useful reaction for the syntheses of heteroatom-containing acetylenic polymers. The reaction was first reported by Truce and Simms in the 1950s: when aryl- or alkylacetylenes were admixed with sodium thiolates, nucleophilic reactions occurred and vinyl sulfides were formed (168). Newton tried to use a molybdenum complex to catalyze the reaction but the product was obtained in a low yield (169). Ogawa (170) and Shimada and co-workers (171) found that rhodium and palladium complexes could effectively catalyze alkyne hydrothiolation, giving vinyl sulfides with linear and branched structures. Love and co-workers developed Rh-based catalysts for the synthesis of vinyl sulfides (172). Although alkyne hydrothiolation can proceed via radical, nucleophilic, and coordination mechanisms with excellent atom economy, the products are often mixtures of regio- and stereoisomers (173). For example, thiol **79** can undergo Markovnikov addition with alkyne **78** to give a branched vinyl sulfide **80**; the reaction can also

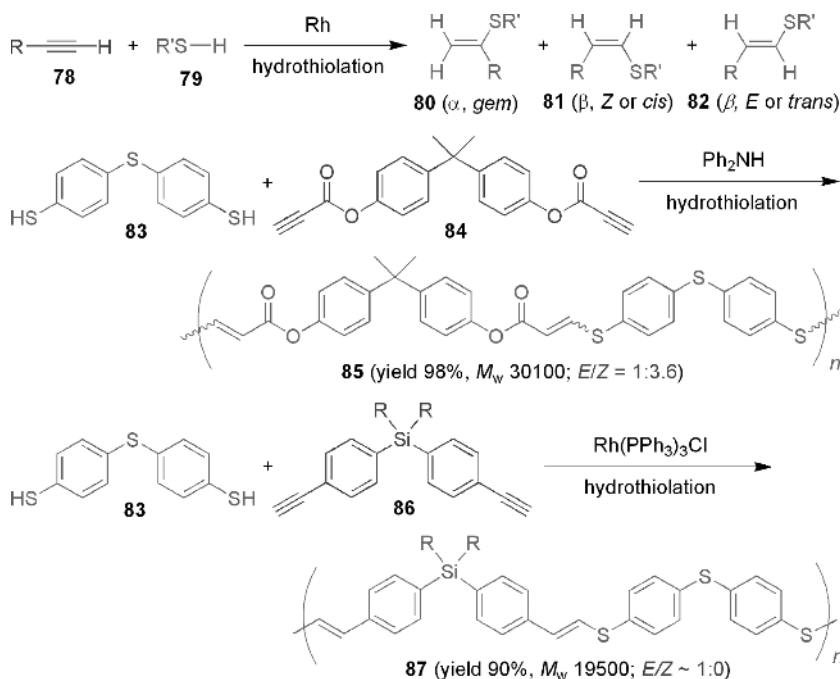


Fig. 21. Polyhydrothiolation of diynes with dithiols.

proceed in an anti-Markovnikov fashion to yield linear adducts with *Z* (**81**) and *E* (**82**) conformations (Figure 21). Clearly, the regio- and stereochemistries are the important issues to be solved for the development of more useful reactions. Synthesis of sulfur-rich polymers by alkyne hydrothiolation has been virtually unexplored, although such polymers are expected to show intriguing photonic properties such as high refractive indexes (RIs). The development of processable polymeric materials with high RI values is a fascinating area of research because of their promising applications in photonic devices such as optical waveguides and holographic image recording systems.

Recently, Tang and co-workers succeeded in developing alkyne hydrothiolation reaction into a useful polymerization technique (174). Dithiol **83** was admixed with bipropiolate **84** in DMF in the presence of a secondary amine such as diphenylamine (Figure 21). After stirring at room temperature for 24 h, polymer **85** with a high molecular weight ($M_w \sim 30 \times 10^3$) was obtained in a nearly quantitative yield. Spectroscopic analysis revealed that the polymer was a linear anti-Markovnikov reaction product with a predominant *Z* conformation (*Z*/*E* = 3.6:1). No branched isomer was obtained at all, indicating that the polyhydrothiolation reaction proceeded in a regioselective fashion. Rhodium complex Rh(PPh₃)₃Cl was found to effectively catalyze polyhydrothiolation of **83** and **86**, giving polymer **87** with a high molecular weight and an exclusive *E*-conformation in a high yield. This is very exciting, because it proves that the stereochemistry of the alkyne polyhydrothiolation can be controlled by the choice of catalyst system and that the Rh-catalyzed polymerization is both regio- and stereoselective.

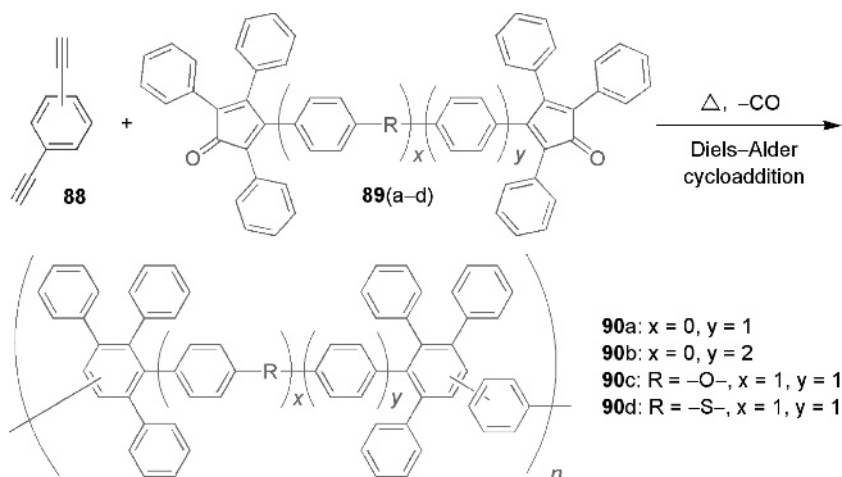


Fig. 22. Polycycloaddition of diynes with dicyclopentadienones.

Oligaruso and Becker (175), Ried and Freitag (176) and Müllen and co-workers (177) have utilized intermolecular Diels–Alder [4+2] cycloadditions of tetraphenylcyclopentadienone with monoyne, diyne, or triyne derivatives to establish effective synthetic routes to large, monodisperse oligophenylenes with potential applications as electronic materials. The preparation of linear PPs was achieved by Stille and co-workers (178,179). The polycycloaddition reactions of *p*- or *m*-diethynylbenzene **88** with bis(tetraphenylcyclopentadienone) **89** at high temperatures (up to 250°C) proceeded with spontaneous extrusion of carbon monoxide, leading to the formation of **90** in high yields (Figure 22). The polymers were almost colorless and amorphous and had high molecular weights (number-average molecular weight $M_n \sim 20,000$ –100,000). The polymers, however, had poor solubility, with only 15% being soluble in common organic solvents. The polycycloaddition reaction is regiorandom: even when *p*-diethynylbenzene **88**(*p*) was used in the reaction, a structurally unambiguous poly(*p*-phenylene) **90**(*p*) could not be obtained. In principle, two regioisomers are possible in each [4+2]-cycloaddition. This is why the polymer chains contain both *p*- and *m*-isomeric units.

Alkyne–azide 1,3-dipolar cycloaddition was systematically studied by Huisgen in the 1980s (180). The area had remained silent until Sharpless and co-workers reported that Cu(I) species efficiently catalyzed the cycloaddition reaction to give regioselective 1,4-disubstituted triazoles. This reaction was coined “click reaction” by Sharpless and co-workers, which enjoys a number of remarkable features, such as wide substrate applicability, high efficiency, excellent regioselectivity, mild reaction conditions, and simple purification procedures (181–183). The click reaction has become a versatile synthetic tool and has been widely used in a diverse area of research, such as bioconjugation, surface functionalization, and materials modification (184–188). The click reaction has also been utilized in polymer science but the emphasis has been on the modification

of preformed polymers via postpolymerization approaches (189–199). The efforts of developing the click reaction into a polymerization technique have met with only limited success. In the early studies, polymer chemists had used click chemistry to construct dendritic and linear polymers. The preparations of dendritic polymers, however, require multistep reactions and tedious product isolations, whereas long reaction time and poor product solubility have been the obstacles to the syntheses of linear polymers via the click reaction route (200).

In the attempted click polymerizations, diynes and diazides have often been copolymerized by using CuSO_4 /sodium ascorbate in the THF/water mixtures (Figure 23) (201,202). The Cu(I)-catalyzed “click” polymerizations of aryldiazides and aryldiynes (aryl = phenyl, pyridyl, fluorenyl, etc.) were sluggish, taking as long as 7–10 days to finish. The products often precipitated from the reaction mixtures even at the oligomeric stage or became insoluble in common organic solvents after purifications, unless very long alkyl chains (e.g., dodecyl groups) were attached to the aryl rings of the polymers. The insolubility is most likely caused by the low solvating power of the aqueous mixtures to the resultant PTAs. This drawback may be overcome if the click polymerization is performed in organic media using a catalyst that is soluble in the organic solvents. Indeed, by using organosoluble catalyst $\text{Cu}(\text{PPh}_3)_3 \text{Br}$, Tang and co-workers succeeded in polymerizing diyne **93** with diazides **94** to obtain soluble, linear PTAs **95** with high molecular weights and 1,4-regioregularity (203).

Experimental and theoretical studies indicate that the reactions are largely affected by the substrate: the alkyne monomers with electron-withdrawing groups adjacent to the carbon–carbon triple bonds facilely undergo the polycycloaddition reaction even in the absence of a metallic catalyst. Tang and co-workers have recently developed a thermally activated, metal-free, click polymerization process for electron-deficient alkyne monomers. Linear poly(aryltriazole)s (**98** and **100**) with high regioselectivity (1,4-content or $F_{1,4}$ up to ~92%) and excellent solubility in common organic solvents are obtained in high yields by simply refluxing the reaction mixtures of bis(arylacetylene)s (**96** and **99**) and diazides (**97**) in polar solvents such as DNF/toluene at a moderate temperature (100°C) for a short period of time (6 h) in an open atmosphere (204,205).

Nonlinear Polymerizations. Nonlinear alkyne polymerizations enable the syntheses of acetylenic polymers with three-dimensional molecular architectures. Polycoupling of aryldiynes with aryltriiodides is an effective way to construct hyperbranched poly(aryleneethynylene)s (*hb*-PAEs). The polymers can also be prepared from AB_2 -type monomers but such approach suffers from the difficulty in the monomer syntheses because of the self-oligomerization between the mutually reactive A and B functional groups (206–208). The $\text{A}_2 + \text{B}_3$ strategy offers the choices of a wider variety of monomers but has the risk of forming cross-linked networks or gels. Control of the polycoupling conditions is thus a necessity for the syntheses of processable *hb*-PAEs with desired structures and properties. Through optimization of the polymerization conditions such as reaction time, monomer and catalyst concentrations, and addition mode of comonomers, Tang and co-workers successfully synthesized *hb*-PAEs **103** containing luminophoric groups such as fluorene and anthracene and azo-cored push–pull nonlinear optical (NLO) chromophores (Figure 24) (209,210).

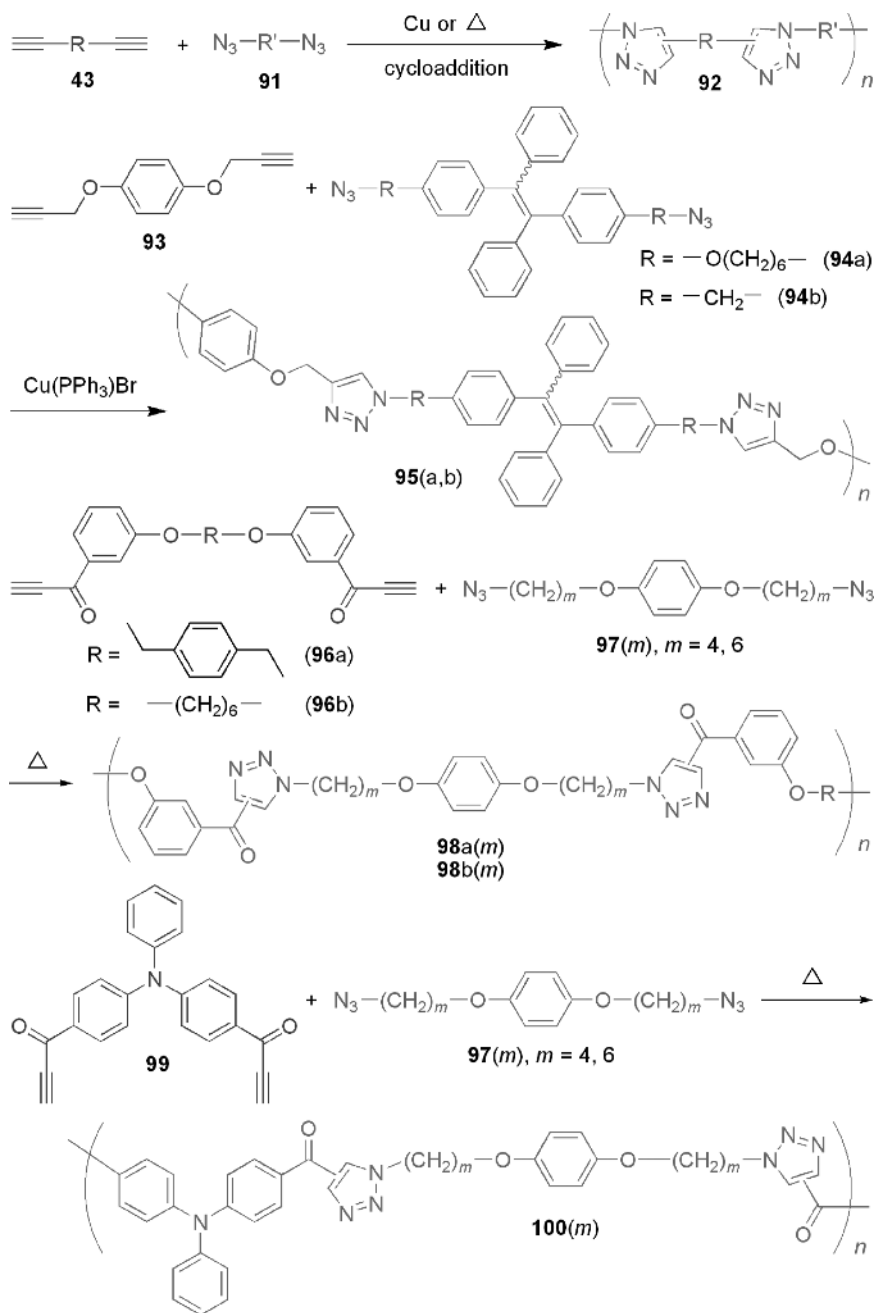


Fig. 23. Click polymerization of diynes with diazides.

Hyperbranched poly(vinylenesilane) **105a** was prepared by Son and co-workers through palladium-catalyzed polyhydrosilylation of diethynylmethylsilane **104a** (Figure 25) (211). The peripheral ethynyl groups of the tacky, soluble, and stable polymer underwent thermo- and photoinduced cross-linking

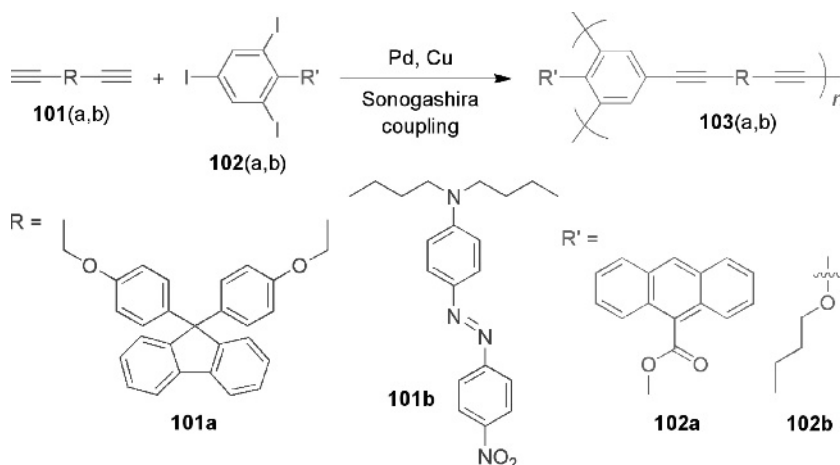


Fig. 24. Polycoupling of diynes with triiodides.

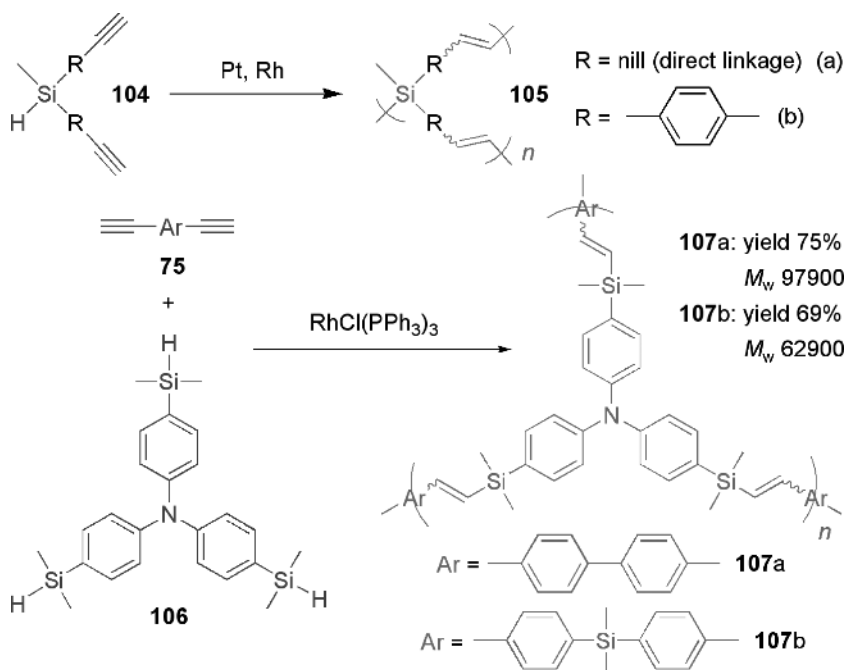


Fig. 25. Examples of alkyne-silane polyhydrosilylation.

reactions. A hyperbranched polymer with σ - π conjugation (**105b**) was prepared by Kwak and Masuda through Rh-catalyzed polyhydrosilylation of AB₂-type silane monomer **104b** (212). The resultant polymer contained 95% *trans* vinylene units and lost merely 9% of its weight when heated under nitrogen to a temperature as high as 900°C. Tang and co-workers synthesized hyperbranched poly(arylenevinylenesilane)s **107** in high yields through

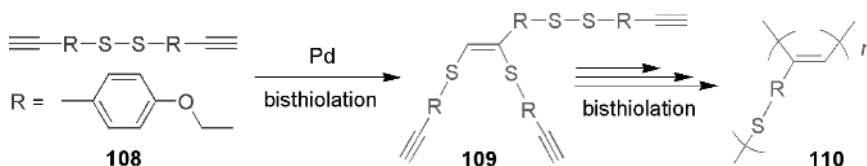


Fig. 26. Polybisthiolation of diethynyl disulfide.

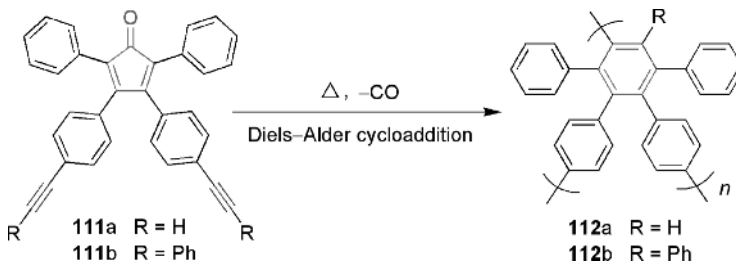


Fig. 27. Polycycloaddition of cyclopentadienonyldiynes.

the $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed $\text{A}_2 + \text{B}_3$ polyhydrosilylation of arylenediynes **75** with arylenetrisilane **106**. Gel permeation chromatography (GPC) measurements of the polymers gave M_w values in the range of $\sim 63,000$ – $98,000$, although the GPC analysis calibrated by the standards of linear polymers (e.g., polystyrene) often greatly underestimates molecular weights of nonlinear hyperbranched polymers. The polymers were film-forming and showed remarkable photonic properties.

In a unique self-addition polymerization, diethynyl disulfide **108**, an $\text{A}_2 \text{ B}_2$ -type monomer, underwent self-bisthiolation reaction in the presence of Pd catalyst (213). Through the formation of oligomeric species (e.g., **109**), hyperbranched polymer **110** with *Z*-substituted dithioalkene units were generated (Figure 26). The M_n and M_w values of polymer **110** were up to 8100 and 57,000, respectively. The stereoregular conformation of **110** was confirmed by ^1H and ^{13}C NMR spectral analyses. The polymer was soluble in common organic solvents, such as benzene, acetone, and chloroform. Insoluble gels were formed when the polymerization reactions carried out for a prolonged period of time.

Müllen reported the syntheses of three-dimensional hyperbranched polyphenylenes (*hb*-PPs) **112** by self-condensation of AB_2 monomers of 3,4-bis(4-ethynylphenyl)-2,5-diphenylcyclopentadienones **111** (Figure 27) (214). The *hb*-PPs are comprised of exclusively pentaphenylbenzene units and possess high DBs. Polymer **112a** is light-brown colored and poorly soluble in common solvents. The poor solubility is probably due to the dense packing of the phenyl rings or the rigid core structure of the polymer. From synthetic point of view, the polymer still contains a multitude of reactive terminal ethynyl groups, due to the steric effect and statistical rule. Polymer **112b** was characterized by dynamic light scattering (DLS) technique and was found to have an average diameter of about 15 nm. Polymers **112** thus can be considered as polydisperse *hb*-PP nanoparticles.

Voit and co-workers found that *hb*-PTAs could be synthesized from AB_2 monomers by 1,3-dipolar cycloaddition reaction. The polymerization of **113** was either initiated by heating or catalyzed by Cu(I) species (Figure 28) (215).

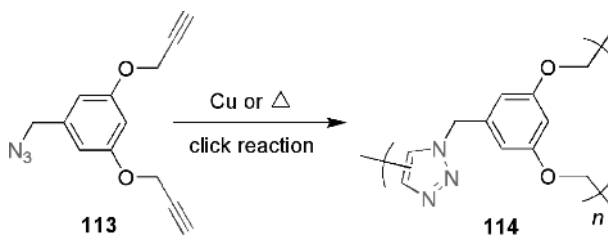


Fig. 28. Click polymerization of azidodiyne.

The thermal approach resulted in the formation of fully soluble 1,4- and 1,5-disubstituted PTAs, whereas the copper-catalyzed system gave insoluble 1,4-disubstituted PTAs. The AB_2 monomers of internal alkynes could be thermally polymerized to soluble *hb*-PTAs with high molecular weights. The AB_2 approach, however, suffers from the complexity in monomer synthesis and the risk of self-oligomerization during the monomer preparation and storage (203–205,216).

Acetylene cyclotrimerization is a century-old reaction for the effective transformation of monoyne molecules to benzene rings (3). Polycyclotrimerizations of diyne molecules can yield *hb*-PPs with repeat units knitted together by robust benzene rings. The diyne polycycloaddition, however, can easily run out of control to give cross-linked insoluble gels (217) and the challenge is thus how to manage to put the reaction under control. Tang and co-workers have taken this challenge and worked on the syntheses of hyperbranched polymers by A_2 -type diyne polycyclotrimerizations (30,31,36,218,222). Through elaborate efforts, especially those in the catalyst exploration and process optimization, Tang's group succeeded in the establishment of controlled polymerization systems and the syntheses of a wide variety of functional hyperbranched polymers by diyne polycyclotrimerizations (41).

The diyne polycyclotrimerization is unique in that it uses only a single type of A_2 monomer (Figure 29). The commonly taken synthetic approaches to hyperbranched polymers have been the utilization of polycondensation reactions of AB_n - ($n \geq 2$) and $(A_2 + B_3)$ -type monomers, where A and B denote the mutually reactive functional groups, for example, carboxy ($-CO_2H$) and hydroxy ($-OH$) groups, respectively. The AB_n approach, however, suffers from the synthetic difficulty in monomer preparation and the self-oligomerization during the monomer storage due to the existence of multiple mutually reactive groups in a single molecule. The $A_2 + B_3$ approach, on the other hand, requires stoichiometric balance of the two monomers in order to obtain polymers with high molecular weights and DB values. In contrast, the A_2 -type diyne monomers are stable at room temperature in the absence of a catalytic species and their polycyclotrimerization reactions are basically a unimolecular event. In other words, there are no complication of self-oligomerization and requirement of stoichiometric balance in the diyne systems, whose polymerizations can thus potentially produce hyperbranched polymers with very high molecular weights and DB values. Moreover, the linkage of the branches by the robust benzene rings in the three-dimensional space enables the synthesis of hyperbranched polymers with high stability and excellent processability, whereas the hyperbranched polymers

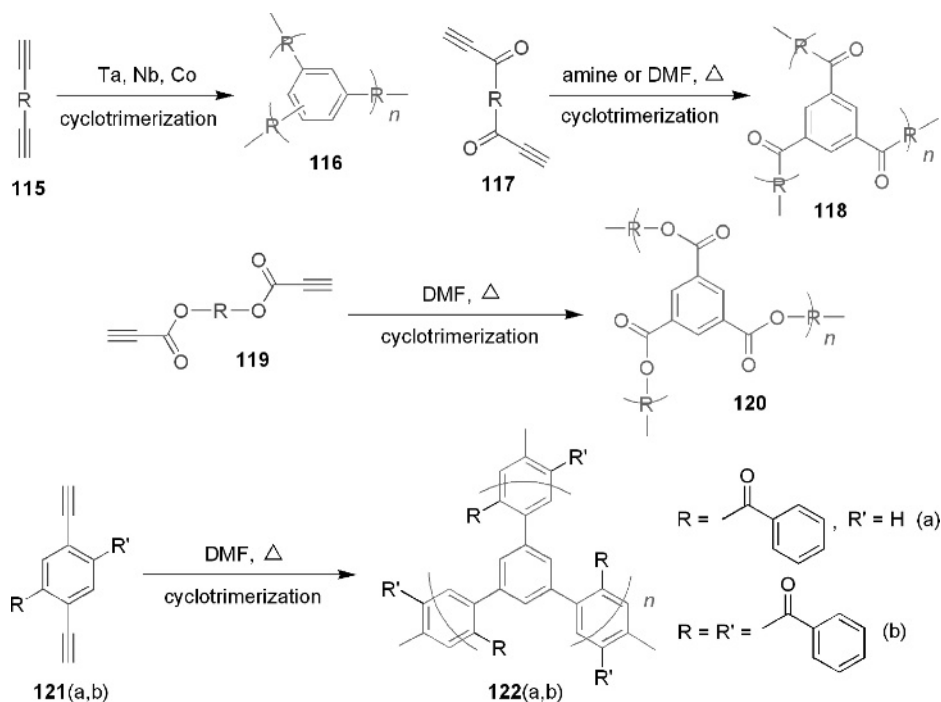


Fig. 29. Polycyclotrimerizations of diynes.

prepared from polycondensation are often unstable (e.g., undergoing hydrolysis degradation), and the linear (unsubstituted) PPs usually become insoluble when their molecular weights reach merely a few thousands, due to the regular packing of their linear chains.

Tang and co-workers have encountered the cross-linking problems during the course of developing the alkyne cyclotrimerization into a useful protocol for the syntheses of hyperbranched polymers. Initially, they used terminal diynes **115** bridged with alkyl chain or aromatic rings as monomers. Cross-linking or gelation was involved in the reactions, but through the molecular engineering of monomer structures and the optimization of polymerization conditions, they succeeded in the syntheses of hyperbranched poly(alkylenephénylene)s or polyarylenes with excellent solubility (223–242). The polymers have been found to show an array of novel properties, such as high thermal stability (up to $\sim 600^\circ\text{C}$), ready photocurability, efficient light emission (Φ_F up to 98%), large optical non-linearity, and low optical dispersion. The Ta- and Nb-catalyzed diyne polycyclotrimerizations can produce polymers with high molecular weights but have little intolerance to polar functional groups. Although the cocatalysts can polymerize diynes carrying certain polar groups, the resultant polymers generally have lower molecular weights and inferior optical and photonic properties than those prepared by the Ta and Nb catalysts due to the presence of hard-to-remove catalyst residues in the polymers.

Through further investigations, Tang and co-workers have found that the polycyclotrimerizations of bis(aroylacetylene)s **117** initiated by nonmetallic catalysts or organocatalysts such as piperidine proceed smoothly in an ionic mechanism and produce hyperbranched poly(aroylarylene)s (*hb*-PAAs) **118** with high DBs in high yields (243,244). The polymerization is tolerant of polar functional groups and is strictly regioselective, giving polymers with sole 1,3,5-regiostructure. The bis(aroylacetylene) monomers are, however, difficult to prepare. It takes many steps of reactions to prepare the monomers and the reactions involve the use of toxic heavy metals such as MnO_2 and CrO_3 . Analysis of the structure of monomer **117** reveals that this polymerization reaction works for diynes whose triple bonds are linked to electron-withdrawing groups. If the carbonyl linkage in the aroylacetylene can be replaced by an ester group, it will make the monomer synthesis much easier, because acetylenecarboxylic acid (or propiolic acid) is a commercially available compound and can be readily esterified with a diol to form a bipropiolate. If the bipropiolate monomer can be readily polymerized, it will pave the synthetic path to facile and economic syntheses of hyperbranched polymers. Tang's group has explored the possibility and demonstrated that polycyclotrimerizations of bipropiolate **119** in refluxed DMF can produce processable hyperbranched polymer **120** with perfectly branched structure and 1,3,5-regioregularity in high yields (245).

Along this line of research endeavor, it is envisioned that this polycyclotrimerization may also work for the monomers with electron-deficient groups linked to the acetylene triple bond via electronically communicable or transmissible units. Tang and co-workers designed a group of new aromatic diynes **121**, in which the carbonyl group is linked to the acetylene triple bond through a benzene ring to make the system electron-deficient. Indeed, polycyclotrimerizations of **121** in refluxed DMF worked well to afford 1,3,5-regioselective, processable, hyperbranched polymers **122** in high yields. This success helps us further understand the polymerization mechanism and shows that there is a vast room for extending the applicability of this polymerization route to other monomer systems (245).

Polymers from Triynes

Coupling Polymerizations. The utility of Glaser–Hay oxidative coupling reaction in the construction of carbon-rich polymers has been actively explored. The challenge has been how to enhance the processability of such polymers, for their linear chains often become insoluble even at the oligomer stage. Synthesis of hyperbranched polymers may help circumvent the processability problem because of the unique globular topology of the polymers, which contain numerous intramolecular voids or large free volumes that facilitate ready solvation. Tang and co-workers have been interested in the design and synthesis of carbon-rich *hb*-PDYs. Such polymers are expected to exhibit novel properties associated with their high density of diyne rods. The rich reactivity of the diyne functional group, for example, may endow the polymers with photosusceptibility, thermal curability, and metal-coordinating capability. To synthesize the *hb*-PDYs, Tang's group took an A_3 -coupling approach: the triyne monomers are knitted together by using Glaser–Hay oxidative coupling reaction. *hb*-PDYs **124**

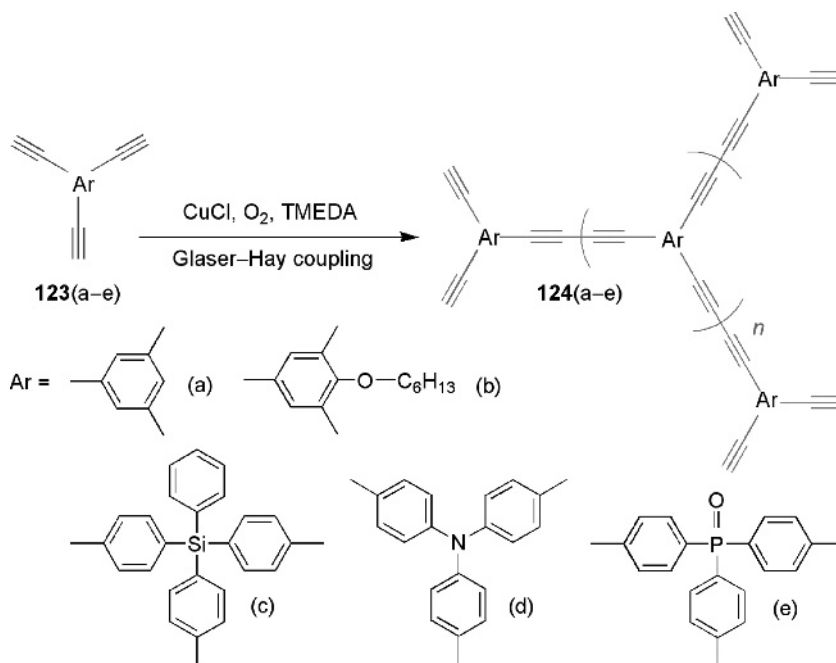


Fig. 30. Polycoupling of triynes.

containing various functional groups such as ether, amine, and phosphorous oxide were synthesized by the homopolycondensation of the corresponding triyne monomers **123** (Figure 30) (246). To prevent network from being formed, the polymerizations were stopped by pouring the reaction mixtures into acidified methanol before gel points.

Click Polymerizations. In their studies on the linear click polymerizations, Tang and co-workers developed a metal-free, thermally initiated, regioselective polycycloaddition process: simply heating a mixture of bis(arylacetylene) (e.g., **96**) and diazide (e.g., **97**) in a polar solvent such as a DMF/toluene mixture readily furnished linear PTAs with high regioregularities ($F_{1,4}$ up to $\sim 92\%$) in high yields (up to $\sim 98\%$) (204). Tang's group went one step further and tried to apply this process to the synthesis of *hb*-PTAs. An $A_3 + B_2$ approach was taken: easy-to-make and stable-to-keep triyne (A_3) and diazide (B_2) were used as monomers (Figure 31), in order to avoid the self-oligomerization problem encountered in the AB_2 systems. The A_2/B_3 monomers (**91/125**) were readily polymerized by the metal-mediated click reactions and the thermally activated cycloaddition reaction (247). The copper- and ruthenium-catalyzed click polymerizations afforded hyperbranched polymers with regular 1,4- and 1,5-linkages, that is, *hb*-1,4-PTA (**126**) and *hb*-1,5-PTA (**128**), respectively, whereas the thermally initiated polymerization system yielded regiorandom polymer *hb-r*-PTA **127**. All the polymers are readily soluble in common organic solvents, such as DCM, THF, and DMSO, representing the first examples of *hb*-PTAs with regioregular structures and macroscopic processability.

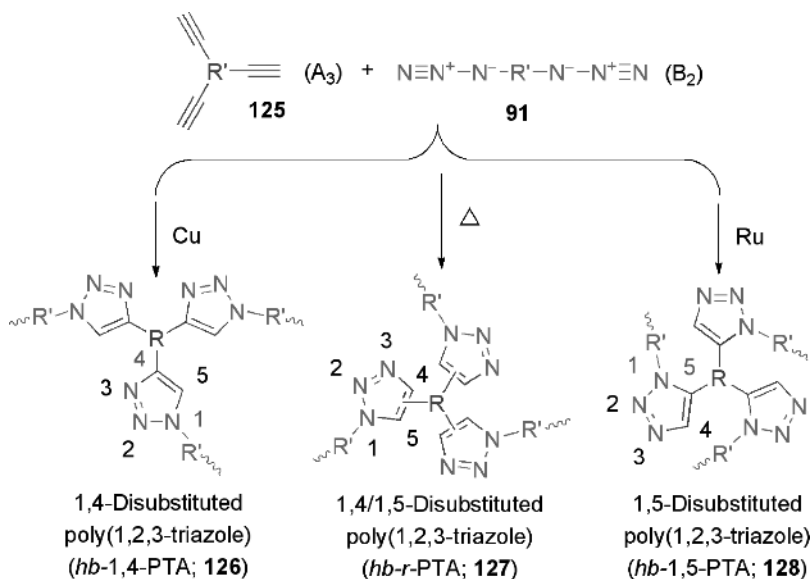


Fig. 31. Metal-mediated and thermally activated regioselective and regiorandom click polymerizations.

The thermal polymerization of **97**(6) and **123d** transformed the azide-alkyne monomers to *hb-r*-PTA **127**(6) in a high yield, whose M_w and PDI were estimated by GPC to be 11,400 and 2.7, respectively. As mentioned above, it is well known that the GPC system often underestimates the molecular weights of hyperbranched polymers. Tang and co-workers employed laser light-scattering technique to measure the absolute M_w of the polymer, which was found to be 177,500, about 14-fold higher than the value estimated by GPC. In an attempt to synthesize regioregular polymers, Tang and co-workers mixed **123d** and **97** with CuSO_4 /sodium ascorbate under “standard” click reaction conditions. Insoluble precipitates were immediately formed, which could not be dissolved in any common organic solvents. The standard recipe for the click reaction is therefore not suitable for the synthesis of processable *hb*-PTAs.

In the standard click system, the CuSO_4 /sodium ascorbate catalyst is used in a THF/water mixture. The incompatibility between the growing *hb*-PTA species and the aqueous medium may have induced the polymers to agglomerate and hence precipitate. To avoid the use of aqueous medium, Tang’s group used a nonaqueous click catalyst of $\text{Cu}(\text{PPh}_3)_3 \text{Br}$ to initiate the click polymerization of triyne **123d** with diazides **97** (Figure 32). The $\text{Cu}(\text{PPh}_3)_3 \text{Br}$ -catalyzed polymerization of **123d** with **97**(4) produced *hb*-1,4-PTA **129**(4) in ~46% yield, which was soluble in common organic solvents, including DCM, THF, DMF, and DMSO. Similarly, the polymerization of **123d** with **97**(6) carried out in the nonaqueous medium gave a soluble *hb*-1,4-PTA **129**(6) in ~52% yield. The Cu(I) catalyst has greatly accelerated the polycycloaddition process (e.g., 80 min at 60°C), in comparison to the thermally activated system (e.g., 72 h at 100°C) (247).

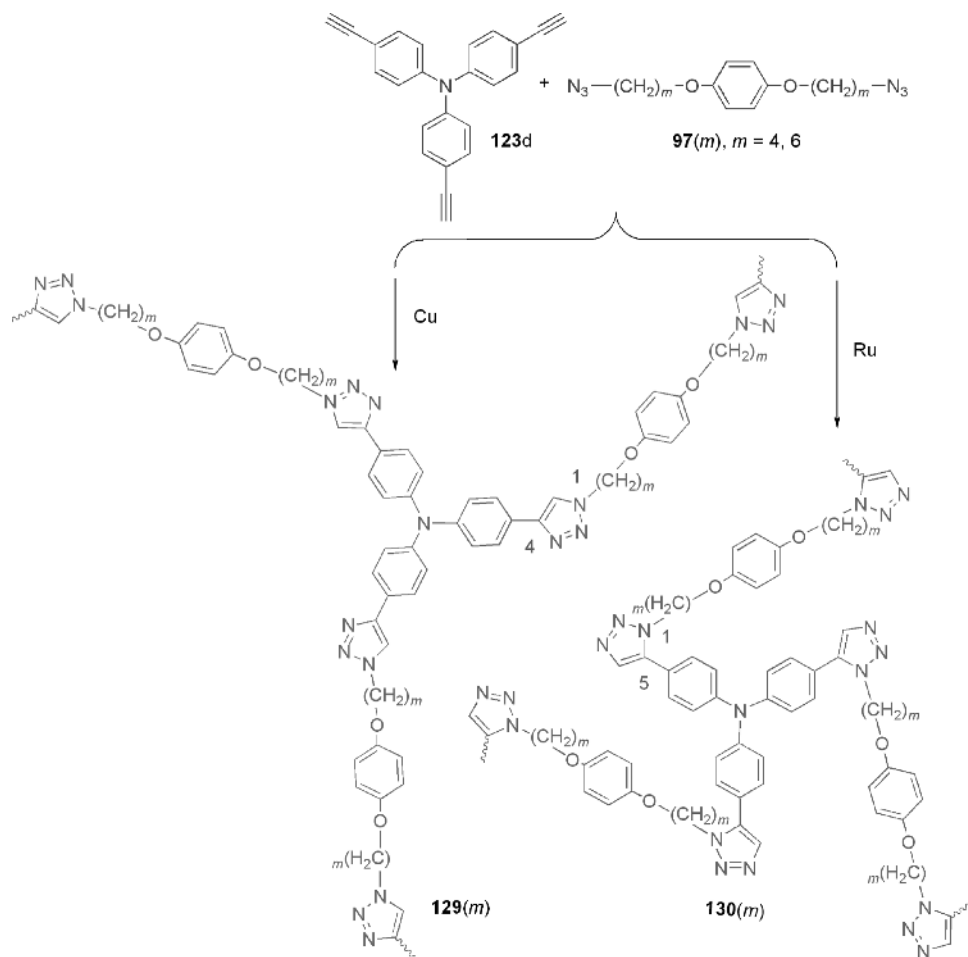


Fig. 32. Copper- and ruthenium-mediated 1,4- and 1,5-regioselective click polymerizations.

The 1,5-regioselective click polymerization of **123d** with **97** catalyzed by $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ proceeded even faster: for example, the polymerization of **123d** and **97(6)** produced soluble *hb*-1,5-PTA **130(6)** in $\sim 75\%$ yield in as short as 30 min. The preparation of the Ru(II) complex, however, is a nontrivial job that requires high synthetic skills (248). Dichloro(pentamethylcyclopentadienyl)-ruthenium(III) oligomer $(\text{Cp}^*\text{RuCl}_2)_n$ is a precursor to $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and can be facily prepared in high yield by refluxing $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and pentamethylcyclopentadiene in ethanol for a few hours. Although it was worried that the stable Ru(III) precursor might not work well as a click catalyst, $(\text{Cp}^*\text{RuCl}_2)_n$ smoothly catalyzed the polycycloaddition of **123d** and **97** at a moderate temperature (40°C), giving soluble *hb*-1,5-PTAs in high yields ($>83\%$) (247).

All the freshly prepared samples of hyperbranched polymers, including the regiorandom *hb-r*-PTA and regioregular *hb*-1,4- and *hb*-1,5-PTAs, are processable: thin solid films can be facily prepared by static casting or spin coating of

their 1,2-dichloroethane solutions onto solid substrates, such as silicon wafers, glass slides, and mica plates. All the polymers are stable, irrespective of the polymerization processes by which they were prepared. For example, the *hb*-PTAs lose 10% of their original weights in the temperature region of 374–407°C, indicative of their strong resistance to thermolysis. No glass transition temperatures were detected by differential scanning calorimetry (DSC) measurements when the polymers were heated up to 200°C.

The *hb*-1,4-PTA prepared by the $\text{Cu}(\text{PPh}_3)_3 \text{ Br}$ catalyst, however, gradually became partially insoluble upon storage under ambient conditions. One possible reason for this solubility change is the postpolymerization reactions of the polymers catalyzed by the metallic residues trapped in the *hb*-1,4-PTA samples. The Cu species may have coordinated with the “old” amino functional groups in the monomer repeat units and/or the “new” triazole rings formed during the polycycloaddition reaction. In a control experiment, a small amount of CuSO_4 /sodium ascorbate was mixed with the *hb*-1,5-PTA prepared from the Ru-catalyzed click polymerization. The polymer became insoluble within a few minutes, although it remained soluble after storage for several months in the absence of the externally added Cu catalyst. The Cu species may have catalyzed the cycloaddition reaction of the azido and ethynyl terminal groups in the periphery of the polymer, making it cross-linked and hence insoluble. Much effort has been devoted to removing the catalyst residues by washing the *hb*-1,4-PTA with amine solvents but the result was unsatisfactory because of the poor solubility of the polymer in the hydrophilic solvents.

Another possible reason for the solubility change of the *hb*-1,4-PTA with storage is the aggregate formation in the solid state. Theoretic simulation shows that, in the optimized conformation, the phenyl and triazole rings of the 1,4-isomer experience little steric interaction and can locate almost in the same plane. During storage, the cyclic plates of the *hb*-1,4-PTA may gradually pack, with the aid of the π - π stacking attractions between their aromatic units. This “physical cross-linking” process progressively knits more polymer molecules together and widens the three-dimensional networks, hence gradually decreasing the polymer solubility. On the contrary, there exists steric repulsion between the phenyl and triazole rings in the 1,5-isomer. The rings are thus twisted out of planarity to alleviate the involved steric effect. This twisted, nonplanar structure makes the cyclic units of *hb*-1,5-PTA difficult to pack in the solid state. The 1,5-regioregular polymers thus can maintain their good solubility for a long period of time. The *hb-r*-PTA prepared by the thermal polymerizations possesses a regiorandom structure and would be difficult to pack in the solid state. In addition, no transition metal catalyst was used in the thermal polymerization process; in other words, no metallic residues left in the polymer. The *hb-r*-PTA thus should have good solubility: indeed, the polymer remained soluble after it had been stored in the solid state under ambient conditions for several months.

Polymer Reactions. Compared to the reactions of linear polymers, hyperbranched polymer reactions are more interesting. Due to the high density of reactive groups in their peripheries, hyperbranched polymers can be postmodified by many functional groups to furnish a variety of polymers with new functional properties. For example, many hydrophilic brushes may be grafted onto the surface of hydrophobic hyperbranched polymers to give individual amphiphilic

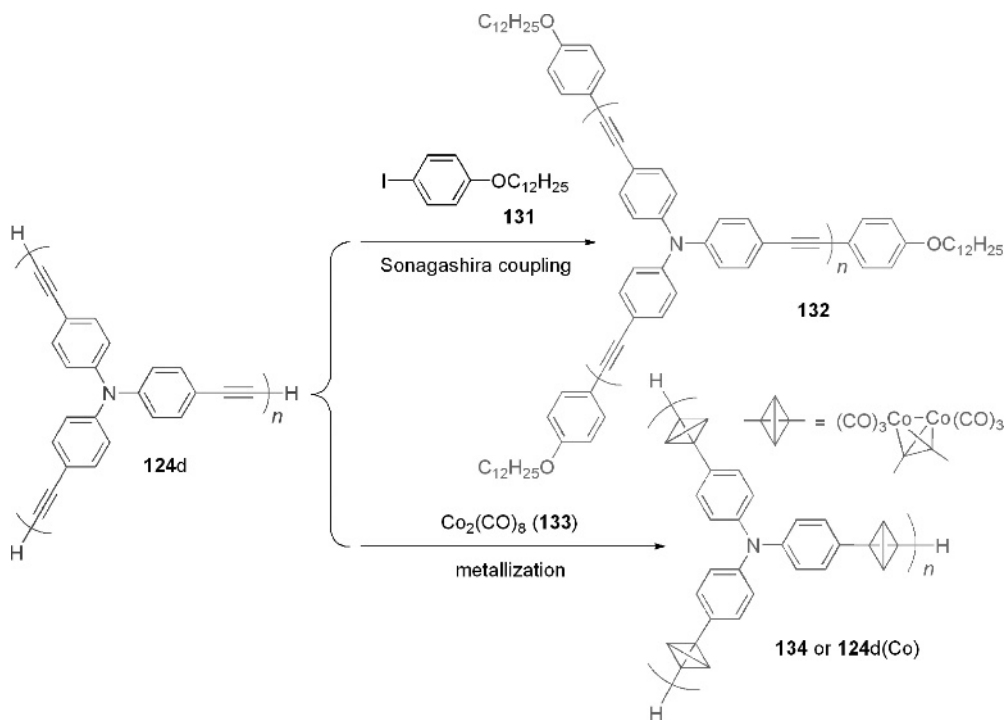


Fig. 33. End-capping and metal complexation of hyperbranched polydiynes.

nanoparticles that can be dispersed in water as macromolecular micelles. Spectroscopic analyses reveal that *hb*-PDYs contain terminal monoyne triple bonds, which allow the peripheries to be decorated by end-capping reactions. This is demonstrated by the coupling of **124d** with aryl iodide **131** (Figure 33) (31). Thanks to the long *n*-dodecyloxy group of the end-capping agent **131**, the end-capped polymer **132** shows much higher solubility than its parent form **124d**. No signal of resonance of the terminal acetylene proton is observed in the ^1H NMR spectrum, indicating that the end-capping reaction has proceeded to completion (246).

As alkynes are well-known and widely used ligands in organometallic chemistry (3), metallization of *hb*-PDYs can therefore be realized through the coordination interactions of their alkyne triple bonds with metallic species. Polymer **124d** contains numerous acetylenic triple bonds, which enable it to be readily metallized by the complexation with, for example, cobalt carbonyls **133**, to give organometallic polymer **134** (Figure 33) (31,246). Upon mixing **124d** with **133** in THF at room temperature, the solution color changed from yellow to brown, accompanied with carbon monoxide gas evolution. The mixtures remained homogenous toward the end of the reaction and the product was purified by pouring the THF solution into hexane. The resultant polymer complex is stable in air and the incorporation of the cobalt metal into the polymer structure is verified by spectroscopic analyses (246). The polymer–metal complex proves to be good precursor for magnetic ceramics. This example also serves as an excellent

demonstration of the utility of polymer reaction in the preparation of highly functionalized materials.

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ACOUSTIC PROPERTIES

Introduction

Sound speed and sound absorption measurements in polymers are useful both as a probe of the molecular structure of polymers and as a source of engineering design properties. As a molecular probe, acoustic properties are related to such structural factors as the glass transition (T_g), cross-link density, morphology, and chemical composition. Thus, acoustic measurements can be used as a measure of any of these factors, or at least to monitor changes that may occur as a function of time, temperature, pressure, or some other variable. As a source of engineering properties, acoustic measurements are used for applications such as the absorption of unwanted sound and the construction of acoustically transparent windows.

A few terms and their units should be defined because not all authors use these terms in the same way.

Acoustic refers to a periodic pressure wave. The term is synonymous with *sonic* and includes waves in the audio frequency range (ie, those that can be heard by the human ear) as well as those above the audio range (*ultrasonic* and *hypersonic*) and below the audio range. Acoustic measurement is a form of dynamic mechanical measurement, though sometimes the latter term is reserved for low frequency (see also DYNAMIC MECHANICAL PROPERTIES).

Absorption is a measure of the energy removed from a sound wave as a result of conversion to heat as the wave travels through the polymer. Absorption is synonymous with *dissipation* and is related to dynamic mechanical terms: damping, loss factor, and loss tangent. Absorption is a material property, usually given the symbol α , expressed in units of dB/cm, where a decibel (dB) is a unit based on ten times the common logarithm of the ratio of two acoustic energies. Alternatively, the natural logarithm can be used, in which case the units of α are Np/cm, where 1 Neper (Np) is equal to 8.686 dB. It is sometimes convenient to consider the amount of absorption for a specimen thickness equal to one wavelength, λ . This quantity $\alpha\lambda$ has units of dB (or Np). In contrast to absorption, the term *attenuation* includes energy loss due to scattering and reflection as well as absorption. Also, attenuation, in units of dB, is not a material property, but depends on specimen thickness and experimental configuration.

Frequency is the reciprocal of the period of the sound wave. Frequency f is expressed in Hertz (Hz), which is defined as one cycle per second. Sometimes frequencies are expressed in terms of radians. Since there are 2π radians in one cycle, the radian or circular (angular) frequency is given by $\omega = 2\pi f$.

Wavelength, λ (meters), is the distance between successive pressure (stress) peaks of the sound wave, and is the spatial periodicity of the wave. Frequency and wavelength are defined for a sinusoidal, harmonic (single-frequency) sound wave. More complicated, transient sound signals can be expressed as a superposition of harmonic waves with different frequencies.

Sound speed is a scalar quantity: the magnitude of the sound velocity vector. Sound speed will be denoted by v in this article, although c is sometimes used in the literature. Units of sound speed are meters per second (m/s).

This article covers the use of acoustics as a molecular probe of polymer structure and describes various acoustic applications of polymers. Enough theory and experimental details are given to make the presentation understandable, but the emphasis is on the experimental results for polymers. Most of the presentation is for small-amplitude waves in solid polymers. References to some specialized topics are given (see also MECHANICAL PROPERTIES; TEST METHODS).

Theory

This section covers the basic principles and governing equations for the experimental results that follow. Only the conclusions are presented here; the derivations are available in the references. Most of the presentation applies to linear wave propagation, ie, where Hooke's law is valid.

In an unbounded isotropic solid, two types of sound waves can be propagated. In the first type, called a longitudinal wave, the polymer vibrates in the direction of wave propagation. In the second type, called a shear wave, the polymer motion is perpendicular to the direction of propagation. Longitudinal waves are sometimes called dilatational, compressional, or irrotational waves. Shear waves are sometimes called distortional, isovoluminous, or transverse waves. These two types of waves propagate independently of one another and are the only two types possible in an unbounded solid.

Associated with each of the two modes of propagation, there is a sound speed and an absorption. Thus, four parameters are required to specify the acoustic properties of a solid isotropic polymer: longitudinal speed, shear speed, longitudinal absorption, and shear absorption.

Elastic Constants. One of the purposes of measuring sound speeds is to determine the elastic constants of the polymer. Longitudinal sound speed v_l , and shear sound speed v_s are related to elastic constants by

$$v_l = [(K + 4G/3)/\rho]^{1/2} \quad (1)$$

$$v_s = (G/\rho)^{1/2} \quad (2)$$

where K is the adiabatic bulk modulus (equal to the reciprocal of the adiabatic compressibility), G is the shear modulus, and ρ is the polymer density. Equations 1 and 2 are strictly valid only when absorption is low. The absorption corrections have been given (1); the analysis proceeds by making the moduli complex, with the real part equal to the modulus and the imaginary part proportional to absorption.

For an isotropic solid, there are only two independent elastic constants. These two can be taken to be K and G as above, but it is sometimes convenient to use other elastic constants, such as Young's modulus E and Poisson's ratio σ . These constants can be calculated from K and G using the standard relations

$$E = 3G/(1 + G/3K) \quad (3)$$

$$\sigma = 0.5 - E/6K \quad (4)$$

When the lateral dimensions of the specimen are much greater than the wavelength, a longitudinal wave is propagated, as in equation 1. When the lateral dimensions are much less than the wavelength, an extensional wave is propagated. For such a wave, the sound speed is given by

$$v_{\text{ext}} = (E/\rho)^{1/2} \quad (5)$$

This type of propagation is most often encountered in the lower frequency range and is an alternative method to equation 3 for determining E .

In a liquid, shear stresses cannot be supported and the only type of wave that is propagated is a bulk wave:

$$v_b = (K/\rho)^{1/2} \quad (6)$$

Other definitions of elastic constants are sometimes used (2). The Lamé constants λ and μ are related to K and G in the following manner:

$$\mu = G \quad (7)$$

$$\lambda = K - 2G/3 \quad (8)$$

Other elastic constants are defined starting from the generalized Hooke's law relation between stress σ and strain ε :

$$\sigma_i = C_{ij} \varepsilon_j \quad (9)$$

where $i, j = 1, \dots, 6$ and the C_{ij} are the elastic stiffness constants. The number of independent constants in the 6×6 C_{ij} matrix depends on the crystal symmetry of the specimen. In the most anisotropic case, there are 21 independent elastic stiffness constants or elastic moduli. As the crystal structure becomes more symmetric, the number of independent constants decreases. For a cubic crystal, there are three independent constants, and for an isotropic solid only two, C_{11} and C_{12} . The C_{ij} matrix in this case is specified by

$$C_{11} = C_{22} = C_{33} = \lambda + 2\mu = K + 4G/3 \quad (10)$$

$$C_{12} = C_{13} = C_{23} = C_{21} = C_{31} = C_{32} = \lambda = K - 2G/3 \quad (11)$$

$$C_{44} = C_{55} = C_{66} = (C_{11} - C_{12})/2 = \mu = G \quad (12)$$

All other terms are zero. In a liquid, there is only one elastic constant K . Note that most polymeric solids are isotropic, either because they are amorphous or because they are polycrystalline, with a random orientation of the crystallites (see AMORPHOUS POLYMERS; SEMICRYSTALLINE POLYMERS).

In comparing elastic constants measured acoustically with those obtained in a static (very low frequency) test, note that acoustic values are measured under adiabatic conditions, while static values are isothermal. The two types of bulk modulus measurements are related by the standard thermodynamic relation

$$\frac{K}{K_T} = \frac{C_p}{C_v} = 1 + \frac{TV\alpha^2 K}{C_p} \quad (13)$$

where K and K_T are the adiabatic and isothermal bulk moduli, C_p and C_v are the specific heat capacities at constant pressure and volume, T is absolute temperature, and α is the cubic thermal expansion coefficient (3). (It is unfortunate that the same symbol α is also used for absorption; in context, there should be no confusion.) For shear modulus

$$G_S = G_T = G \quad (14)$$

ie, the adiabatic and isothermal moduli are equal. This result follows from the fact that shear deformation occurs at constant volume. The magnitude of K/K_T is on the order of 1.1 for polymers, and increases as the temperature is raised above the glass-transition temperature (4). This effect is more pronounced in polymers than in metals.

In addition to the adiabatic or isothermal difference, acoustically determined elastic constants of polymers differ from static values because polymer

moduli are frequency-dependent. The deformation produced by a given stress depends on how long the stress is applied. During the short period of a sound wave, not as much strain occurs as in a typical static measurement, and the acoustic modulus is higher than the static modulus. This effect is small for the bulk modulus (on the order of 20%), but can be significant for the shear and Young's modulus (a factor of 10 or more) (5,6).

Strain dependence should also be considered when comparing acoustically measured elastic constants with statically measured values. As an example, for polyethylene at room temperature, the modulus is independent of strain up to a strain of about 10^{-4} (7). Beyond this point, the modulus decreases as the strain increases. Typically, acoustic measurements are made in the strain range 10^{-6} – 10^{-9} , where the moduli are strain-independent, but static measurements often exceed the linear strain limit (8).

Sound Absorption. The absorption of sound in polymers can be high, in certain ranges of temperature and frequency, up to four orders of magnitude higher than typical for metals. The mechanisms of the high absorption are various molecular structural relaxation processes involving motion of the entire long molecular chains, or of selected short molecular segments. Second-order transitions (9) are associated with the various molecular relaxation processes, where a given molecular relaxation motion fully participates in the thermodynamic response of the polymer at temperatures above the transition temperature, and does not participate (is "frozen") at temperatures below the transition temperature.

The average time required for the specific molecular motion is an important parameter of the relaxation process. This time is called the relaxation time, τ , and it is a function of temperature and pressure. When the frequency of the dynamic stress (acoustic or vibration) is in the range of $1/\tau$, the strains in the polymer lag the applied stress, because of structural molecular relaxation, which leads to conversion of mechanical energy to heat, and to damping of the acoustic wave (or mechanical vibration). This type of mechanical response of the polymer is called *viscoelastic behavior* (see VISCOELASTICITY). At low frequencies, $f \leq 1/\tau$, the molecules have time to respond to the applied stress and the structural molecular relaxation completely follows the applied stress. Therefore, stress and strain are in phase and mechanical energy loss is low. The sound speeds, and elastic constants, in this frequency region are denoted by the subscript 0. At high frequencies, $f \geq 1/\tau$, the period of the applied stress is too short for the given molecular relaxation process to occur. Stress and strain are again in phase, sound absorption is low, and the sound speeds and elastic constants in this frequency range are denoted by the subscript ∞ . The high frequency sound speeds are greater than the low frequency values, because of increased stiffness of the polymer at high frequencies (no molecular relaxation). It follows from the above discussion that sound speeds and elastic moduli of a polymer are frequency dependent in temperature (and pressure) ranges where a transition occurs. Also, at frequencies $f \approx 1/\tau$ there is a peak in the sound absorption per wavelength, $\alpha\lambda$.

The glass transition (qv), in the amorphous portions of the polymer, is the transition that dominates the acoustic properties of many polymers. At

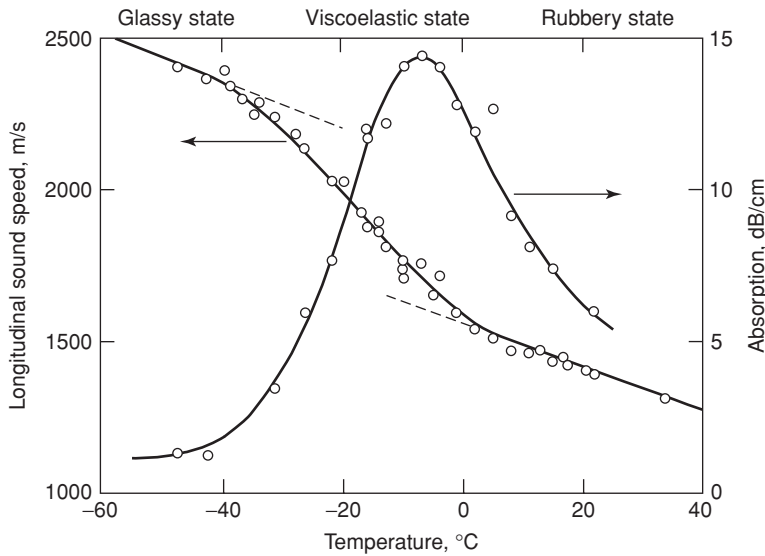


Fig. 1. The glass transition for poly(carborane siloxane)—longitudinal sound speed and absorption vs temperature at 1 MHz. Adapted from Ref. 49.

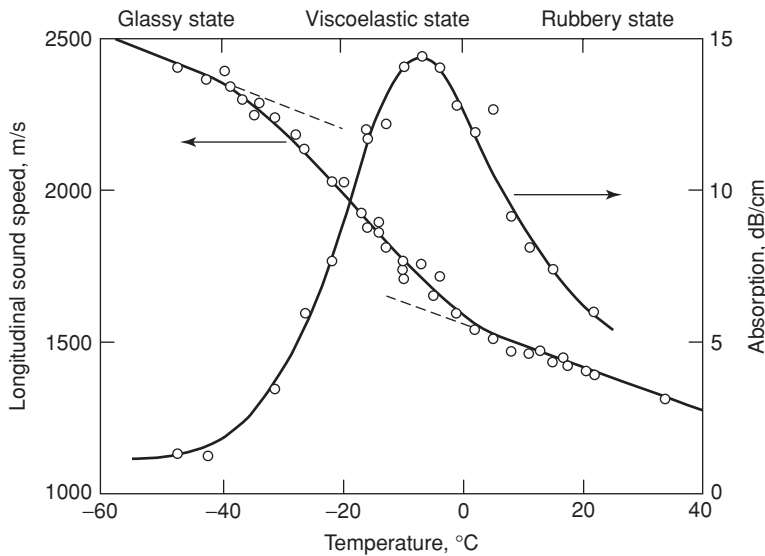


Fig. 2. The glass transition for a polyurethane (PTMG2000/MDI 3/BDO/DMPD)—shear modulus($\circ$) and loss factor($\square$) vs frequency at room temperature. Adapted from Ref. 50.

temperatures below the glass-transition temperature, T_g , or at frequencies $\geq 1/\tau_g$, the sound speeds have “glassy” values. At temperatures above T_g , or at frequencies $\leq 1/\tau_g$ the mechanical response of the polymer is ‘rubbery.’ (As shown in Figs. 1 and 2.)

The discussion that follows, of sound propagation in a lossy polymer, is limited to the case where the stress-strain relation in the polymer is linear. The effect of loss mechanisms on the mechanical response of polymers is included by modifying the stress-strain relations (eq. 9). At small strains, at which the behavior of the polymer is linear, the stress-strain relations are modified according to the Boltzman Superposition Principle (3,10). This principle states that the stress at a given point in the polymer is a function of the entire strain history at that point. Therefore, to each strain term in equation 9 is added an integral that represents contributions to the stress at a given time from strain increments at earlier times.

For example, the stress-strain relation for shear strain in an isotropic material is $\sigma = G\varepsilon$. For a viscoelastic material this relation is modified as follows:

$$\sigma(t) = G_{\infty}\varepsilon(t) - \int_0^{\infty} M(\Delta t)\varepsilon(t - \Delta t) d\Delta t \quad (15)$$

where $\sigma(t)$ and $\varepsilon(t)$ are the shear stress and strain, at a given point in the material, at time t , and G_{∞} is the high frequency (instantaneous) shear modulus. $M(\Delta t)$ is an 'after-effect,' at time t , of the strain at time $(t - \Delta t)$. Physically $M(\Delta t)$ is a relaxation function, since it describes the relaxation of molecular process excited by an imposed strain. Other stress-strain relations are modified similarly.

The Boltzman Superposition Principle is one starting point for inclusion of structural relaxation losses. An equally valid starting point is to include in equation 9 time derivatives (first-order and higher) of stress and strain. It can be shown that this approach is equivalent to the above integral representation (10). Finally, modified stress-strain relations, to describe viscoelastic response, have also been formulated using fractional derivatives (11).

A characteristic feature of viscoelastic response is the phase lag between the strain and the applied stress, due to the loss mechanisms. This phase difference is described by defining complex wave numbers, sound speeds, and elastic moduli, as follows. The relations that follow are developed specifically for a shear wave propagating through an absorbing polymer. Similar relations can be developed for longitudinal and extensional waves. Sound signals are either single-frequency (harmonic) waves, or transient signals that can be represented as a superposition of harmonic waves of different frequencies. A harmonic wave is a particularly simple case of wave motion, since in this case all quantities (stress, strain, particle displacement, etc) vary harmonically, at the same frequency. When the modified stress-strain relations are used to derive the equation for sound wave motion, the solution for a progressive, plane, harmonic wave is (11,12),

$$p = p_0 e^{-\alpha_s x} e^{i(k'_s x - \omega t)} \quad (16)$$

where p is the acoustic pressure at distance x from the reference point where the pressure is p_0 , $k'_s = 2\pi/\lambda_s$ is the real part of the shear wave number, where λ_s is the shear wavelength, and α_s is the sound attenuation coefficient, for shear waves, in nepers per meter. From equation 16 it follows that sound attenuation

can be formally included in the wavenumber by defining a complex wavenumber,

$$k_s^* = k_s' + ik_s'' = k_s' + i\alpha_s \quad (17)$$

The expression for the shear wave now has the same form, $p = p_0 \exp[i(k_s^* x - \omega t)]$, as in a lossless medium. The complex wavenumber defines a complex sound speed for the material as follows:

$$v_s^* = \frac{\omega}{k_s^*} \quad (18)$$

The propagation of the wave as a function of space and time is still determined by the phase velocity, v_s , which is related to the real part of the wavenumber, $v_s = \omega/k_s'$.

The elastic moduli of a lossy material are also complex quantities. The relation between the complex shear wave speed and the complex shear modulus is the same as the relation between the corresponding real quantities (eq. 2),

$$G^* = G' - iG'' = \rho v_s^{*2} \quad (19)$$

From equations 17–19 it follows that the sound attenuation coefficient is related to the complex elastic modulus,

$$(k_s'^2 - \alpha_s^2) + i(2k_s'\alpha_s) = \frac{\rho\omega^2}{G'(1+r^2)}(1+ir) \quad (20)$$

where r is called the loss factor, and is the ratio of the imaginary to the real part of the modulus,

$$r = \tan \delta = \frac{G''}{G'} \quad (21)$$

Equations 18–20 can be solved for the real and imaginary parts of the complex shear modulus (1),

$$G' = \rho v_s^2(1 - r^2)/(1 + r^2) \quad (22)$$

$$G'' = 2\rho v_s^2 r/(1 + r^2) \quad (23)$$

A material is characterized as low loss when the attenuation per wavelength, $\alpha\lambda$, is small, $\alpha\lambda \ll 1$ or $\alpha \ll k'$. Then the loss factor is small, $r \ll 1$, and the above relations simplify to

$$k_s'^2 = \frac{\rho\omega^2}{G'} \quad \text{and} \quad \alpha_s \lambda_s = \pi r \quad (24)$$

where the shear wavelength $\lambda_s = 2\pi/k_s'$. Equation 24 is an approximation that overestimates G' by 40% when $\tan \delta = 1$, and by 1% when $\tan \delta = 0.1$. From the above equations it follows that the complex modulus is closely related to the sound speed and absorption. In particular, the frequency dependence of the

real part of the elastic modulus (G') is similar to the frequency dependence of the corresponding sound phase velocity (v_s). Also, the frequency dependence of the loss factor, $\tan \delta$, is similar to the frequency dependence of $\alpha\lambda$, as shown in Figures 1 and 2.

Techniques for measuring the complex sound speeds and moduli of polymers are described in the section on test methods. The data shows that the real and imaginary components of the elastic moduli are frequency dependent. The frequency dependence is strongest for materials with high values of the loss factor r . Materials with frequency-dependent elastic moduli are called *dispersive*, and measurements and theory show that sound absorption mechanisms lead to *dispersion*. The real and imaginary part of an elastic modulus are related by the Kramers–Kronig relations, which are presented in the next section.

Kramers–Kronig Relations. The Kramers–Kronig (KK) relations are derived from the basic causality condition that the output strain cannot precede the input stress in any physical material (13–15). These relations apply to the complex, frequency-dependent elastic moduli of any material, and relate the real and imaginary components of the modulus. For example, for the complex shear modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, the Kramers–Kronig relations are

$$G'(\omega) - G_\infty = \frac{1}{\pi} PV \int_{-\infty}^{+\infty} d\omega' \frac{G''(\omega')}{(\omega' - \omega)} \quad (25)$$

$$G''(\omega) = -\frac{1}{\pi} PV \int_{-\infty}^{+\infty} d\omega' \frac{G'(\omega') - G_\infty}{(\omega' - \omega)}$$

where PV is the principal value of the integral and G_∞ is the high frequency ($\omega \rightarrow \infty$) modulus. Similar relations hold for the complex bulk modulus, $K^*(\omega)$. The KK relations are significant to the acoustic designer because they show that it is not possible to select the modulus (G') and the loss factor ($\tan \delta = G''/G'$) of a material independently. The KK relation can also be used to check the consistency of experimental data. Lack of agreement between the measured loss factor and that calculated from the modulus is an indication of some experimental error. Likewise, an analytical model for a complex modulus must obey KK in order to be a physically meaningful relation.

A useful, approximate local version of the KK relation was developed by O'Donnel and co-workers (14). This approximation relates the attenuation coefficient α to the frequency derivative of the phase velocity, $dv/d\omega$, as follows:

$$\alpha(\omega) = \frac{\pi\omega^2}{2c^2} \frac{dv}{d\omega} \quad (26)$$

Equation 26 applies both to shear and longitudinal waves, where α and v are related to the real and imaginary parts of the appropriate modulus by equations 22 and 23. Examples of application of the KK relations are given in References (16) and (17). The KK relations are particularly useful for discussion of the acoustical and mechanical behavior of polymers in the viscoelastic state. In this state

polymers have a high loss factor, and are used for underwater sound attenuation and for vibration damping. Equation 26 shows the trade-offs that have to be made in choosing a viscoelastic material for any specific sound attenuation or vibration damping applications. For example, it follows from equation 26 that, for shear waves, a high value of α_s requires a large $d\nu_s/d\omega$ in the viscoelastic region, which points to a material with a large relaxation strength $(G_\infty - G_0)/G_0$ and a narrow range of relaxation times. However, experience shows that in materials where the viscoelastic region occurs over a narrow range of frequencies the relaxation times, and therefore $\alpha_s(\omega)$, are strongly temperature dependent.

Equation of State. An equation of state in this context is a relation between pressure, volume, and temperature in a polymer, or a relation between any two of these variables holding the third constant. Frequently, these equations involve the bulk modulus. Given the equation of state of a polymer, one can correlate much experimental data and extrapolate to high pressure, where measurement is difficult.

By making reasonable assumptions about the form of the intermolecular potential, it was possible to calculate bulk modulus as an analytic function of volume (18). The calculation agrees fairly well with experimental data, and with the assumption that volume is the primary factor determining bulk modulus and, by extension, sound speed.

The Gruneisen parameter is widely used in polymer equation-of-state calculations. Bulk modulus is primarily a function of volume. The volume of a polymer can be changed by varying either the pressure or the temperature, leading to two equivalent expressions for the Gruneisen parameter γ :

$$\gamma = \frac{1}{2} \left(\frac{\partial K}{\partial p} \right)_T \quad (27)$$

$$\gamma = -\frac{1}{2\alpha} \left(\frac{\partial \ln K}{\partial T} \right)_p \quad (28)$$

For solid polymers, equations 27 and 28 give approximately the same value (19).

The Gruneisen parameter also plays a role in nonlinear acoustics, and it has been shown that there is a relation between the Gruneisen parameter and ultrasonic absorption: the larger γ is, the higher the absorption (19).

Transitions. In polymer science, a change from one state to another is a transition. An important transition is the glass to rubber transition. Processes occurring at temperatures below the glass transition are called secondary transitions, even if it is not known what the two states are. The transition is identified as such through its effect on some physical property, like dynamic mechanical damping. In acoustics, processes of this type are generally called relaxations (see GLASS TRANSITION; VISCOELASTICITY).

Acoustic properties vary with frequency. Assuming this behavior can be described by a single time called the relaxation time, the frequency dependence of either longitudinal or shear waves is given by

$$v^2 = v_0^2 + (v_\infty^2 - v_0^2) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (29)$$

$$\frac{\alpha\lambda}{\pi} = \frac{(v_{\infty}^2 - v_0^2)\omega\tau}{v_0^2 + v_{\infty}^2\omega^2\tau^2} \approx \frac{v_{\infty}^2 - v_0^2}{v_{\infty}^2} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (30)$$

where the subscripts 0 and ∞ refer to low and high frequency limiting values, respectively, and τ is the relaxation time (20). Note that $\alpha\lambda$ is a maximum for $\omega\tau = 1$. This absorption peak is identified with a particular relaxation process or transition in the polymer.

It is generally assumed that the temperature dependence of the relaxation time is of the Arrhenius form:

$$\tau = \tau_0 \exp (\Delta H/RT) \quad (31)$$

where ΔH is the activation energy for the relaxation process, R is the gas constant, and τ_0 is a constant. Since $\tau = 1/\omega = 1/2\pi f$ at the absorption maximum, an Arrhenius plot of $\ln f$ vs $1/T$ has a slope of $-\Delta H/R$. Each point on the plot is the reciprocal temperature of the absorption peak for a given logarithmic measurement frequency. Arrhenius plots are a particularly revealing way of examining acoustic data and interpreting results in terms of molecular structure. If the Arrhenius plot is not a straight line, it is assumed that ΔH is a function of temperature.

A significant result in equations 29 and 30 is that the acoustic properties depend only on the product $\omega\tau$, not on either variable separately. Since τ is a function of temperature, as shown in equation 31, the results of changing frequency are indistinguishable from those of changing temperature (neglecting any changes in v_0 and v_{∞}). The applicability of time-temperature superposition directly follows from the form of these equations. The analytic form of the temperature dependence of the relaxation time is, however, not specified in equations 29 and 30.

The discussion so far has been limited to the single relaxation time model. In polymers, however, the measured absorption and sound speed vs frequency curves are much broader than predicted by the single relaxation time model. This observation is interpreted to mean that there is a continuous distribution of relaxation times in polymer relaxation. There has been considerable analysis of various empirical distributions of relaxation times (21). Arrhenius plots are still valid in this case, but the activation energy is interpreted as an average value. Because of the distribution of relaxation times in polymers, measurements over a broad frequency range (several decades) are required to map out a given relaxation. Experimentally, it is difficult to cover such a wide range of frequencies without using several different pieces of equipment. Acoustic measurements are then sometimes supplemented with dielectric measurements. The governing equations are strictly analogous and, in many cases, dielectric and acoustic data can be displayed on the same Arrhenius plot. A full discussion is given in Reference 21.

Hysteresis Absorption. In the vicinity of a polymer transition, the absorption vs frequency at first increases, and then decreases. In a region removed from a transition, however, absorption typically increases linearly with frequency. This behavior is referred to as hysteresis absorption and is observed in both crystalline and amorphous polymers, and also in such materials as metals and rocks.

An absorption proportional to frequency can be expressed as $\alpha = cf = cv/\lambda$, or $\alpha\lambda = \text{a constant}$, ie, absorption per wavelength independent of frequency is another way of describing hysteresis absorption.

It is generally assumed that the description of polymer properties requires a continuous distribution of relaxation times. Numerous forms of the distribution function have been assumed, often for mathematical simplicity or on the basis of physical intuition. It has been found that a fractional power law distribution of relaxation times of the form τ^{-m} leads to hysteresis absorption with $\alpha\lambda = m\pi/2$ (Np), when $m \leq 1$ (3). The disadvantage of this model is that attempts to justify this distribution of relaxation times on a molecular basis quantitatively have not been successful. Mathematically, almost any experimental result can be expressed in terms of a distribution of relaxation times, but there may not be any physical significance to the distribution.

It has been suggested that the origin of the hysteresis absorption is in the time delay of reorienting the polymer among the large number of metastable equilibrium positions possible (8). The magnitude of the hysteresis absorption should depend on free volume because of two competing effects: the number of segments that reorient themselves decreases with decreasing volume, and the fraction of these segments that does not return to their original orientation increases with decreasing free volume. The second effect generally dominates, and the hysteresis absorption increases with decreasing free volume. The form of the volume dependence of the hysteresis absorption was originally assumed to be a simple linear dependence (8), but is probably more complicated (22).

Inhomogeneous Media. The inhomogeneities considered here are on the macroscopic rather than microscopic scale. The first topic considered is layered media. To begin with, consider a flat boundary between two media of different acoustic properties. When an acoustic wave traveling through one medium encounters at normal incidence the boundary with another medium, some of the acoustic energy is reflected and some transmitted (12). The sound power transmission coefficient T is given by

$$T = \frac{4Z_1Z_2}{(Z_1 + Z_2)^2} \quad (32)$$

where the subscripts refer to the two media, and the acoustic impedance Z is given by

$$Z = \rho v \quad (33)$$

Thus, the transmission properties depend on the impedance match of the two media. For a flat plate in a liquid medium

$$\frac{1}{T} = \cos^2 k_2 l + \frac{1}{4} \left(\frac{Z_2}{Z_1} + \frac{Z_1}{Z_2} \right)^2 \sin^2 k_2 l \quad (34)$$

where $k = \omega/v$, subscript 2 refers to the plate, subscript 1 refers to the liquid, and l is the thickness of the plate (12). The extension of these results to multiple layers of plane parallel plates at oblique angles of incidence, including the effect

of absorption, has been considered by several authors (23,24). Some work has been done to determine polymer properties from the acoustic properties of plate transmission (25). Reflections from multiple concentric cylinders (26) and from spheres (27) have also been examined.

Another class of inhomogeneous materials of increasing practical importance is fiber-reinforced composites (qv). Usually the matrix is a polymer, such as epoxy. The reinforcement may be polymeric, such as Kevlar, or nonpolymeric, ie, glass, steel, or graphite. For a unidirectional composite with transverse isotropy, there are five independent elastic constants or moduli: C_{11} , C_{13} , C_{33} , C_{44} , and C_{66} , (28,29). Absorption measurements are particularly difficult to make on such composites. Frequently, the measured attenuation has a significant contribution as a result of scattering from the reinforcement; this is sometimes referred to as geometric dispersion.

Foamed materials can be considered to be the opposite of fiber reinforcement (see CELLULAR MATERIALS). In a foam, the gas inclusions make the matrix softer and weaker. The introduction of even small amounts of air into a polymer can have a dramatic effect on acoustic properties. One approach to modeling the effect of a small air content ϕ on the acoustic properties of a rubber is to use Kerner's theory of composites (30):

$$K = K_0(1 - \phi)/(1 + 3K_0\phi/4G_0) \quad (35)$$

$$G = 3G_0(1 - \phi)/(3 + 2\phi) \quad (36)$$

$$\rho = \rho_0(1 - \phi) \quad (37)$$

where the subscript 0 refers to solid rubber and the Poisson's ratio of rubber is assumed to be one-half. Longitudinal and shear sound speeds can be calculated from these equations. Absorptions can be included by making the moduli complex. In addition to Kerner's model, other models for polymer composites with microscopic inclusions have been developed (31–33). One application of such composites is for absorption of underwater sound (34). Also, this type of composite can be used as a sound-absorbing lining, at ultrasonic frequencies, in immersion tanks (35).

Nonlinear Wave Propagation. It is assumed that most acoustic measurements are made in the linear wave propagation region, ie, where Hooke's law applies. Polymers as a class, however, are more nonlinear than other solids. Nonlinear wave propagation is therefore significant in some cases.

Extensive studies of nonlinear propagation in fluids have been made (36). Although derived for fluids, the results have been applied to a number of solid polymers (37,38). In these studies, the isentropic equation of state for pressure p , in terms of density ρ , is expanded to the form

$$p - p_0 = A[(\rho - \rho_0)/\rho_0] + (B/2)[(\rho - \rho_0)/\rho_0]^2 + \dots \quad (38)$$

The quantity B/A is the parameter of nonlinearity. From thermodynamic evaluations,

$$\frac{B}{A} = 2\rho_0 v \left(\frac{\partial v}{\partial p} \right)_T + \frac{2v\alpha T}{\rho_0 C_p} \left(\frac{\partial v}{\partial T} \right)_p \quad (39)$$

where α is the thermal-expansion coefficient. The extension of this analysis to solids involves third-order elastic constants (39). There are few measurements of third-order elastic constants for polymers. One method for determining these constants is to measure the velocities of longitudinal and shear waves in the material as a function of various applied static stresses. Hughes and Kelly (40) give the following values for polystyrene: $\ell = -18.9 \pm 0.3$, $m = -13.3 \pm 0.3$, $n = -10.0 \pm 0.1$, in units of GPa. It is found that the third-order elastic constants are related to the Gruneisen parameter. Relationships have also been found between B/A and the Gruneisen parameter (41). This is another manifestation of the fact that the Gruneisen parameter is a fundamental measure of the nonlinear behavior of a polymer.

One particular interest in nonlinear propagation in polymers is for what is known as a parametric sonar. In this application, two colinear high frequency beams of slightly different frequency are propagated through a medium. In a perfectly elastic medium, the two waves would propagate indefinitely without interacting. In a real medium containing nonlinearity, however, there is an interaction that produces waves with the sum and difference frequencies of the two beams. Thus, a low frequency beam is generated with the highly directional character of a high frequency beam. Polymers are particularly attractive in this application because of their high nonlinearity and high absorption. Hence, the efficiency of the frequency conversion is high, and the high frequency source components are absorbed relatively quickly while the low frequency difference wave propagates much further (37).

Additive Properties. It is reasonable to assume that different chemical groups should contribute differently to the macroscopic properties of polymers. Rigid aromatic groups would be expected to raise the elastic modulus (and sound speed), while flexible aliphatic groups would be expected to lower the modulus. A quantitative expression of this idea is known as the method of additive properties and has been extensively developed and reviewed by Van Krevelen (42). In this method it is assumed that various polymer properties are determined solely from the additive contributions of their constituent groups. The groups are assumed to have unique properties that are independent of their environment. The uniqueness assumption has proven to be valid in many cases.

The simplest example of additive properties states that the molar mass M of a polymer is the sum of the molar masses of the component groups in the repeat unit. A similar equation holds for the molar volume and leads to an expression for the polymer density,

$$M = \sum N_i M_i, \quad \rho = \frac{\sum N_i M_i}{\sum N_i V_i} \quad (40)$$

Table 1. Group Contributions to U_H and U_R

Group	$U_H, (\text{cm}^3/\text{mol})(\text{cm/s})^{1/3}$	$U_R, (\text{cm}^3/\text{mol})(\text{cm/s})^{1/3}$
$-\text{CH}_2-$	880	675
$-\text{CH}(\text{CH}_3)-$	1,875	1,650
$-\text{CH}(\text{C}_6\text{H}_5)-$	4,900	4,050
$-\text{CHCl}-$	1,725	1,450
$-\text{C}(\text{CH}_3)(\text{COOCH}_3)-$	4,220	3,650
$-\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_5-$	11,000	8,700
$-\text{O}-$	400	300
$-\text{OCOO}-$	1,575	1,200
$-\text{CONH}-$	1,750	1,400

where M_i is the mass of the i th component group, N_i is the number of such groups in the repeat unit, and V_i is the molar volume of the i th component group.

As applied to sound speed, the method of additive properties begins with work on liquids, where it was empirically found that

$$R = Vv^{1/3} \quad (41)$$

where V is molar volume, v is sound speed, and R is a constant, for each liquid, known as Rao's constant or the molar sound speed (43). R is an additive property, but v is not. Since a liquid cannot support a shear stress, the sound speed in a liquid can be calculated by equation 6, so that, in terms of modulus, Rao's rule (eq. 41) can be written as

$$R = V(K/\rho)^{1/6}, \quad K = (M/V)(R/V)^6 \quad (42)$$

In applying Rao's rule to solid polymers, it should be kept in mind that the longitudinal sound speed (eq. 1) includes not only a bulk modulus term, but also a shear modulus term that must be taken into account (5). This has been done for both linear and cross-linked polymers (44–47). Van Krevelen has named the additive variable for bulk modulus the Rao function, U_R , and for shear modulus the Hartmann function, U_H . The bulk and shear moduli can then be calculated from the equations,

$$K = (M/V)(U_R/V)^6 \quad \text{and} \quad G = (M/V)(U_H/V)^6 \quad (43)$$

Group contributions to U_R and U_H for some common molecular groups, taken from Van Krevelen (42), are listed in Table 1. The bulk and shear moduli for various polymers calculated using the values from Table 1 are in good agreement with experimental values (42). Sound speeds can be predicted from the calculated elastic moduli and densities.

A limitation of the above method is that some of the required group properties are not available. This is particularly a hindrance when trying to predict the properties of polymers with novel compositions. To overcome this limitation, a new additive contribution method has been developed (48) in which the polymer

properties are expressed in terms of topological variables or connectivity indices. In this method properties are determined primarily from the summation of contributions of atoms and bonds instead of groups. The pertinent properties of the handful of elements found in most polymers have been determined, allowing for the prediction of properties for most polymers having a known structure.

Sound as a Molecular Probe

Acoustic measurements have been employed as a molecular probe of polymer structure to study different aspects of molecular structure: transitions, curing (UV, visible light, thermal) (qv), density, and chemical composition in both synthetic and biological polymers.

Transitions.

Glass Transition. The acoustic properties of polymers, when plotted over broad ranges of frequency and temperature, are usually dominated by the glass transition. Typical data are shown in Figures 1 (49), and 2 (50). The change in slope of the sound speed at about -40°C is independent of frequency and is equal to the dilatometric value of T_g . This method of determining T_g has been applied to a number of polymers (51–53). The change in slope at -40°C occurs as a result of the discontinuity in the thermal expansion coefficient and the strong dependence of modulus on density. The value of T_g determined in this manner is dependent on the density, but independent of frequency. It is important to keep in mind the difference between the glass-transition temperature, T_g , which is a fixed number, and the glass transition, which is a process that occurs at different temperatures depending on the frequency of the measurement.

Figure 1 shows the variation, in the glass-transition region, of the longitudinal sound speed and absorption with temperature at a fixed frequency, for poly(carborane siloxane). Figure 2 shows the real part of the shear modulus and the loss factor as a function of frequency, at a fixed temperature, for a polyurethane. From equation 24 it follows that the variation of the shear sound speed and absorption is similar. The longitudinal sound speed changes from ~ 1500 m/s in the rubbery state to ~ 2300 m/s in the glassy state. The change in the shear sound speed in the polyurethane is from ~ 50 to ~ 900 m/s. The large change in the shear sound speed through the glass-transition region is typical for polymers.

In small amounts, crystallinity raises T_g by limiting the motions of the amorphous regions. As the degree of crystallinity increases, the glass transition, which occurs only in the amorphous regions of the polymer, tends to be masked and may even be difficult to determine, as in the case of polyethylene. At the glass transition of an amorphous polymer, some 10–50 repeat units become free to move in cooperative thermal motion of individual chain segments, involving large-scale rearrangements of the chain backbone. Below the glass transition, these large-scale motions become frozen and cannot occur. Major changes in many physical properties, including acoustic properties, take place at the glass transition (16).

Most studies of glass transition have focused on the absorption. By repeating the measurements of Figure 1 at higher frequencies, an Arrhenius plot of

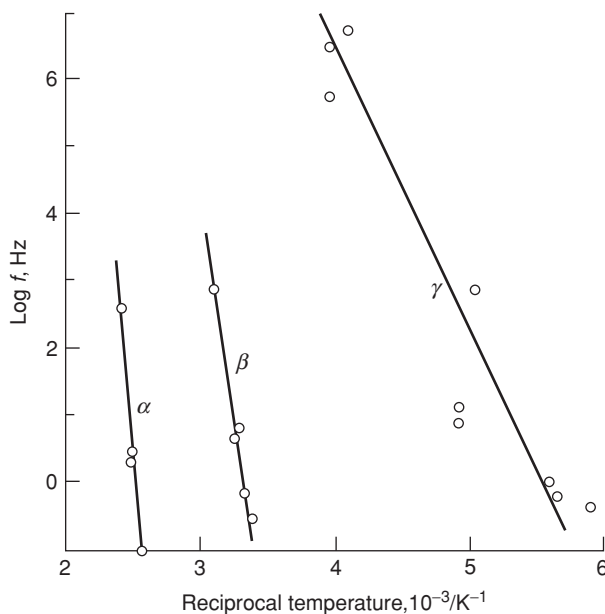


Fig. 3. Arrhenius plot for α , β , and γ transitions in polytetrafluoroethylene.

the log of test frequency vs reciprocal temperature of peak absorption can be made, yielding an activation energy of about 100 kJ/mol; this is a typical value for glass transitions, albeit on the low side. A compilation of literature data for seven semicrystalline polymers has been given (54). An example of the results for polytetrafluoroethylene is shown in Figure 3. For the glass (ie α) transition, the activation energy is 700 kJ/mol, the highest value in this group. Note that an Arrhenius plot, such as Figure 3, is a convenient way to keep track of multiple transitions in a given polymer and in correlating data from various sources and various experimental techniques. Acoustic measurements over a limited range of temperature and frequency may indicate a relaxation, but it is not always clear what mechanism is producing the effect. A plot like Figure 3 is very useful in identifying the relaxation.

In the case of isotactic polypropylene, two glass transitions were found acoustically—as well as by using other techniques (55). It was shown that whereas the crystalline phase is isotactic, the amorphous phase, which gives rise to the glass transitions, includes atactic as well as isotactic chains. The atactic amorphous phase has the lower T_g .

Through consideration of Arrhenius plots of the glass transition of 14 polymers, the empirical observation was made that the lines for the various polymers all seemed to converge in one of two regions: 10^8 Hz for the more sterically restricted polymers, and 10^{18} Hz for sterically nonrestricted polymers (56). This observation shows that there is a direct relation between dilatometric T_g and activation energy: the higher the T_g , the higher the activation energy. In addition to the data discussed (54,56), an even more complete summary of acoustic data on solid polymers has been compiled (57).

The glass transition provides the behavior that has the most practical significance. Secondary transitions are too small to have much effect and polymers are not generally practical to use at their melting point. The glass transition shows a large change through the transition and can be used both above and below the transition. The glass transition is a second-order phase transition, in which the primary thermodynamic functions are continuous but their first derivatives are discontinuous. For example, the specific heat capacity vs temperature is continuous through the glass transition but the derivative of the specific heat is discontinuous. The sound speeds and elastic moduli are continuous but their derivatives are discontinuous.

The most successful phenomenological model of the frequency dependence of the elastic constants around the glass transition is the Havriliak–Negami (HN) model (58)

$$(G - G_{\infty})/(G_0 - G_{\infty}) = 1/(1 + (i\omega\tau)^{\alpha})^{\beta} \quad (44)$$

where G_0 is the relaxed modulus (the rubbery modulus in this case), G_{∞} is the unrelaxed modulus (the glassy modulus in this case), τ is the average relaxation time, and α and β are dimensionless parameters with values between 0 and 1 that, roughly, describe the width and asymmetry of the glass transition.

One application of the HN equation is that one can demonstrate an empirical relation between the height and width of the loss factor peak at the glass transition. Using measured properties of a number of polyurethanes and calculations using equation 44, it was shown (59) that high loss factor peaks are narrow and broad peaks are low. A simple relation was found between the height and width of the peak in shear sound absorption per wavelength, $\alpha_s\lambda$, as a function of frequency—namely, the product of height times width is a constant equal to 1.5 decades of frequency. These relations are important in design of polymer treatments for sound absorption and vibration damping. An example of the above relations is shown in Figure 4.

It is commonly observed that the temperature and frequency dependence of polymer relaxations are related. This is expressed qualitatively as the time–temperature superposition principle, or the frequency–temperature equivalence, or the method of reduced variables. A mathematical way to describe this behavior is to note that if the dispersion relation for the relaxation [eqs. 29,30, and 44] depends on frequency and temperature only through the product of frequency and a function of temperature, $\omega\tau(T)$, then the effect of a change in frequency is indistinguishable from a change in temperature. In other words, a measurement at low temperature is equivalent to a measurement at high frequency and a measurement at high temperature is equivalent to a measurement at low frequency—“equivalent” meaning that the same elastic constants and sound speeds are obtained. A material for which this equivalence holds is called thermorheologically simple. Polymers are thermorheologically simple to a greater or lesser extent. The principle is extremely useful as it allows a wide frequency range to be obtained by simply changing temperature; a frequency range that would be obtained directly only with great difficulty, if at all. A plot of modulus vs log frequency, such as Figure 2, is called a master curve.

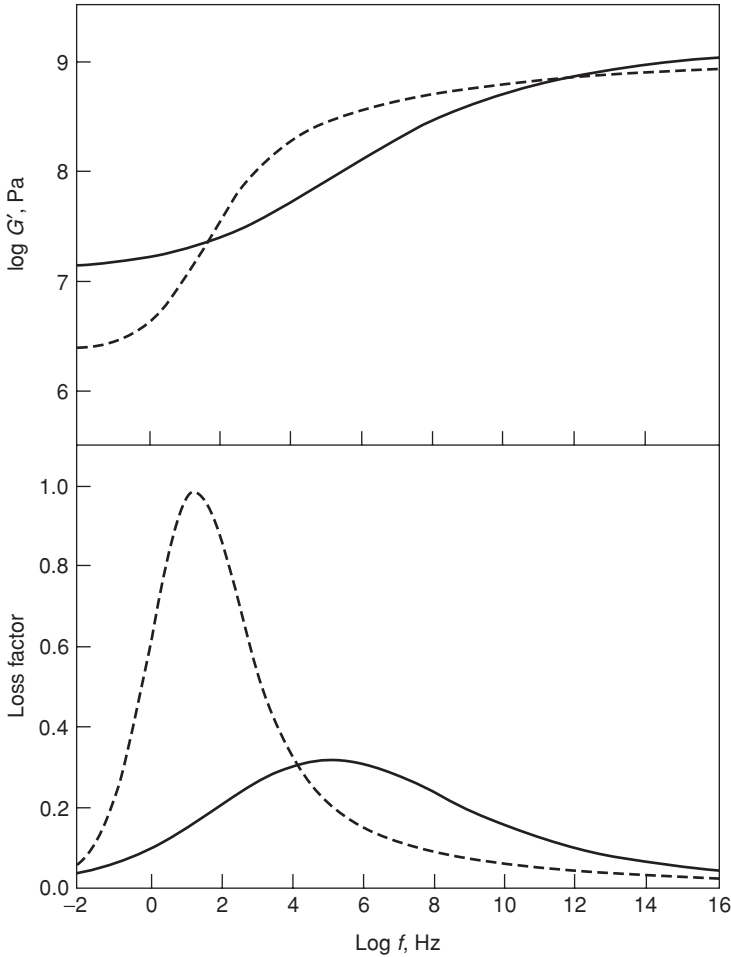


Fig. 4. Phase-separated polyurethane (solid line) compared with phase-mixed polyurethane (dashed line). The shear modulus and the loss factor are plotted as a function of frequency, through the glass-transition region. From Ref. 50.

The relation between temperature and frequency dependence is described by a function known as the shift factor, defined as the change in log frequency that is equivalent to a change in temperature. The most common analytical form of this equation is the WLF equation (3,60)

$$\log a_T = - \frac{c_1(T - T_0)}{c_2 + (T - T_0)} \quad (45)$$

where a_T is the change in log frequency due to a change in temperature from a reference temperature T_0 to a measurement temperature T , and c_1 and c_2 are constants for a given polymer and reference temperature. [An extensive listing of c_1 and c_2 values is given by Ngai and Plazek (61).] This equation has been found

to apply in general to polymers above their glass-transition temperatures. Below the glass-transition temperature, the Arrhenius equation has been found to be applicable (21)

$$\log a_T = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (46)$$

where ΔH is the activation energy and R is the gas constant. The combination of a master curve and a shift factor curve then contains all of the temperature- and frequency-dependence information for the given polymer.

As the temperature of a polymer is raised through the glass-transition of a polymer, the moduli and sound speeds change from the high value of the glassy state to the low value of the rubbery state. There has been considerable study of the relation of the glass-transition temperature to the molecular structure of the polymer, which then relates to the elastic constants of the polymer. Examples include molecular weight, polarity, and steric effects (62). T_g increases asymptotically with increasing molecular weight according to the relation (63)

$$T_g = T_{g,\infty} - A/M_n \quad (47)$$

where $T_{g,\infty}$ is the glass-transition temperature at infinite molecular weight, A is a constant for each polymer, and M_n is the number-average molecular weight. The presence of polar groups in the polymer increases the T_g . For example, poly(*cis*-1,4-isoprene) (natural rubber), with the chemical structure $-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-$, has a glass-transition temperature of -73°C while polychloroprene (neoprene), with the chemical structure $-\text{CH}_2\text{CH}=\text{C}(\text{Cl})\text{CH}_2-$, has a T_g of -50°C . The substitution of a chlorine atom for a methyl group (with comparable size) raises the transition temperature. A correlation has been observed between the log of the average relaxation time τ in the HN equation and the reciprocal of the glass-transition temperature (64).

Secondary Transitions. Most acoustic studies of polymer transitions have been of the glass transition, but some work has been done on secondary transitions, ie, those occurring below the glass transition. One transition that has received a fair amount of study is the β relaxation in polycarbonate (65). The transition has an activation energy of 40 kJ/mol and arises from a combination of phenylene and heteroatom motion. This value, one-half to one-third the value for a glass transition, is typical of secondary transitions which involve smaller segments of the polymer. This study also found a correlation that often, but not always, exists between acoustic and dielectric measurements. The two sets of data fall on the same line and sometimes cover complementary frequency ranges. Activation energies for some secondary transitions are even smaller. The δ relaxation in poly(ethyl methacrylate), owing to ester ethyl group rotation, has an activation energy of only 9 kJ/mol (66). A study of the activation energy for the δ relaxation in polychlorotrifluoroethylene showed it to be 30 kJ/mol, and possibly associated with an uncoiling of the polymer chain. This work emphasized the usefulness of pressure as a complementary variable to temperature and frequency in the study of molecular relaxations in polymers (67).

Most of the polymers discussed so far have been linear and either amorphous or semicrystalline. The γ transition in some cross-linked epoxies is similar to that of linear polymers (68). The activation energy is 40 kJ/mol and is due to the motion of the glycol ether group.

In a detailed discussion of secondary transitions in glassy, amorphous polymers, it is shown that the β transition in polymethacrylates is caused by motion of the entire $-\text{COOR}$ group (69). This same study notes that the Arrhenius plot lines for secondary transitions of various polymers all converge to a common frequency, about 10^{13} Hz; this is the same type of empirical behavior observed for the glass transition (56).

Melting Transition. The final transition to be considered is the melting transition. Measurements at 12 MHz on linear polyethylene show that there is an absorption peak in the vicinity of the melting point and that the sound speed decreases rapidly in this region (70). Other studies show that the absorption peak does not shift with frequency and therefore is not a relaxational process (71); this type of behavior can indicate a fluctuation mechanism. The loss factor can be high in the molten region, but the shear modulus is very low. Therefore, polymers are not generally used in the molten state for damping applications.

Curing. Early measurements on polyesters, phenolic, and melamine polymers made during the curing process showed a significant rise in sound speed as the materials passed from the uncured stage, through the gel stage, to the fully cured condition (72). Absorption increased during the gel stage and then dropped in the fully cured stage (see GEL POINT). Increasing the cure temperature increases the final sound speed and decreases the final absorption. Later work on epoxies has emphasized the difficulty in making such measurements because of temperature changes caused by the reaction exotherm, the increase of T_g , as curing proceeds, and the viscoelastic nature of the epoxies (73).

Most cure studies are done on solid polymers that have undergone various cure cycles. One study focused on the γ relaxation in diamine-cured epoxies (74). This relaxation is due to the motion of the glycol ether group, $-\text{CH}_2\text{CHOHCH}_2\text{O}-$, and is common to epoxies made with different resins and curatives. An advantage of the acoustic method is that the measurements can be made below T_g , so that the measurement process does not alter the molecular structure being measured. It was found that the absorption curve increased in height, width, and temperature as the cure temperature was raised. The activation energy was found to be dependent on the degree of cure, increasing from about 60 kJ/mol during the early stages of cure to as much as twice that value (depending on the curative) in the postcured state, as a result of steric hindrance (75).

In a curing study on resole-type phenolic, no correlation between sound speed and curing temperature was found, but both longitudinal and shear absorption decreased as the cure temperature increased (76). This behavior was related to a transition in the phenolic at about 70°C.

Another study considered the effect of cross-link density on the acoustic properties of some diamine-cured aliphatic epoxy polymers (77,78). In this case, the cross-link density was varied by altering the chain length of the aliphatic curative. The acoustic properties in the vicinity of the glass transition were found to shift—unaltered in shape—by an amount equal to the glass-transition

temperature. Thus, a plot of sound speed and absorption vs $T - T_g$ gave universal curves for all polymers. In contrast, it has been shown that when the cure temperature and time are varied for another epoxy system, not only does the molecular relaxation shift, but there are also structural changes (79). Also, ultrasonic systems have been developed to monitor the cure of epoxy resins and to characterize the cure state. This is done by measuring the ultrasonic signal velocity and ultrasonic attenuation throughout the cure process (80,81).

Density. For organic liquids, it is observed that the higher the density, the higher the sound speed. Similar behavior is found with solid polymers. For polyethylene, a plot of extensional sound speed vs density is shown in Figure 5 (82). The data appear to be well represented by a straight line, though Rao's relation for liquids (eq. 41) would suggest that $\nu^{1/3}$ should be plotted, rather than ν . The scatter in the data is such that it is inconclusive whether the linear or the cubic relation gives the best result (5,83). In the polyethylene studies, the chemical composition of the polymer was the same. Different densities resulted primarily from different degrees of crystallinity. Another study considered variations in chemical composition and plotted longitudinal sound speed vs density for 14 different polymers (52). Good correlation was found, except for the halogenated polymers. In a study of resole-type phenolic, it was found that the longitudinal sound speed correlated with density not only at room temperature, as the other studies had found, but also as a function of temperature, all on the same plot (76).

From a practical point of view, it is important to remember the correlation between sound speed and density when comparing data from different sources for the same polymer. As can be seen from Figure 5, even small changes in density produce large changes in sound speed. This type of behavior was mentioned previously in connection with the effect produced in the vicinity of the glass transition. Also, because of the direct relation between density and crystallinity, sound speed measurements provide a means of measuring or monitoring polymer crystallinity.

From a fundamental point of view, sound speed can be said to depend primarily on volume because of the volume dependence of the intermolecular potential. Any mechanism that changes the volume of the polymer will change the sound speed by an amount determined by the volume change, and not by the mechanism producing the volume change. This is true for such diverse mechanisms as degree of crystallinity, branching, cross-linking, and temperature and pressure changes.

Sound Speed. A number of studies have been made on the effect of variations in molecular structure on sound speed. Replacing the hydrogen atoms in polyethylene with fluorine atoms lowers the sound speed, in line with the expectation that there will be a reduction in intermolecular attraction due to the larger size of the fluorine atoms (53). In this case, the sound speed also decreases because the polymer density increases. Similarly, in a series of poly(alkyl methacrylates), the sound speed decreases as the alkyl side-chain length increases (84). Again, there is a volume increase that reduces the intermolecular attraction.

The introduction of a phenylene group into an epoxy polymer structure raises the sound speed. These polymers and other phenylene-containing polymers, such as polycarbonate, polysulfone, and poly(ether sulfone), all have relatively high sound speeds (65). The aromatic ring imparts a conformational

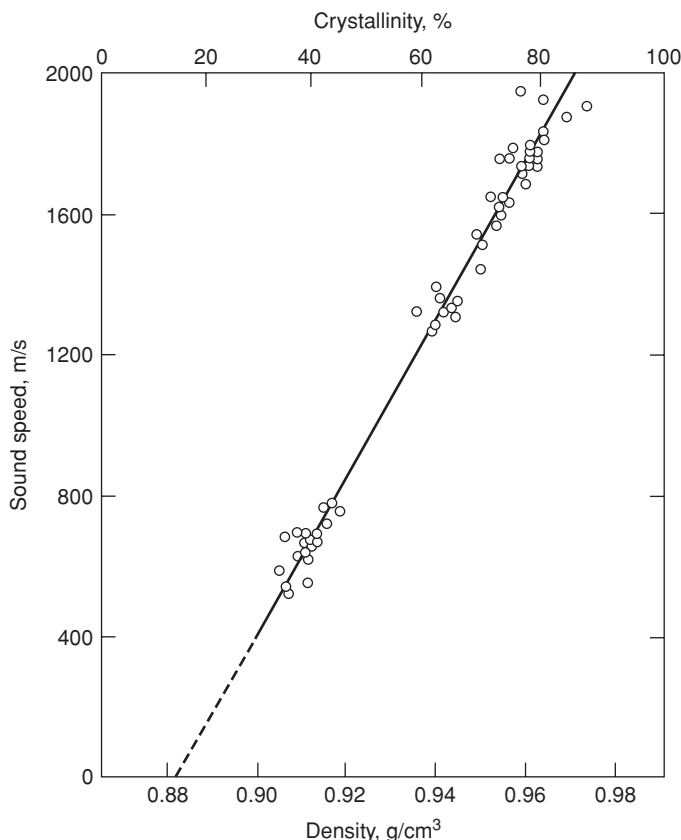


Fig. 5. Extensional sound speed vs density and crystallinity for polyethylene.

rigidity to the backbone structure of these polymers, which is responsible for the high sound speed.

So far, the molecular variations discussed were made in homopolymers. A number of studies have been made on multiple-component systems, either chemical combinations such as copolymers or physical combinations such as plasticized polymers. As an example of the former, the sound speed in copolymers of methyl methacrylate and methacrylic acid increases in a regular manner as the mole fraction of methacrylic acid increases (85).

Several studies have been made of the effect of various plasticizers (qv) on poly(vinyl chloride) (86–88). In addition to shifting the glass transition, the plasticizers lower the sound speed. Since the sound speed in the plasticizers is less than that in poly(vinyl chloride), this is not surprising. Water can be considered as a plasticizer. Its effect on poly(methyl methacrylate) is the lowering of sound speed expected from a plasticizer (89).

The sound speed in polymer blends (qv) varies with composition in a manner similar to that in copolymers. For blends of polystyrene and poly(vinyl methyl ether), the sound speed increases as the weight percent of the higher-sound-speed polystyrene increases, but the relation may not be linear because of phase

inversion caused by polymer incompatibility (90) (see COMPATIBILITY). The effect of carbon black (qv) on sound speed in rubber is more complicated than in blends, but the qualitative effect is to increase the sound speed (91). In contrast, the addition of iron oxide to rubber decreases the sound speed (92). In this case, the higher density of the filler dominates, rather than the higher modulus. A decrease in sound speed is also observed when voids are present (79). In this case, the lower modulus of the voids dominates, rather than the lower density.

Additive Properties. Many of the studies cited have considered the effect on the sound speed, of substituting one component for another or an aromatic for an aliphatic. One is thus led to the possibility that there is a certain sound speed associated with each chemical component. This is indeed the case, as was first demonstrated for liquids, and then for solid polymers.

For liquids, it was empirically found that the Rao constant R of equation 41 was an additive property, which was expressed in terms of individual atom values (43). Since the measurements also showed that aromatic compounds have higher sound speed than aliphatic compounds, an R value was also assigned to the carbon-carbon double bond. It was later pointed out that better results are found by considering bonded atom groups such as C-H, C-C, O-H, etc (93). A further refinement was to use radical increments, $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{C}_6\text{H}_5$, etc (94).

In an extensive account of the application of the method of additive properties to numerous polymer properties, component values determined from measurements on organic liquids were used and good agreement between predicted and measured sound speeds were found (42). This approach has now been applied to numerous linear polymers (45,46,95).

Results have also been obtained for the density and bulk modulus of cross-linked epoxies (44). Agreement is about the same as for linear polymers. Finally, shear modulus has been related to an additive property (47). These results, along with the additive results for density and bulk modulus, show how both longitudinal and shear sound speeds are related to molecular components.

Biological Polymers. Although biopolymers are structurally and morphologically different from the polymers discussed so far, biopolymers are similar in their long-chain polymeric nature. Also, many of the techniques of studying other polymers apply to biopolymers. Perhaps the most common observation on the acoustic properties of biopolymers is that the absorption is a linear function of frequency, ie, a hysteresis absorption (96,97). Because of its appearance in very different biopolymers, hysteresis is presumed to arise whenever there is a broad spectrum of relaxation times (96), perhaps through the same mechanism postulated for other polymers (97).

In measurements on liver tissue, the absorption was found to be high, compared with blood, and sensitive to variation of protein structure (96). By making measurements on tissue that had successively more extensive destruction of the gross tissue structure, it was found that the absorption is largely independent of cellular and subcellular structure. Absorption occurs primarily at the macro-molecular level. A comprehensive compilation of ultrasonic properties of mammalian tissues that gives absorption results for 30 different tissue types has been prepared (98). One conclusion of this work was that since tissue condition or preparation or both may influence ultrasonic properties, *in vivo* measurements should be encouraged. Most measurements in biopolymers have been made with

longitudinal waves, but some data are available for shear sound speed and absorption (99). Some progress has been made in characterizing the pathological state of a tissue in a study that also examines hysteresis absorption and presents a theory in terms of a distribution of relaxation times (100).

The dynamic elastic properties of soft tissues, and methods of measurement (including acoustic techniques) are reviewed by Sarvazyan (101). The corresponding review for hard tissues is given by Lees (102). Propagation of acoustic waves in human tissue is of interest because acoustic waves, both at audio and ultrasonic frequencies, are widely used in medicine for imaging and identification of tumors. Recently, nuclear magnetic resonance techniques have been developed for imaging the propagation of shear waves in biopolymers (103).

Applications

In this section, results of acoustic measurements that are used directly in some applications are presented without molecular interpretation.

Sound Speed. Representative sound speeds measured at room temperature, ambient pressure, and at frequencies in the MHz range are given in Table 2, taken from various sources (49,76,85,87,104–106,108,109). (Abbreviations for polymers listed in Table 2 are given in Tables 3 and 4.) The longitudinal speeds vary from about 1000 to 3000 m/s, a range intermediate between that of metals (3000–6000 m/s) and that of liquids (900–1500 m/s). Shear speeds vary from about 700 to 1400 m/s, a range lower than the 1600 – 3300 m/s range for metals. Densities are also listed in Table 2 because the speed in a given polymer varies with density. Owing to the usual variations from batch to batch of polymer, the sound speeds given in Table 2 can easily differ by 1% or more from other measurements.

Table 2 is representative of the variation in speeds found from one polymer type to another. Considerable variations within one type can also occur. For example, within a series of epoxy polymers (47,77), the longitudinal speed can vary from 2000 to 3000 m/s. For poly(vinyl chloride), plasticizers (87) can lower the longitudinal speed from 2380 to 1490 m/s. The variation of sound speed with density (crystallinity) has already been mentioned (82) and is illustrated in Figure 5.

Many sound speed measurements in polymers have been made as a function of temperature, usually over a range of 100 K or less. Qualitatively, the speeds decrease as the temperature increases. Except in the vicinity of a transition, the decrease is usually linear and of greater magnitude than for metals. Representative values of the rate of decrease of sound speeds with temperature are given in Table 5. Measurements were made over a 300-K temperature range for poly(ethylene terephthalate) (111) and for styrene–butadiene–styrene block copolymers (112). Measurements for a series of polyimides were made over a 600-K range (113).

Cryogenic temperature measurements of both longitudinal and shear speeds have been made for many polymers. For polyethylene, polytetrafluoroethylene, polyformaldehyde (acetal resin), and polyamides (114,115) at low temperature, there is a plateau in the temperature dependence where sound speed

Table 2. Sound Speeds^a for Various Polymers

	Density, g/cm ³	Longitudinal, speed v_l , m/s	Shear speed v_s , m/s	Ref. ^b
General polymers ^c				
Poly(methacrylic acid)	1.285	3350		85
Phenolic polymer	1.22	2840	1320	76
Epoxy polymer	1.205	2820	1230	
Polyhexamethylenedipamide	1.147	2710	1120	
Polycaprolactam	1.146	2700	1120	
Poly(methyl methacrylate)	1.191	2690	1340	
Polypropylene	0.913	2650	1300	
Polyphenylquinoxaline	1.209	2460	1130	76
Polyoxymethylene	1.425	2440	1000	
Polyethylene, high density	0.957	2430	950	
Polystyrene	1.052	2400	1150	
Poly(vinyl chloride)	1.3916	2376		87
Poly(vinyl butyral)	1.107	2350		
Polysulfone	1.24	2297		104
Poly(phenylene oxide)	1.08	2293		104
Polycarbonate	1.19	2280		104
Poly(ethylene oxide)	1.208	2250		
Poly(4-methyl-1-pentene)	0.835	2180	1080	105
Polyurethane, polyether-based	1.104	2130		49
Poly(acrylonitrile-butadiene-styrene)	1.023	2040	830	105
Polyethylene, low density	0.922	1970		
Poly(vinylidene fluoride)	1.779	1930	775	
Polyurethane, polybutadiene-based	1.008	1660		49
Poly(carborane siloxane)	1.041	1450		
Polytetrafluoroethylene	2.177	1380		
Polydimethylsiloxane	1.045	1020		
Epoxy polymers ^d				
DGEBA/DETA	1.190	2910		106
DGEBA/TETA	1.184	2810		106
BDGE/MPDA	1.227	2579		77
DGEBA/D	1.162	2520		107
BDGE/PDA	1.179	2423		77
BDGE/HDA	1.152	2301		77
BDGE/DDA	1.094	2033		77
DGEPG/TETA	1.116	1561		106
DGEPG/DETA	1.108	1561		106
Urethane polymers ^d				
PTMG650/TDI/TMAB	1.118	1744		108
PTMG650/TDI/MBOCA	1.119	1717		108
PTMG1000/TDI/TMAB	1.089	1632		108
PTMG1000/TDI/MBOCA	1.085	1606		108
PTMG2000/TDI/TMAB	1.047	1545		108
PTMG2000/TDI/MBOCA	1.045	1547		108
PTMG2692/TDI/TMAB	1.035	1523		108
PTMG2692/TDI/MBOCA	1.035	1523		108
Filled polymers				
DGEBA/TETA/39% glass spheres	1.050	2879		106
Poly(vinyl chloride) + DOP	1.290	2120		87
Poly(isobutylene-isoprene) + carbon	1.130	1973		
Polychloroprene + carbon	1.420	1720		
1,2-Polybutadiene + carbon	1.100	1567		
cis-1,4-Polyisoprene + carbon	1.120	1524		

^aMeasurements made at room temperature, ambient pressure, and frequencies in the MHz range.^bTaken from Ref. 109 except as noted.^cSee Table 3.^dSee Table 4.

Table 3. Trade Names of Some Common Polymers

ABS	Generic abbreviation for a terpolymer of acrylonitrile, butadiene, and styrene
Cycolac	Poly(acrylonitrile–butadiene–styrene) or ABS (Marbon)
Delrin	Poly(methylene oxide) or polyformaldehyde (DuPont)
Kel-F	Poly(chlorotrifluoroethylene) (3M)
Kynar	Poly(vinylidene fluoride) (Pennwalt)
Lexan	Polycarbonate (General Electric)
Lucite	Poly(methyl methacrylate) (ICI)
Marlex	Polyethylene (and other polymers) (Phillips Petroleum)
Mylar	Poly(ethylene terephthalate) (DuPont)
Nylon	Generic description of a polyamide, including nylon-6 (polycaprolactam) and nylon-6,6 (polyhexamethylene adipamide)
Plexiglas	Poly(methyl methacrylate) (Rohm & Haas)
Teflon	Poly(tetrafluoroethylene) (DuPont)
TPX	Poly(4-methyl-1-pentene) (Mitsui)
Zytel	Poly(hexamethylene adapamide) or nylon-6,6 (DuPont)

Table 4. Abbreviations for Epoxy and Polyurethane Polymers

BDGE	Butanediol diglycidyl ether
BEPD	2-Butyl-2-ethyl-1,3-propanediol
D	Tri(2-ethyl hexoate) salt of tri(dimethyl amino methyl) phenol
DDA	Dodecanediamine
DEPD	2,2-Diethyl-1,3-propanediol
DETA	Diethylenetriamine
DGEBA	Diglycidyl ether of bisphenol A
DMPD	2,2-Dimethyl-1,3-propanediol
DOP	Diethylphthalate
EMPD	2-Ethyl-2-methyl-1,3-propanediol
HDA	Hexanediamine
MBOCA	Methylene bis(<i>o</i> -chloroaniline)
MDI	4,4'-Diphenylmethane diisocyanate
MDIL	Modified MDI (liquid)
MPDA	<i>m</i> -Phenylene diamine
PDA	Propanediamine
PPG	Polypropylene glycol
PTMG	Poly(tetramethylene ether) glycol
PTMAB	Poly(tetramethylene diaminobenzoate)
RDGE	Resorcinol diglycidyl ether
TDI	Toluene diisocyanate
TETA	Triethylenetetramine
TMAB	Trimethylene-bis- <i>p</i> -aminobenzoate
Z	Aromatic eutectic mixture of methylene dianiline, MPDA, and phenyl glycidyl ether
13BDO	1,3-Butanediol
14BDO	1,4-Butanediol

Table 5. Temperature Dependence of Sound Speeds^a

Polymer	$-dv_l/dT$, m/(s·K)	$-dv_s/dT$, m/(s·K)	Ref.
Polysulfone	1.38		104
Polystyrene	1.5	4.4	110
Poly(phenylene oxide)	1.52		104
Poly(methyl methacrylate)	2.5	2.0	109
Polyphenylquinoxaline	3.0	1.3	76
Polycarbonate	3.58		104
Poly(acrylonitrile–butadiene–styrene)	4.1	1.5	105
Poly(4-methyl-1-pentene)	4.2	1.8	105
Phenolic polymer	7.1	4.0	76
Polyethylene, high density	9.6	6.8	109
Polypropylene	15.0	6.7	109

^aMeasurements made in the vicinity of room temperature, at ambient pressure, and at frequencies in the MHz range.

becomes independent of temperature. All relaxation processes have become frozen out. For poly(methyl methacrylate), however, there is no plateau (116). Even at very low temperature, the methyl group attached to an ether link can rotate. Fluoropolymers also exhibit more complicated behavior (117). Some measurements in the range 0.2–2 K on two epoxy polymers indicate a peak rather than a plateau (118).

Measurements as a function of frequency are not common because of the experimental difficulties. Most data are available only at three or four frequencies covering about one decade. Qualitatively, the speeds increase as the frequency increases. Longitudinal measurements on vulcanized rubber compounds at five frequencies from 0.04 to 10 MHz are available (119), as well as longitudinal and shear results for a nitrile–butadiene vulcanizate at 2, 5, and 10 MHz (120). By using time–temperature superposition, longitudinal and shear measurements at 0.5, 1, and 2 MHz as a function of temperature on an epoxy polymer have been extended to a very wide frequency range (121).

Measurements as a function of pressure are available in a few cases. Qualitatively, the speed increases as the pressure increases. Most studies have only gone as high as 200 MPa. Measurements have been made on polystyrene (122), poly(methyl methacrylate) (122), polyethylene (122), polyisobutylene (123), natural rubber vulcanizate (124), plasticized poly(vinyl chloride) (125), and polychlorotrifluoroethylene (67). Other measurements have been made up to 300 MPa for high density polyethylene (126), and up to 500 MPa for poly(methyl methacrylate) (127). Finally, measurements to 1 GPa have been made for polystyrene (126) and poly(methyl methacrylate) (128). For the latter, $dv_l/dp = 2.66$ m/(s·MPa) and $dv_s/dp = 1.07$ m/(s·MPa).

Absorption. Representative sound absorptions measured at room temperature, ambient pressure, and a frequency of 2 MHz are given in Table 6. The longitudinal absorptions vary from 1 to 10 dB/cm and the shear absorptions vary from 4 to 25 dB/cm. These values are higher than for metals. The measurements in Table 6 were not made near the glass transition; much higher values are

Table 6. Absorptions for Various Polymers^a

Polymer	Longitudinal absorption, dB/cm	Shear absorption, dB/cm	Ref.
Poly(methyl methacrylate)	1.4	4.3	8
Poly(4-methyl-1-pentene)	1.4	6.7	105
Polyethylene, high density	3.3	25.0	8
Polyphenylquinoxaline	3.5	15.0	76
Phenolic polymer	4.1	19.0	76
Poly(ethylene oxide)	7.1		8
Polyurethane, polyether-based	7.5		49
Polyurethane, polybutadiene-based	9.1		49

^aMeasurements made at room temperature, ambient pressure, and a frequency of 2 MHz.

found near the glass transition. For one epoxy, the peak longitudinal absorption at 2 MHz was 30 dB/cm (77). Rubber compounds typically have the highest peak absorptions. At 10 MHz, peak longitudinal absorptions vary from 150 dB/cm for butadiene–styrene rubber to 450 dB/cm for butyl rubber (91,119). Absorption measurements are sensitive not only to the temperature and frequency of the test, but also to the state of the polymer owing to such factors as plasticization (86,88,89,93) and crystallinity (71).

Absorption measurements as a function of temperature have been made over moderate temperature ranges for a variety of polymers, including vulcanized rubbers (91,119,120), poly(methyl methacrylate) (128), poly(4-methyl-1-pentene) (105), poly(acrylonitrile–butadiene–styrene) (ABS) (105), epoxy polymers (47,77), polyphenylquinoxaline (76), phenolic polymer (76), fluoropolymers (53), polycarbonate (65), polysulfone (65), and poly(ether sulfone) (65). Measurements over a wide temperature range have been made for polyethylene (70) and polyimides (113).

Measurements as a function of frequency indicate hysteresis behavior when not in the vicinity of a transition (8,128). By using time–temperature superposition, a wide range of frequencies covering the glass transition of natural rubber has been obtained (124). Other frequency measurements, covering less than one decade, have been made for various polymers (65,89,91,120).

Measurements as a function of pressure have been made in a few cases. For poly(methyl methacrylate) (128), the hysteresis shear absorption at 1 GPa is about one-fourth of that at ambient pressure. For plasticized poly(vinyl chloride) (125), polyisobutylene (123), and natural rubber vulcanizate (124), upon the application of pressure, the glass transition peak shifts to higher temperature with a lower but broader peak.

Elastic Constants. For the polymers listed in Table 2 for which both longitudinal and shear sound speeds are given, the elastic constants have been calculated at room temperature, ambient pressure, and a frequency of 2 MHz; these are listed in Table 7. The moduli values are approximately 1 order of magnitude lower than those for metals. The range of Poisson's ratio values is somewhat higher than that for metals. A review of elastic properties of polymers is given by Hartmann (130).

Table 7. Elastic Constants for Various Polymers^a

Polymer	Density, g/cm ³	Bulk modulus K' , GPa	Shear modulus G' , GPa	Young's modulus E' , GPa	Poisson's ratio σ	Ref. ^b
General polymers						
Phenolic polymer	1.22	7.02	2.13	5.79	0.36	76
Epoxy polymer	1.184	7.13	1.83	5.05	0.38	
Polyhexamethylene adipamide	1.147	6.53	1.43	3.99	0.40	
Polycaprolactam	1.146	6.45	1.43	4.00	0.40	
Poly(methyl methacrylate)	1.191	6.49	2.33	6.24	0.34	
Polypropylene	0.913	4.37	1.54	4.13	0.34	
Polyphenylquinoxaline	1.209	5.21	1.54	4.20	0.37	76
Polyoxymethylene	1.425	6.59	1.43	4.01	0.40	
Polyethylene, high density	0.957	4.54	0.91	2.55	0.41	
Polystyrene	1.052	4.21	1.39	3.76	0.35	
Poly(4-methyl-1-pentene)	0.835	2.67	0.97	2.61	0.34	105
Poly(acrylonitrile- butadiene-styrene)	1.023	3.33	0.70	1.96	0.40	105
Poly(vinylidene fluoride)	1.779	5.18	1.07	3.00	0.40	
Polycarbonate	1.194	4.57	0.99	2.77	0.40	129
Poly(vinyl chloride)	1.386	5.41	1.59	4.34	0.37	129
Polysulfone	1.236	4.92	1.05	2.94	0.40	129
Poly(phenylene oxide)	1.073	3.86	1.07	2.94	0.37	129
Polytetrafluoroethylene	2.18	2.79	1.16	3.06	0.32	114
Epoxy polymers						
RDGE/PDA	1.2711	8.65	2.64	7.19	0.36	47
RDGE/MPDA	1.3023	8.23	2.62	7.11	0.36	47
RDGE/HDA	1.2299	7.88	2.14	5.89	0.38	47
DGEBA/PDA	1.1844	7.28	1.97	5.42	0.38	47
DGEBA/MPDA	1.2033	6.78	2.00	5.46	0.37	47
DGEBA/HDA	1.1595	6.52	1.69	4.67	0.38	47
RDGE/DDA	1.1667	6.38	1.29	3.63	0.41	47
DGEBA/Z	1.202	6.27	1.81	4.95	0.37	121
DGEBA/DDA	1.1255	5.34	1.15	3.22	0.40	47
Filled polymers						
Polyester + water	1.042	2.94	0.44	1.26	0.43	
Polyepoxide + glass spheres	0.718	2.57	1.18	3.07	0.30	
Polyepoxide + glass spheres	0.793	2.40	0.83	2.23	0.35	
Polyepoxide + glass spheres	0.691	2.14	0.95	2.48	0.31	

^aMeasurements made at room temperature, ambient pressure, and at frequencies in the range 1–2 MHz.

^bTaken from Ref. 109 except as noted.

In addition to the measurements given in Table 7, other data are available, including polyethylene as a function of density (crystallinity) (5); natural rubber vulcanizate compressibility as a function of temperature, pressure, and frequency (124); bulk and shear moduli as a function of temperature for various polymers (47,53,131,132); and the pressure and temperature dependence of the bulk modulus of poly(methyl methacrylate) (128) and polystyrene (110).

Table 8. Extensional Modulus and Loss factor at Room Temperature^a

Polymer	ρ , g/cm ³	E' , GPa	$\tan \delta$	f_{av} , kHz	Ref.
General polymers at various frequencies					
Polyethylene	0.964	3.58		9	82
Polyethylene	0.907	0.27		3	82
Poly(2,6-dimethyl-1,4-phenylene oxide)	1.06	2.39	0.01	10	133
Poly(ethylene terephthalate)	1.380	2.70	0.01	0.1	111
Poly(ethylene terephthalate)	1.335	1.77	0.02	0.1	111
Polyurethanes at 1 kHz					
1 PPG777/3 MDIL/1 14BDO	1.170	1.17	0.22		134
1 PTMG1000/3 MDI/2 BEPD	1.106	0.47	0.41		50
1 PTMG1000/3 MDI/2 EMPD	1.119	0.38	0.42		50
1 PPG1000/3 MDIL/1 14 BDO	1.154	0.34	0.67		134
1 PTMG2000/6 MDI/4 DMPD	1.108	0.30	0.47		50
1 PTMG1000/3 MDI/2 DMPD	1.123	0.29	0.55		50
1 PTMG1000/3 MDI/2 DEPD	1.073	0.18	0.76		50
1 PTMG1000/3 MDI/1 14BDO	1.139	0.10	0.26		50
1 PTMG1430/3 MDI/1 14BDO	1.105	0.044	0.14		50
1 PPG2000/3 MDIL/1 14BDO	1.101	0.016	0.39		134
1 PTMG1000/4 MDI/3 DMPD	1.092	0.009	0.55		50
1 PTMG2000/3 MDI/2 BEPD	1.064	0.009	0.37		50
1 PTMG650/2 TDI/1 PTMAB	1.087	0.009	0.47		135
1 PTMG2000/3 MDI/2 DMPD	1.074	0.009	0.35		50
1 PTMG1000/2 TDI/1 PTMAB	1.073	0.007	0.27		135

^aData for the polyurethanes is in the viscoelastic region of the glass transition.

Table 8 gives values of the real part of the extensional modulus (eqs. 3 and 5) and the loss factor. The values for most of the polymers are outside the glass-transition region, while the values for polyurethanes are typical of the glass-transition region. The high values of $\tan \delta$ are of interest for sound absorption and for vibration damping.

Data on the frequency dependence of elastic moduli was obtained by Lagakos co-workers (129), who used different techniques to determine the Young's modulus E' both at kHz and at MHz frequencies. Their values for the frequency derivative of E' are given, for selected polymers, in Table 9. These values are typical for the region outside the glass transition.

In addition to chemical composition, the morphology of the polymer also affects the elastic constants. For example, the moduli of crystalline regions of a polymer are different from the amorphous regions of the same chemical composition. Also, especially in the polyurethanes, the degree of microphase separation influences elastic constants. In this case there are soft segments and hard segments (not necessarily crystalline) that are mixed or separated to varying degrees and this affects the elastic constants. An example is shown in Figure 4, where a phase-separated polyurethane (PTMG1000/MDI 3/BDO) is compared with a phase-mixed polymer (PTMG1000/MDI 3/DMPD). The data in this figure illustrates the general trend that a phase-mixed polyurethane will have low rubbery modulus and a phase-separated polyurethane will have a high rubbery

Table 9. Frequency Derivatives of Young's Moduls

Polymer	ρ , g/cm ³	$dE'/d \log f$, GPa/decade	Ref.
Poly(methyl methacrylate)	1.187	0.509	129
Polypropylene	0.901	0.469	129
Poly(tetrafluoroethylene)	2.160	0.145	129
Polyethylene	0.951	0.116	129
Poly(methylene oxide)	1.424	0.099	129
Poly(hexamethylene)	1.141	0.097	129
Polysulfone	1.236	0.069	129
Polycarbonate	1.194	0.047	129
Polystyrene	1.048	0.037	129

modulus. The glassy modulus is about the same in both cases. Associated with the low rubbery modulus is a high, narrow loss peak, while a low, broad loss peak is associated with the high rubbery modulus.

Elastic constants for unidirectional fiber composites with transverse isotropy have been measured for some composites (qv) with an epoxy matrix. Depending on whether glass fibers (28) or carbon fibers (qv) (29) are used, C_{11} varies from 40 to 300 GPa and C_{12} is only about 5 GPa. The other elastic constants are generally intermediate. For the most part, the elastic constants are fiber-dominated.

The Gruneisen parameter, used in equation-of-state calculations, has been determined from acoustic measurements in a number of cases. For high density polyethylene (126), the Gruneisen parameter was calculated from the pressure dependence of the sound speed. It was found that γ varied from 3.5 to 5.5 over the temperature range -55 to 15°C , in good agreement with the room temperature value of 5.1 found from the temperature dependence of the acoustically determined bulk modulus (109). For poly(methyl methacrylate) and polystyrene, little temperature dependence was found, both polymers having $\gamma \sim 4$. Other measurements of γ using the temperature dependence of the bulk modulus include 7.6 for phenolic polymer (76), 4.4 for polyphenylquinoxaline (76), 5.1 for poly(4-methyl-1-pentene) (105), 7.2 for poly(acrylonitrile-butadiene-styrene) (105), 5.2 for poly(methyl methacrylate) (128), 4.4 for polystyrene (110), and 11.0 for isotactic polypropylene (109).

Underwater Acoustics. Acoustically transparent materials are used in a number of underwater applications, including transducer windows, sonar domes, potting compounds, and hydrophone support structures. A commonly used class of material for these purposes is called Rho-C rubber (BF Goodrich trademark), because the impedance, $Z = \rho c$ (where c is sound speed), matches that of water. A disadvantage of Rho-C rubber is that it does not possess structural rigidity. A material sometimes used when rigidity is required is poly(acrylonitrile-butadiene-styrene). Transmission loss measurements from 100 kHz to 2 MHz, at room temperature, show that a 2-mm-thick sheet of ABS has a transmission loss at normal incidence that averages 1 dB (136). This is slightly higher than that for the rubber, but still low enough for most applications. ABS has more angle

dependence than Rho-C rubber and thus does not have quite as large a field of view. Another rigid window material is poly(4-methyl-1-pentene), which, because of its low density (0.835 g/cm^3), has an impedance closer to seawater than does ABS. The calculated transmission loss for poly(4-methyl-1-pentene) is less than for ABS at normal incidence, but greater than ABS for incident angles greater than about 45° (105). Another approach to acoustically transparent structural materials is the combination of more or less flexible epoxy polymers with different types of microballoons (106). Sound speeds varying from 2890 to 1560 m/s are obtained. Many trade-offs are possible, depending on the transmission loss and rigidity required.

Acoustic lenses are used in applications such as high resolution sonar and underwater imaging for salvage, as well as for medical imaging, materials inspection systems, and ultrasonic microscopy. Three types of lenses are common: (1) single refractive element, liquid-filled lens, (2) single-element thin solid lens, and (3) two-element athermal solid lens (a low sound speed and high sound speed material in contact designed so that the focal length is independent of temperature over a wide range). The liquid lenses are limited to an angular resolution of 0.5° and have a temperature-dependent focal length. For single-element thin solid lenses of polyhexamethyleneadipamide, polyethylene, and polystyrene, as well as two-element athermal lenses of poly(phenylene oxide)–polydimethylsiloxane, beam widths on the order of 0.35° over a 30° field of view can be obtained (137). Even higher angular resolution has been achieved using a four-element solid lens, consisting of two doublets of polystyrene–polydimethylsiloxane (138). For this lens, a resolution of 0.2° over a 20° field of view with good temperature properties was obtained. Multilayer systems have potential use for both acoustic windows and lenses. Transmission loss measurements and calculations for one-, two-, and three-layer systems utilizing various polymers have been made (23,24).

Anechoic (echo-reducing) coatings to reduce tank-wall reflections are needed in many underwater acoustic test facilities. One effective design utilizes butyl rubber loaded with metal particles (usually aluminum flakes) prepared so that the final product contains small gas pockets surrounding the particles (139). Even more effective than thin sheets of this material is a gradual transition from water to coating in the form of cones of the coating material. Although thicker than the sheets, the cone structure gives more than 25 dB echo reduction from 20 kHz to 1 MHz at normal incidence. Coatings for the 2–7 MHz range of interest in materials inspection and medical applications have made use of polydimethylsiloxane loaded with ferric oxide (a dense filler) and microballoons (both glass and phenolic) (135), as well as paraffin wax and polychloroprene (140).

For a parametric sonar receiver in water, the insertion of a polydimethylsiloxane cylinder in front of the receiver improved the parametric conversion gain by 20 dB and reduced the beam width by a factor of 2–3 (37).

Miscellaneous. Vibration damping is typically effected with a polymer used in the vicinity of the glass transition. Different temperature and frequency ranges are covered by using different homopolymers, blends, copolymers, plasticizers (qv), and other fillers. The application of time-temperature superposition to damping materials has been demonstrated for various polymers (141). One way of achieving a very broad transition region is through the use of interpenetrating polymer networks (142). The structure of interpenetrating polymer networks, and

their acoustic and damping properties are reviewed in Reference 143. Data on the complex shear and Young's moduli for various commercial damping treatments are presented by Nashif co-workers (144). Closed-cell polyurethane foams (145) and solution blends (146) also have potential for broad application. See Reference 147 for a comprehensive review of this application (see also CELLULAR MATERIALS).

Airborne noise applications include acoustically transparent open-cell polyurethane foam (148) for use as a microphone windscreen, and acoustically absorbing polyurethane foam (149) for noise abatement. Polyester-based foam has superior mechanical properties and acoustical absorption, but poor humid aging. Polyether-based foam has better humidity resistance and is inexpensive, but has less absorption.

Also, some studies have been done on the effect of insonification on polymerization reactions. In one case, it was found that insonification produced a rapid increase in conversion during free-radical polymerization of methyl methacrylate (150).

A class of polymer materials that has extensive applications in acoustics and vibrations is that of electroactive polymers. In these polymers there is coupling between mechanical deformation and electric fields. An applied stress produces both strains and charge separation, which leads to an output voltage between opposite surfaces of the polymer. Conversely, an applied electric field produces strains in the polymer. The induced strain has a linear and a quadratic term in the applied electric field. The linear term is characteristic of piezoactive response and the quadratic term corresponds to electrostrictive response.

Examples of polymers that have a piezoactive response are poled poly(vinylidene fluoride) (PVDF) (151) and its copolymers with trifluoroethylene co(VDF-TrFE) (152), and the family of odd nylons (153) (see PIEZOELECTRIC POLYMERS). These are partially crystalline materials in which the crystalline regions have a permanent electric dipole moment. These polymers show ferroelectric switching behavior indicating that after poling they have a net polarization. The piezoelectrically induced strain, linear in the field, for the fluorinated polymers is up to 0.3% for fields of 30 V/ μm (0.8 kV/mil). Recent extensive measurements of the piezoactive coefficients for PVDF, including temperature and frequency dependence, are given in Reference 154. Applications of PVDF and copolymers include (155) high frequency loudspeakers, transducers (single and arrays) for generating and receiving ultrasound (for nondestructive testing and medical imaging), and acoustically transparent, small (point) size hydrophones for imaging underwater ultrasonic fields (156,157). Also, PVDF transducers are used as industrial acoustic and vibration sensors (154).

The strain dependence for electroded polymers that is quadratic in the field consists of two terms: one a Maxwell stress due to the attraction of free surface charge on the electrodes, and the other electrostriction, which is a change of dielectric function with strain (158), related to dipole moments induced by the applied electric field. This quadratic term occurs for all materials and does not require a permanent polar moment. A large ambient electrostriction of 4% strain has been reported for irradiated copolymers of VDF/TrFE (159), terpolymers of VDF/TrFE/CTFE (160), and for polyurethanes (161). For the case of the fluorinated copolymers the irradiation or the addition of the third monomer for the

terpolymers is hypothesized to create defects and decrease the size of correlation of the polarization regions, allowing the dipoles more freedom to respond to the electric field. This results in large dielectric constants on the order of 80 (159). An electrostrictive strain of 4% deformation for polyurethanes has been measured by both optical (161,162) and capacitance methods (161,163). The frequency range for the electrostrictive response is found up to 1 kHz for polyurethanes. A space charge distribution is indicated as the electrostrictive mechanism for these polymers (164). The fluorinated terpolymers and copolymers are highly crystalline and can impart a higher stress than that of these lower-modulus urethane elastomers. Other dielectric elastomer systems that have been shown to have large electric field coupling yielding strains of 100% are acrylics and silicones. These polymers have a low modulus and their deformation has been shown to be accounted for by the quadratic Maxwell stress term (165). The design and performance of an underwater flexensional projector transducer based on an electrostrictive copolymer of VDF/TrFE is described by Z. Y. Cheng and co-workers (166).

Electrets are another type of electrically active polymer. These are materials that contain embedded electrical charges (155). Electret films are extensively used as membranes in microphones. The embedded electrical charges in the electret film eliminate the need to supply an external d-c bias voltage to the microphone.

Test Methods

A comprehensive review of measurement techniques is presented by Capps (167), who also gives data for the complex Young's modulus for a range of polymers. This data includes the rubbery, transition, and glassy regions, and parameters for time-temperature superposition (eq. 45). The measurement techniques fall broadly into three categories: wave propagation methods, resonance methods, and forced-vibration nonresonance methods. The resonance and forced-vibration techniques are designed to measure directly the complex Young's and shear moduli, and the acoustic properties of the polymer are calculated from this data.

Wave-Propagation Methods.

Immersion Technique. A test method known as the immersion technique will be described in some detail. Other test methods will then be discussed in contrast to this method. The immersion technique is relatively simple to use and provides both longitudinal and shear sound speeds and absorption over a range of temperatures, generally in the MHz frequency range, to 1% accuracy in sound speed.

In this method, acoustic waves are generated by a piezoelectric transducer, which converts an oscillating electric field to a mechanical oscillation. Detection of acoustic waves that have traveled through a polymer specimen is done with the same type of transducer. Depending on its use, a transducer is called a transmitting transducer (transmitter) or receiving transducer (receiver). Common transducer materials are quartz and various polycrystalline ceramics, such as lead zirconate titanate (PZT), polarized in a strong electrostatic field.

Measurements are made by sending acoustic pulses, typically less than 1 ms duration, through a specimen. Pulses, rather than continuous waves, are used because it is easy to determine the time it takes for a pulse to go through a specimen by looking for the beginning of the pulse. In the immersion technique, the specimen, transmitter, and receiver are all immersed in a liquid. Pulses are sent from one transducer to the other both with and without the specimen in the path of the sound beam. From the changes in the detected signal when the specimen is removed, the speed and absorption can be calculated.

The specimen is in the shape of a circular or rectangular slab. When a specimen of lateral dimensions several times the acoustic wavelength is supported with its face perpendicular to the path of the sound beam, longitudinal waves are generated in the specimen (119,125,168). A variation of this method is to hold the specimen at an angle to the sound beam. In this way, both longitudinal and shear waves are generated in the specimen. If the angle at which the specimen is held is greater than the critical angle, the longitudinal wave is totally internally reflected and only the shear wave is propagated (29,86).

In a typical immersion apparatus, when making shear measurements, the specimen is rotated with respect to fixed transducers to obtain shear waves. In the apparatus described here, the transducers are rotated about the fixed specimen (109,169). Eight specimens are mounted on the periphery of a circle and are moved into and out of the path of the sound beam. Especially when making measurements as a function of temperature, it saves time when eight specimens are immersed at once.

PZT transducers, 2.5 cm in diameter, are used in this apparatus. The larger the transducer diameter at a given frequency, the better collimated the acoustic beam (170). In this case, at 1 MHz, the diffraction attenuation is negligible and specimen alignment is not critical. The resonant frequency of the transducer is proportional to its thickness, 0.25 cm, and is 0.75 MHz. The maximum output of the transducer is at its resonant frequency, but it can be operated below resonance without much loss, and can be operated at harmonics of the resonant frequency to obtain higher frequency measurements. In this manner, the apparatus has been used to make measurements over the frequency range 0.1–10 MHz, though most of the data are taken at 2 MHz.

An ideal immersion liquid has a very low sound speed, is liquid over a wide temperature range, and is safe. A low viscosity silicone fluid was chosen for this apparatus. This liquid can be used to make measurements over the temperature range –50 to 150°C.

For measurements of the longitudinal speed the specimen is oriented with its face perpendicular to the sound beam. With the specimen between the transducers, the detected pulse is displayed on the oscilloscope and the position, for example, of the first peak of the pulse is noted. The specimen is then removed from the path of the sound beam. Since the speed in the immersion liquid is less than the speed in the polymer, the signal will take a longer time to reach the receiver, and the pulse will move to the right on the oscilloscope screen when the specimen is removed. The difference in transit times t for the specimen and for an equal thickness of liquid is determined from this shift in position. For a specimen of thickness L , the transit time is L/v_l , where v_l is the longitudinal speed of the specimen. The transit time through an equal thickness of liquid is L/v_{liq} , where

v_{liq} is the speed in the liquid. Therefore,

$$\Delta t = L/v(\text{liq}) - L/v_l \quad (48)$$

so that v_l can be calculated, since v_{liq} in this case (49,109) is given by

$$v(\text{liq}) = 976 - 2.5(T - 25) \quad (49)$$

for v_{liq} in m/s and T in $^{\circ}\text{C}$.

Shear speed is measured by rotating the transducers so that the sound beam strikes the specimen at an angle. At off-normal incidence, both shear and longitudinal waves are generated. When both waves are present, they overlap in the received signal and are difficult to separate. However, if and only if $v_{\text{liq}} < v_l$, there is a critical angle beyond which there is total internal reflection of the longitudinal wave, and only the shear wave propagates through the specimen. It is for this reason that a low sound speed immersion liquid is desirable. Shear speed v_s is calculated in a manner similar to that for v_l . The procedure is more involved only because the path length through the specimen is somewhat greater than the specimen thickness (109).

Longitudinal absorption is found by comparing the amplitude of the received signal with no specimen in place to that of the signal with a specimen held perpendicular to the sound beam. The amplitude will be less with the specimen in place, both because the absorption in the polymer is greater than in the liquid and because some of the sound energy is reflected when it strikes the specimen. The amount of reflection can be calculated so that the absorption can be determined (109). Shear absorption proceeds in a similar manner (109). Immersion apparatuses can be used to measure sound speeds to an accuracy of 1% or better, and absorption to 10% or better.

Delay Rod Techniques. In the delay rod technique, the acoustic path of liquid between the transducers and the specimen in the immersion apparatus is replaced with solid rods of quartz or metal (120). The purpose of the delay rods (also called buffer rods) is to give enough separation between pulses that the complete pulse can be sent by the transmitter before the beginning of the pulse arrives at the receiver. This technique eliminates stray r-f pickup by the receiver. A very thick specimen could be used for the same purpose, but polymers are generally highly absorbing, so that thin specimens are necessary in order to detect the transmitted signal. Since there is no liquid to freeze, this technique has been used down to liquid helium temperature (114,115).

Two problems are encountered with the delay rod technique. First, there must be a good bond between the transducers and the delay rods and also between the delay rods and the specimen. Second, shear measurements cannot be made with the same transducers used for longitudinal measurements. Various bonding agents have been used. For longitudinal waves, silicone liquid, stop-cock grease, and glycerin have been successfully used. For shear waves, which are more highly damped, the problem is more critical. A low molecular weight poly(α -methylstyrene) liquid and mixtures of phthalic anhydride and glycerol are effective. All of these bonding agents have the advantage of being relatively easy

to remove so that the transducer can be recovered intact. An epoxy bond can give good coupling, but is difficult to remove.

Longitudinal and shear measurements are made separately with different sets of transducers. Quartz transducers are often used. Quartz crystals produce different types of vibrations depending on how they are cut. An X-cut quartz crystal is used for generating longitudinal waves. Y-cut or AC-cut quartz crystals are used to generate shear waves.

Speed and absorption measurements can be made in a similar manner to those in the immersion technique or by using a null method (114). In this method, the pulse input to the transmitter is split in two. The pulse that has traversed the specimen is then mixed with an out-of-phase signal directly from the pulsed oscillator. By properly delaying and attenuating the direct signal, a null is obtained. Using this technique, an accuracy of 0.5% in speed can be obtained.

Multiple Echo Techniques. In multiple echo techniques, pulses of sound that traverse the specimen are partially reflected at the face of the specimen and bounce back and forth with continually diminished amplitude. From the time it takes for the echo to travel from one face to the other and the reduction in its amplitude during this trip, the speed and absorption can be calculated. Since the pulse must make several trips through the specimen, this technique cannot be used for highly absorbing materials. On the other hand, the technique is very accurate.

In one version of this technique (171) that has been successfully applied to polymers (124), two transducers are bonded directly onto the specimen. Two independently controlled pulses are applied to the transmitter. The first pulse generates a series of signals at the receiver corresponding to the directly transmitted signal and its subsequent echoes. The second pulse generates a similar set of signals. The second pulse is then delayed and attenuated so that the envelope of the directly transmitted signal coincides with that of the first echo of the first pulse. By adjusting the frequency of the measurement, the coincident signals can be made to interfere destructively and cancel each other out. The required frequency depends on the transit time through the specimen and allows accurate determination of the transit time. Absorption is obtained from the attenuation required to match the amplitude of the direct pulse with the first echo. Sound speed measurements can be made to an accuracy of 0.1% and absorption to ± 1 dB.

Another version of the multiple echo technique (172,173) that has been used to make very accurate sound speed measurements in polymers makes use of a single transducer bonded directly to the specimen (110). Pulses are reflected from the opposite face and return as echoes to the front face. By adjusting the pulse repetition rate, an echo from a later pulse can be made to overlap a multiple echo from an earlier pulse. When the repetition rate is adjusted to obtain an in-phase condition, constructive interference will result in a maximum amplitude in the superimposed signals. A value of sound speed accurate to 0.05% can be obtained by observing several repetition rates that yield an in-phase condition at the transducer resonant frequency and by repeating the measurements at some other frequency, eg, 10% below resonance, and on other specimens that differ only in thickness.

Laser Ultrasonics. Ultrasonic waves can be both generated and detected in solids using lasers. Laser ultrasonic systems have been developed for measuring the velocity and attenuation of ultrasound in materials. A high-power pulsed laser is used to generate a broadband ultrasonic pulse, and the time of flight and amplitude of this pulse are measured at one or more points on the material, using a low power, continuous laser (174). The advantages of the laser system are

- (1) The system is noncontact, so it does not load the sample and can be configured for fast scanning of the sample surface.
- (2) The sound generation/detection regions are small, and the system can be modeled as a point source/point receiver system.
- (3) The ultrasonic signals are broadband and the sound speed and attenuation are measured over a range of frequencies.

A disadvantage of the laser system is its relatively low generation and detection efficiency.

Brillouin Scattering. The scattering of light by sound waves, a phenomenon first suggested by Brillouin, has become a practical tool with the advent of the laser. Sound waves are present in solids as a result of collective thermal vibrations, called thermal acoustic phonons. Since the phonons have a velocity relative to the photons, the scattered light is Doppler-shifted by an amount directly proportional to the sound speed. Brillouin scattering is observed for both longitudinal and transverse (shear) phonons. The Brillouin scattered lines are, to a first approximation, Lorentzian in shape. The width of the line is related to the phonon lifetime, or absorption coefficient. Brillouin scattering is thus a method of measuring sound speed and absorption in the 1–10-GHz frequency range.

Measurements of Brillouin scattering using a Fabry–Perot interferometer have been made on poly(methyl methacrylate) and poly(vinyl chloride) as a function of temperature through the glass transition (175). Only longitudinal measurements were obtained with this arrangement; shear waves could not be detected. Improved measurement methods using multiple-pass Fabry–Perot interferometry have been demonstrated for polystyrene (176), poly(4-methyl-1-pentene) (177), and several other amorphous polymers (178).

Through the use of thin films 0.1–0.3 mm thick, Brillouin scattering was measured in nontransparent polymers, such as polyethylene and poly(ether sulfone) (179). This technique is also useful for studying shear waves in polymers.

Surface Acoustic Waves. All of the discussion so far has dealt with the propagation of acoustic waves in bulk polymers. In addition to longitudinal and shear waves, however, a surface or Rayleigh wave, called a surface acoustic wave, can also be propagated.

A surface acoustic wave probe for polymers has been developed (180). Periodic distortions in piezoelectric substrates are induced by application of r-f energy to sets of interdigitated electrodes laid down on the substrate by standard photolithographic and etching techniques. There are 50 finger pairs, each finger 1 mil wide, with 2 mil spacings between adjacent fingers. This device has a wavelength of 100 μm and an operating frequency of about 32 MHz. The probe

has been used to detect melting, glass, and secondary transitions in thin films of various polymers.

Low Frequency Techniques. For measurements below about 100 kHz, different test methods have been developed. Progressive wave techniques have been used to measure waves in rubber rods or strips. The specimen must be sufficiently long so that there are no reflections from the end of the specimen. An electromechanical shaker is used to excite one end of the specimen and a phonograph needle pickup is moved along the length of the specimen. From the amplitude vs distance measurement, the absorption is calculated. From the phase difference between shaker and pickup, the speed is calculated. This type of apparatus is generally used to measure extensional waves, governed by Young's modulus, over a frequency range from 100 Hz to 40 kHz (181). A modification of this technique has been used to measure torsional waves, governed by the shear modulus, over a frequency range from 1 to 8 kHz (182). Since these measurements must be repeated at each frequency, this method is time consuming. The method is also limited in accuracy and the range of materials that can be measured.

A pulse technique for the kilohertz frequency range is described in Reference 17. In this method the sample was immersed in a large water-filled tank, and a large area projector and hydrophone were used, operated in a pulse mode. The longitudinal sound speed and absorption were determined from measurements of signal amplitude and time of flight. Measurements were made on a polyurethane rubber sample, $35 \times 35 \times 5.2$ cm, over the range 12.5–75 kHz and 3.9–39.6°C. (The water-filled tank is also designed to operate at pressures up to 100 psi.) Also, the dynamic shear modulus was measured, using a rheometer, and the dynamic bulk modulus was determined from the longitudinal and shear measurements.

Resonance Techniques. Resonance methods (183–185) are used for measurements below about 100 kHz. The complex modulus (usually Young's or shear) is determined over a limited frequency range at a number of fixed temperatures, usually over one to three decades of frequency and over the useful temperature range of the material. From the measured data, reduced frequency plots at constant temperature are generated by the application of the time-temperature principle (3). In these plots, the real and imaginary parts of the complex modulus are plotted over many decades of frequencies, typically, as many as six or more decades of frequency than were actually measured.

Resonance techniques have been extensively used to find polymers with high loss factors, for sound absorption and vibration-damping applications, and to determine relations between acoustic and elastic properties and molecular composition and morphology.

The complex dynamic Young's modulus can be determined from the response of a bar-shaped test specimen in a forced-resonance method (186). A shaker drives one end of the specimen (nominally $100 \times 6 \times 6$ mm). Miniature accelerometers are used to measure the driving point acceleration at the shaker and the response of the test specimen as shown in Figure 6. The output signals from the accelerometers are analyzed by a dual-channel fast Fourier transform spectrum analyzer. The analyzer determines the acceleration ratio and phase difference of the two accelerometers, and also provides a random noise source to drive the shaker over a frequency range of 25 Hz to 20 kHz. The measured data are always sampled and

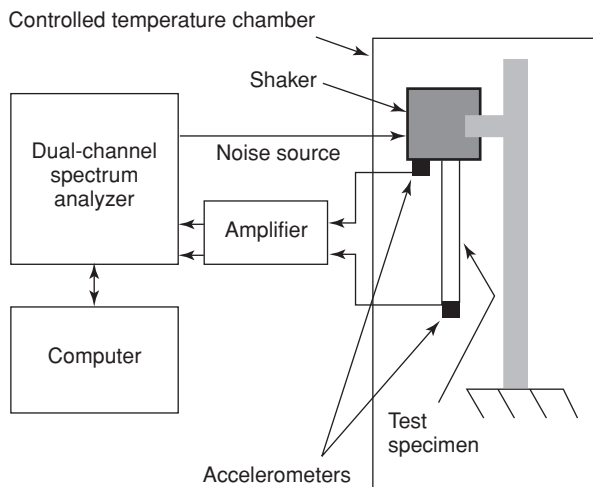


Fig. 6. Schematic diagram for the resonance apparatus.

rms-averaged at least 8 times, for low noise data, and up to 256 times, for noisy data. The displayed amplitude ratio versus frequency goes through a number of resonant peaks from which the sound speed (governed by the Young's modulus) and absorption (loss factor) are computed. The measurements are made over a temperature range of -60 to 70°C at 5° intervals.

The acceleration at selected locations on the sample can also be measured using a laser Doppler vibrometer (LDV) (187). The advantage of the LDV is that it is a noncontact measurement and does not disturb the vibration of the sample. Reference 187 describes a measurement setup that operates in the frequency range 500 – 2500 Hz, temperature range 0 – 40°C , and at pressures up to 500 psi.

Forced-Vibration Nonresonance Methods. In the forced, nonresonant method (183,188) sensors are used to measure the drive force and resulting displacement at one end of the sample. The complex modulus (shear or Young's) is determined from the amplitude ratio and relative phase of the force to the displacement. There are similarities between the resonance and nonresonance techniques. The complex modulus is measured over a limited frequency range at a number of fixed temperatures, and the time-temperature superposition principle is used to generate a plot of the complex modulus over many decades of frequency. The applications of the data are similar.

In a forced, nonresonant method, the complex dynamic Young's modulus can be determined from the response of a beam mounted in a single-cantilever fixture (188) as shown in Figure 7. A thin sample (nominally $1.2 \times 10 \times 3$ mm) is clamped at both ends. One end is attached to a shaker through a driveshaft. The force and displacement are measured at the driven end at fixed frequencies. The low frequency/low mass bending solution is used together with the measured input impedance to infer the Young's modulus and loss factor. Sixteen discrete frequencies from 0.01 to 200 Hz are available, with an operating temperature range from -100 to 300°C .

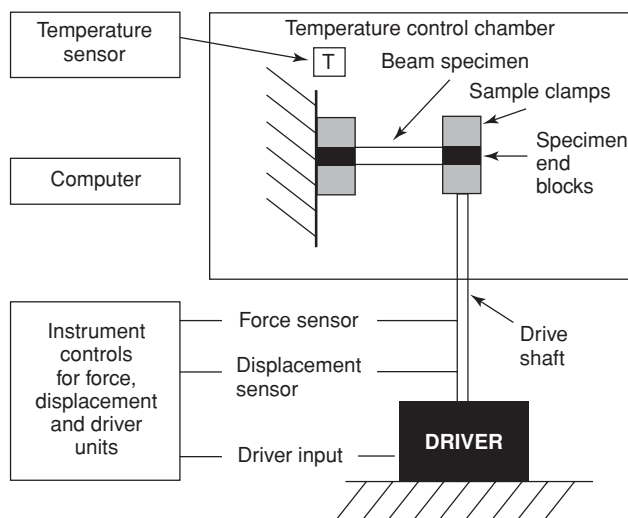


Fig. 7. Schematic diagram for the single cantilever beam apparatus for measurement of the complex Young's modulus. (A forced vibration nonresonance method.)

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ACROLEIN POLYMERS

Introduction

Acrolein (propenal), $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$, is the simplest unsaturated aldehyde. Its synthesis from glycerol and some of its typical reactions were already known in 1843 (1). It was observed at that time that the fluid acrolein spontaneously changed upon standing to a white, solid product, which was called dis-acryl, and it was suspected that this solid was a polymer. There was little interest in this monomer and polymer until acrolein became available on a technical scale in 1942 (2). Then intensive research on the suitability of the compound in organic syntheses and polymerizations began, and today acrolein is frequently used

Table 1. Physical Properties of Monomeric Acrolein

Property	Value
formula weight, C_3H_4O	56.06
melting point, $^{\circ}C$	-86 to -87
normal boiling point, $^{\circ}C$	52.7
dT/dp , $^{\circ}C/Pa$	2.66
vapor pressure, at $20^{\circ}C$, kPa	28.7
evaporation enthalpy, at 101.3 kPa, kJ/kg	542.2
density, $20^{\circ}C$, g/cm^3	0.8389
refractive index, n^{20}_D	1.4017
viscosity, $20^{\circ}C$, mPa·s	0.329
solubility	
acrolein in H_2O , $20^{\circ}C$, wt %	21.4
H_2O in acrolein, $20^{\circ}C$, wt %	7.1
water azeotrope	
wt % acrolein	97.4
wt % H_2O	2.6
boiling point, $^{\circ}C$	52.4
uv absorption in hexane, λ_{max} , nm	335

for synthesizing various technically important substances. Homopolymers and copolymers of acrolein have not achieved significant commercial use.

Physical Properties of Monomer

Acrolein is a colorless liquid with a low viscosity and an extremely pungent smell. Hydroquinone is most frequently used as a stabilizer to prevent autoxidation and spontaneous polymerization. Metallic copper or copper compounds also act as stabilizers. Nevertheless, upon prolonged storage, a turbidity or white precipitate of polymeric material with ill-defined structure may be formed. A selection of the most important physical properties of acrolein appears in Table 1; other data are available in refs. 3–5.

Chemical Properties of Monomer

Acrolein is very reactive; reactions can be carried out at the aldehyde group as well as at the $C=C$ double bond. Furthermore, acrolein may act as a diene and dienophile in Diels-Alder reactions (2,5–7). Only a few of these features are being utilized for technical syntheses.

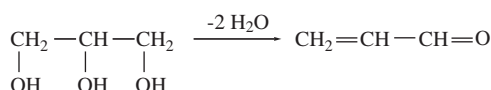
The gas-phase oxidation of acrolein yielding acrylic acid is feasible (4,5,7–9), but it is more advantageous to oxidize propene directly without isolating acrolein as an intermediate (5,10). The conversion of acrolein to propanal, propanol, or glycerol is of practical interest (5,7). The syntheses of pyridine and β -picoline from

acrolein and ammonia in the gas phase at 350–400°C are also of some technical importance (5,11,17).

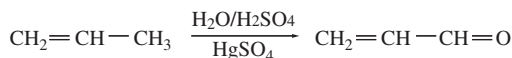
Pyran derivatives, which can be obtained by Diels-Alder reactions (5), can be utilized as intermediates in the synthesis of epoxy resins (qv) (18). Large amounts of acrolein are used for producing DL-methionine (19), an essential amino acid used as a feed supplement for poultry and cattle. For this purpose, the enantiomers need not be separated.

Manufacture of Monomer

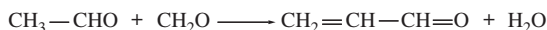
The oldest method of synthesizing acrolein is based on the acid-catalyzed thermalolysis of glycerol at ca 190°C. Today, this reaction is no longer carried out on a technical scale, but is still used for laboratory synthesis (20):



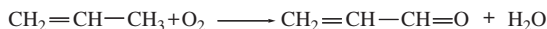
Also, the reaction of gaseous propene with a suspension of HgSO_4 in aqueous sulfuric acid results in high yields of acrolein (21).



The first commercially suitable synthesis was developed by Degussa AG in FRG (2,22,23). This process is based on the condensation of formaldehyde and acetaldehyde in the gas phase at 300–320°C with alkaline silica gel as a catalyst:



A more economical, gas-phase oxidation of propene, has replaced this process (4,5,7):



At temperatures of 350–450°C and pressures of 0.1–0.2 MPa, a mixture of gaseous propene, air, and steam in the molar ratio 1:20:2 is passed over a solid catalyst. Special catalysts have been described by Degussa, Nippon Kayaku, Nippon Shokubai, and Farbwerke Hoechst (4,5,7,24). Conversions are 90–98%. Acetaldehyde and acrylic acid, which are by-products, can be removed by distillation. Technical-grade acrolein is 95–97% pure; it contains 3–5% water, 0.2 wt % hydroquinone as a stabilizer, and only trace amounts of other contaminants.

affords oily resinous products (42–46). However, less is known about the mechanism of formation, structure, and molecular weight of these polymers. In anhydrous media, anionic initiators bring about a chain-growth polymerization. Suitable initiators are, for example, naphthylsodium, tritylsodium, butyllithium, potassium benzophenone, tertiary phosphines, or alkali cyanides (46,47). The catalytic effect of NH_3 (48), pyridine (49), imidazole (50,51), and lithium-organic cuprates (52) has also been described.

Polymers synthesized by anionic initiation do not have the same regular structure as those prepared under radical conditions. Most of the repeat units reflect addition across the carbonyl, but there are also some units of vinyl addition, and an uncertain amount of 1,4-addition fragments (46,47,53–55).

In contrast, polymers synthesized in THF at -40 to -50°C with sodium cyanide as a catalyst are exclusively comprised of repeat units from polymerization at the carbonyl (56,57).

Copolymers of acrolein with methyl vinyl ketone (58), acrylamide (58), acetaldehyde (59), benzaldehyde (59), and others are accessible via anionic polymerization (qv). Block copolymers (qv) of acrolein–butadiene or acrolein–isoprene blocks (60–62) and grafting of acrolein onto imidazole-containing polymers have been described (63–65).

Cationic Homopolymerization and Copolymerization. Only a few investigations deal with the cationic polymerization of acrolein. This polymerization is best carried out in bulk at 0 to -80°C with BF_3 etherate or triethyloxonium tetrafluoroborate as catalysts (30–32,46). The exact structure of these polymers is not known; they show both vinyl and carbonyl addition and contain branches. When the polymerization is stopped at low conversion, the products are soluble in chloroform, THF, or pyridine. Upon prolonged storage, they tend to become insoluble. These polymers soften between 80 and 110°C .

Copolymerizations with styrene or epichlorohydrin, for example, are also feasible under cationic conditions. Some acrolein derivatives, such as acrolein acetals, 2-vinyl-1,3-dioxolane (66–70), diallylidene pentaerythritol, or acrolein oxime (27,71–73), can also be radically or ionically polymerized or copolymerized. However, in some cases during the chain-growth reactions, side reactions and isomerization take place, yielding cross-linked or chemically nonuniform polymers.

Properties of Polymers

The chemical structure and the physical and chemical properties of the acrolein polymers depend upon the mechanism of polymerization. Polymers formed by spontaneous or thermal polymerization are colorless-to-yellow powders or a horny mass of undefined structure. They are insoluble, infusible, and of no practical interest.

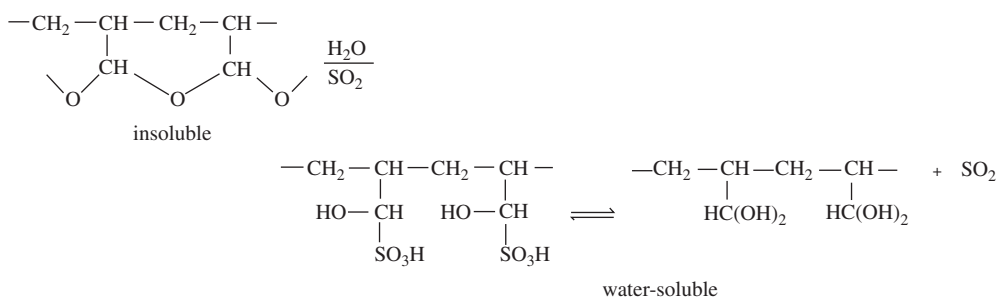
Most acrolein polymers that have been studied have been obtained by radical or anionic polymerization (29,46,74,75). Polymer products from radical polymerizations are colorless, light powders. They are infusible, insoluble in

common solvents, and have densities of 1.32–1.37 g/cm³. Degrees of crystallinity and tacticity have not yet been determined. For molecular-weight determinations, the insoluble polyacroleins must be converted to soluble derivatives. Depending upon the polymerization conditions, the molecular weights can be 300,000 or more. In contrast, polymers from anionic polymerizations are soluble in many organic solvents. They soften between 90 and 150°C, and molecular weights can be determined by the usual techniques (see MOLECULAR-WEIGHT DETERMINATION).

Polyacrolein as a Reactive Polymer. Polyacroleins synthesized by radical polymerization contain one pendent aldehyde group per repeat unit. The carbonyl group can be chemically modified under mild conditions. In contrast to polyacrolein itself, most of the derivatives obtained by this chemical modification are soluble in organic solvents, or even in water. This means that the reactions start out from a heterogeneous medium and form a homogeneous solution with increasing conversion.

The aldehyde groups may be reduced or oxidized or they may react with alcohols and amines to form acetals and imines, respectively. Polyacroleins react quantitatively with hydroxylamine and phenylhydrazine. The Cannizzaro reaction occurs upon treatment with alkali to yield polymers with pendent hydroxymethyl (–CH₂OH) and carboxylic acid (–COOH) groups (76–78). Specific metal complex-forming moieties can also be introduced by reactions with the carbonyl groups (79).

Reactions with sodium bisulfite and sulfurous acid offer the opportunity of producing water-soluble addition compounds of polyacrolein:

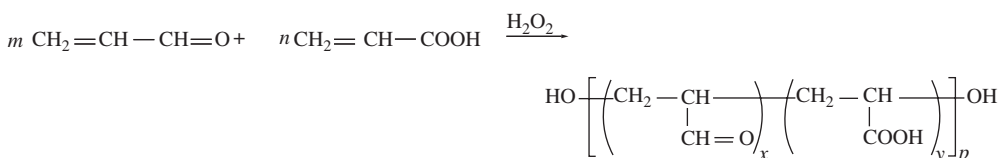


By dialysis, the equilibrium can be shifted to an SO₂-free, water-soluble polyacrolein hydrate (80–83).

The carbonyl groups of the insoluble polymers and the aldehyde hydrate groups of the aqueous solutions are quite reactive. They undergo addition and condensation reactions not only with many low molecular-weight reagents, but also with different polymers, eg, with poly(vinyl alcohol), collagen (qv), and gelatin (qv) (82,84–86). According to this principle, proteins, enzymes (84,87,88), lectins (89), red blood cells, lymphocytes, and leukemia cells (90–94) can also be fixed covalently to polyacroleins. These conjugates can be utilized for affinity chromatography and cell separation (see CHROMATOGRAPHY, AFFINITY).

Economic Aspects

Monomeric acrolein is used as a starting material for various technically important syntheses, such as production of methionine (19), pyran derivatives, or glycerol. Acrolein homopolymers from free-radical polymerization may have uses, for example, as biocidal or biostatic agents similar to monomeric acrolein, although they are not soluble in either aqueous or organic environments (95). Copolymers of acrolein and formaldehyde formed by condensation polymerization with a basic catalyst have been found to be water-soluble biocides (96). By oxidative copolymerization of acrolein with acrylic acid, a product of commercial interest is obtained (97–102). This copolymer has both pendent aldehyde and carboxylic acid groups:



Because during the polymerization part of the acrolein is oxidized and incorporated as acrylic acid units, $m + n = x + y$, but $x < m$ and $y > n$.

This material has the Degussa trade name POC, and is a strong complexing agent which has attracted interest as a sequestering agent for water treatment.

Of the great variety of methods for modifying the carbonyl groups of polyacrolein, thus far only a few have been used for research purposes on the laboratory scale. The possible application of polyacroleins or copolymers as polymeric reagents, polymeric complexing agents, and polymeric carriers should be recognized.

The binding capacity of polyacrolein microspheres toward several amino ligands have been studied (103). Amino ligand-microsphere conjugates may be used in various biological applications (see POLYMERIC DRUGS).

Analytical and Test Methods

Ir spectroscopy is a simple, qualitative test for characterizing polyacroleins (46,53–55). Radical and cationic polymerizations yield homopolymers that exhibit typical sharp bands at 1700 cm^{-1} ($5.85 \mu\text{m}$) for the C=O bond vibration and 2700 cm^{-1} ($3.65 \mu\text{m}$) for the CH bond vibration of the aldehyde group. A broad unstructured band between 1180 cm^{-1} ($8.5 \mu\text{m}$) and 900 cm^{-1} ($11 \mu\text{m}$) indicates the presence of ether and acetal bonds. Anionic polymerization methods yield polymers that show only a weak band at $1700\text{--}1660 \text{ cm}^{-1}$ ($5.85\text{--}6.0 \mu\text{m}$) and 3120 cm^{-1} ($3.25 \mu\text{m}$). Because of the solubility characteristics of polyacrolein, ^1H and ^{13}C spectra can be obtained only for anionically initiated homopolymers (47) and copolymers with small acrolein content made under radical conditions. The microstructure of polyacroleins prepared by ionizing radiation and by sodium hydroxide catalysis has been studied by solid-phase ^{13}C -nmr (104).

The quantitative determination of carbonyl groups is of special interest. For this purpose, chemical methods are used based on reactions with hydroxylamine (54,105) or dinitrophenylhydrazine (106). Soluble and insoluble polymers can be analyzed with these reagents. Fuchsin-sulfurous acid forms a blue color with polyacrolein (80–82). This reaction may serve as a qualitative test for free aldehyde groups.

Standard methods for molecular-weight determination (qv) can be utilized only for soluble homopolymers and copolymers. The crucial point, however, is establishment of a calibration curve (55,107). Insoluble polymers must first be converted to soluble derivatives via chemical modification (108,109). For routine measurements, the reaction of polyacrolein with sulfur dioxide in water has proven effective. The resulting water-soluble addition compound is suitable for viscometry after addition of sodium chloride (29). Different derivatives may also be used for molecular-weight determination, provided that the conversion is known and chain degradation can be ruled out.

Health and Safety Factors

Monomeric acrolein must be handled with utmost caution because of its high flammability and irritating effect on eyes and mucous membranes. The TLV for safe, continued 8 h exposure is 0.1 ppm by volume in air. Concentrations as low as 0.5 ppm cause a distinct lacrimatory effect; concentrations of 5 ppm are completely intolerable, although the toxification threshold is much higher. Because of its extreme lacrimatory effect, acrolein serves as its own warning agent (5). Because polymeric acrolein may be useful as a biocidal agent and the insoluble polymers are highly reactive, caution should also be taken with both homopolymers and copolymers.

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ACRYLAMIDE POLYMERS

Introduction

The terminology used to describe acrylamide-containing polymers in the technical literature varies in its precision. In order to avoid confusion, throughout this article the term “poly(acrylamide)” is reserved for the nonionic homopolymer of acrylamide, whereas the term “polyacrylamides” or “acrylamide polymers” refers to acrylamide-containing polymers, including the homopolymer and copolymers. Specific nomenclature is used for particular copolymers, for example, poly(acrylamide-*co*-sodium acrylate).

The diverse class of water-soluble and water-swelling polymers comprising polyacrylamides contains some of the most important synthetic polymeric materials used to improve the quality of life in our modern society. Acrylamide-containing polymers fall into three main categories: nonionic, anionic, and cationic. The projected annual sales growth rate of polyacrylamides between 1999 and 2002 is 4–7% (1). The multi-billion-dollar global market value of this class of materials makes it an economically important segment of the chemical industry.

Poly(acrylamide) is made by the free-radical polymerization of acrylamide, which is derived from acrylonitrile by either catalytic hydrolysis or bioconversion. The unique chemistry of acrylamide, its favorable reactivity ratios with many comonomers, and the ability of poly(acrylamide) to be derivatized allows for a substantial variety of polymers to be tailor-made over a wide range of molecular weights (approximately 10^3 – 50×10^6 Da), charge densities, and chemical functionalities.

A very large number of applications for acrylamide-containing polymers have been extensively reviewed (2–7). One major application area for polyacrylamides is in solid–liquid separations. The largest market segments therein are for use as flocculants and dewatering aids for municipal wastewater, thickening aids for industrial wastewater, secondary clarification and clarification of potable water, solids removal from biological broths, and animal feed recovery from waste. Because of major concern for the environment, the allowable suspended solids in most effluent streams are becoming more restricted by government regulations. New technologies for producing cationic polymers with a wide range of charge levels, novel structures, and very high molecular weights have addressed this need. These polymers have greatly improved the dewatering performances of centrifuges, screw presses, and belt presses used for such purposes. This has resulted in drier dewatered solids, which has translated into lower costs to either landfill or incinerate the solids.

The largest volume applications for polyacrylamides in paper mills are in on-machine wet-end processes. Paper retention aids and drainage aids are used to flocculate or bind fillers, fibers, and pigments. Glyoxalated cationic polyacrylamides are used as strengthening agents and promoters for paper sizing. Other papermaking applications include off-machine processes for recovering fiber from recycled paper waste and for deinking.

High molecular weight polyacrylamides have also traditionally been used in the minerals processing industry. Recent polymer technology developments, including ultra high molecular weight and novel anionic polyacrylamides, have

yielded important materials. These products are used as flocculants in coal mining, the Bayer process for alumina recovery (red mud flocculants), precious metals recovery, and the solid-liquid separation of underflow streams in a variety of mining processes. Novel chemical modifications of low molecular weight polyacrylamides have resulted in materials that are used as modifiers in the selective separation of metal sulfides and magnetite and as depressants and flotation aids.

One large market segment for anionic polyacrylamides had traditionally been in enhanced oil recovery. However, low oil prices have resulted in a large decline in such applications. Since 1990, polymer flooding has virtually disappeared in the United States. However, during 1999 crude oil prices started to increase.

Other significant application areas for polyacrylamides include soil conditioning and erosion control, drag reduction, sugar processing, additives in cosmetics, and superabsorbents.

Physical Properties

Solid Polyacrylamides. Completely dry poly(acrylamide) is a brittle white solid. It is nontoxic, unlike the monomer. Dry polyacrylamides (including copolymers) are commercially available as nondusting powders and as spherical beads. These products can contain small amounts of additives that aid in both the stability and dissolution of the polymers in water. Commercially available acrylamide copolymer powders, which are typically dried under mild conditions, will usually contain about 5–15% water depending on their ionicity. The powders are hygroscopic, and generally become increasingly hygroscopic as the ionic character of the polymer increases. Cationic polymers are particularly hygroscopic.

Some physical properties of nonionic poly(acrylamide) are listed in Table 1. The tacticity and linearity of the polymer chain is claimed to be dependent on the polymerization temperature. Syndiotacticity is favored at low temperatures (20). Linear polymer chains are reportedly obtained below 50°C, but branching begins to occur as the temperature is increased above this level (21). A wide range of values of the glass-transition temperature (T_g) of poly(acrylamide) have been published. This is because the measured value is highly sensitive to the presence of water and also to the presence of nonacrylamide species along the polymer backbone. For example, small amounts of acrylate groups can arise from hydrolysis of the amide group during or after polymerization. This can dramatically change the T_g .

Solution Properties. The amide group ($-\text{CONH}_2$) in poly(acrylamide) provides for its solubility in water and in a few other polar solvents such as glycerol, ethylene glycol, and formamide. We can acquire a sense of poly(acrylamide)'s affinity for water by examining a few characteristic parameters. Theta (Θ) conditions for a polymer delineate a particular combination of solvent and temperature at which the polymer acts in an ideal manner (22), ie, the chains behave as random coils. The Θ temperature of poly(acrylamide) in water has been determined to be -8°C (23). Thus, water at 25°C is a solvent of intermediate quality for poly(acrylamide). Aqueous methanol (40 vol%), however, is a Θ solvent for poly(acrylamide) at 25°C (24). The Flory χ parameter, which

Table 1. Physical Properties of Solid Poly(acrylamide)

Property	Value	Reference
Density	1.302 g/cm ³ (23°C)	8
Glass-transition temperature (T_g)	195°C	9
Critical surface tension (γ_c)	52.3 mN/m (= dyn/cm) (20°C)	10
Chain structure	Mainly heterotactic linear or branched, some head-to-head addition	11–14
Crystallinity	Amorphous (high molecular weight)	15
Solvents	Water, ethylene glycol, formamide	16
Nonsolvents	Ketones, hydrocarbons, ethers, alcohols	17
Fractionation solvents	Water–methanol	18
Gases evolved on combustion in air	H ₂ , CO, CO ₂ , NH ₃ , nitrogen oxides	19

Table 2. Physical Properties of Poly(acrylamide) in Solution

Property	Value	Conditions	Reference
Steric hindrance parameter (σ)	2.72	Water @ 30°C	26
Characteristic ratio (C_∞)	14.8	Water @ 30°C	26
Persistence length (γ)	1.52 nm	Water @ 25°C	— ^a
Partial specific volume (v)	0.693 cm ³ /g	Water @ 20°C	27
Theta temperature (Θ)	−8°C	Water	23
Theta conditions	0.40 v/v methanol/water	25°C	24
Flory χ parameter	0.48 ± 0.01	Water @ 30°C	25
Refractive index increment (dn/dc)		Water @ 25°C	28
	0.187 cm ³ /g	$\lambda = 546.1$ nm	
	0.185 cm ³ /g	$\lambda = 632.8$ nm	

^aCalculated from the values of K_0 (Mark–Houwink–Sakurada prefactor under Θ conditions) and Θ_0 (viscosity constant) found in Ref. (21), using the relationship: $\gamma = (\frac{M_0}{2b})(\frac{K_0}{\Theta_0})^{2/3}$, where M_0 is the monomer molecular weight (71 g/mol), and b is the monomer length (0.25 nm).

is a measure of the relative affinity between the polymer segments with each other vs with the solvent, is 0.5 under Θ conditions. The Flory χ parameter of poly(acrylamide) has been determined to be 0.48 in water at 30°C (25). These and other properties of poly(acrylamide) in solution are collected in Table 2.

Poly(acrylamide) is soluble in liquid water at all concentrations, temperatures, and pH values. However, at high pH (>10.5) the polymer will begin to hydrolyze on standing (29). Poly(acrylamide) is generally soluble in most salt solutions but can phase separate in some highly concentrated salt solutions, such as (NH₄)₂SO₄. Each amide group in poly(acrylamide) has roughly 2 strongly bound water molecules (30) associated with it, whereas the entire first hydration sheath contains a total of about 4–5 water molecules per monomer (31). This may be compared to poly(sodium acrylate), which has 4 strongly bound water molecules per repeat unit (32) and a total of 11 water molecules of hydration per repeat unit (33). Certain salts, however, can alter the hydrogen bonding between the primary amide groups and water in individual chains. For example, addition of potassium

iodide [7681-11-0] to a poly(acrylamide) solution can increase the solution viscosity slightly (34). The inferred coil expansion involves a change in the hydration sheath of the polymer.

The amide group is capable of strong hydrogen bonding, which has effects on both the monomer and polymer properties. The relative rates of acrylamide polymerization in various organic solvents (35–37) are influenced by solvent–monomer interactions, which depend on the polarity and hydrogen bonding ability of acrylamide. Hydrogen bonding has been evidenced (with nmr) to occur mainly with the carbonyl oxygen in the acrylamide (38,39).

The hydrogen bonding ability of the amide group is also well worth considering when rationalizing the solution properties of polymers containing acrylamide. Two examples are presented here. The slow evolution of hydrogen-bonded aggregates (see the following) have been implicated in explaining the time dependence of the viscosities of poly(acrylamide) solutions in aqueous media (12,40). Second, it is well known that copolymers of acrylamide and sodium acrylate exhibit maximum values of the mean square radius (R_g), second virial coefficient (A_2), and intrinsic viscosity $[\eta]$ at 60–70 mol% acrylate content (41). This can be rationalized from a consideration of intermolecular hydrogen bonding and electrostatic interactions.

Copolymers of acrylamide with ionic comonomers are also generally quite soluble in water. However, the solution properties of ionized copolymers of acrylamide are substantially different from those of the homopolymer. The incorporation of ionic comonomers leads to all of the traditional polyion effects such as chain expansion and viscosification at low ionic strength (polyelectrolyte effect), ionization-dependent dissociation constants, counterion condensation, ion exchange with charged surfaces, and specific binding of certain multivalent ions. For example, anionic copolymers containing carboxylate groups will precipitate at certain multivalent salt concentrations (42–44). Poly(sodium acrylate) can phase separate in the presence of divalent salts when there are about 0.8 equivalents of the divalent cations (45). The phase behavior of acrylamide–acrylic acid copolymers in mixtures of mono and divalent salts has been studied (46). Trivalent cations (eg, Al^{3+} and Cr^{3+}) are even more efficient at precipitating polyions containing carboxylate groups (47). Under the right conditions, these physical crosslinks can be used to form a reversible gel. This strategy has been employed in mobility control systems used in oil recovery (48).

The rate of dissolution of polyacrylamides can depend on the agitation conditions, dissolved salts, the material form of the polymer (eg, solid or emulsion), state of hydration, and the presence of other components. While salts only weakly affect the dissolution rate of poly(acrylamide), ionic copolymers tend to dissolve decidedly more slowly in salt solutions than in pure water. Increasing the mechanical energy input typically speeds up the dissolution process; however, mechanical degradation (chain scission) of very high molecular weight chains can occur. Flows with elongational components (eg turbulent and porous media flows) are usually most egregious in this regard. The coil-to-stretched transition initiated at a critical elongation rate in these flows can be responsible for such phenomena as drag reduction (49) and apparent viscosity enhancement in porous media flow (50,51). However, chain scission can also occur at a second critical elongation rate. These critical elongation rates are functions of the degree of

polymerization, the solvent quality, and the polymer concentration (52–56). Care is often taken to avoid mechanical degradation of the polymer during mixing [especially in impeller-type mixers (57), gear pumps, and orifice flow], filtration, and flow through a packed column [eg, in high performance size-exclusion chromatography (HPSEC) analysis], all of which expose the polymer chains to some elongational flow kinematics.

Linear polyacrylamides in solution adopt nearly random coil configurations that are partially permeable (draining) to solvent. The coils are unassociated in dilute solution. The average shape of the isolated coils has been described as an ellipsoidal or bean-shaped structure (58). The individual chains are quite flexible, as is common with most vinyl polymers. This is indicated from several parameters shown in Table 2, such as the persistence length, steric hindrance parameter (σ), and characteristic ratio (C_∞). The persistence length of 1.52 nm for poly(acrylamide) in water is quite similar to the average intrinsic (bare) persistence length (~ 1.4 nm) of many vinyl polymers (59).

One measure of the size of a polymer in solution is its mean square radius (R_g), sometimes referred to as its radius of gyration. The mean square radius scales with the weight-average molecular weight (M_w) to a fractional power (a_r) for a homologous series of polymers all within the same topology class (eg, linear chains); $R_g = K_r M_w^{a_r}$. The K_r and a_r values depend on the polymer, solvent, and temperature. Suggested values derived from the literature for poly(acrylamide) and a few copolymers are listed in Table 3.

Solution Rheology. Solutions of polyacrylamides tend to behave as pseudoplastic fluids in viscometric flows. Dilute solutions are Newtonian (viscosity is independent of shear rate) at low shear rates and transition to pseudoplastic, shear thinning behavior above a critical value of the shear rate. This critical shear rate decreases with the polymer molecular weight, polymer concentration, and the thermodynamic quality of the solvent. A second Newtonian plateau at high shear rates is not readily seen, probably because of mechanical degradation of the chains (12). Viscometric data for dilute and semidilute poly(acrylamide) solutions can often be fit to a Carreau model (63,64). It is wise to remember the cautions that were cited previously about mechanical degradation of the high molecular weight components of a polyacrylamide sample when analyzing rheological data.

The viscosities of fully dissolved, high molecular weight poly(acrylamide)s in aqueous solutions have often, but not always, been seen to change with time over the periods of days to weeks. Typically, the solution viscosity decreases with time. Extensive studies of this instability phenomenon have been made (12,40) and it was concluded that the evolution of intramolecular hydrogen bonds and the resulting change in macromolecular conformation were responsible for the time dependence, and not any molecular weight degradation. The instability can be avoided completely when the polymers are dissolved in formamide, aqueous ethylene glycol, or 2% 2-propanol in water. Competing viewpoints do exist about the interpretation of this solution aging (65,66).

The intrinsic viscosity $[\eta]$ of a polymer in solution is a measure of its molecular volume divided by its molecular weight. The $[\eta]$ value can be empirically correlated to the viscosity-average molecular weight (M_η) via the Mark–Houwink–Sakurada relationship (67): $[\eta] = K_\eta M_\eta^{a_\eta}$. Poly(acrylamide) and

Table 3. Suggested R_g - M_w Correlations for Polyacrylamides in Solution $R_g = K_r M_w^{a_r}$ (R_g in nm)

Polymer	Solvent	Temp., °C	MW range (10^6 Da)	$10^2 K_r$, nm	a_r	Reference
Poly(acrylamide)	Water	25	0.83–13.4	0.725	0.64	23
Poly(acrylamide)	0.1 M NaCl + 0.2% NaN ₃	20	0.16–8.2	0.749	0.64	60
Poly(Na acrylate ₂₉ -co-acrylamide ₇₁)	0.1 M NaCl		0.96–6	2.50	0.60	44
Poly(Na acrylate ₂₀ -co-acrylamide ₈₀)	1 M NaCl pH 9	Ambient	0.1–3.0	4.06	0.55	61
Poly(acrylamide ₇₀ -co-AETAC ₃₀)	1 M NaCl + biocide		0.5–2.7	3.30	0.54	62

ionic copolymers of acrylamide follow this empirical relationship, which is often used to estimate the polymer molecular weight. Table 4 lists suggested literature values of K_η and a_η for poly(acrylamide) and several copolymers in a variety of solvents.

At high concentrations of univalent ions ($\sim 1 M$), the solution properties of ionic copolymers of acrylamide tend to resemble those of the homopolymer, but they are not exactly the same. Considering the intrinsic viscosity data, the exponents a_η for anionic and cationic polyacrylamides in high salt concentrations tend to cluster between 0.7 and 0.8, which is similar to that for poly(acrylamide) (12,23,60–62,71–75). However, the prefactors (K_η) vary over a larger range, and this cannot be rationalized simply by considering only the degree of polymerization. This means that there are real differences in the short-range interactions along the chains, which depend on the copolymer composition.

The polymer concentration (c) dependence of the zero-shear-rate viscosity (η_0) for aqueous poly(acrylamide) solutions of various viscosity-average molecular weights does not seem to follow the entanglement model, wherein polymer chain interpenetration would dominate the viscometric behavior, and a master curve should result when η_0 is plotted against cM_η . Instead, the data can be better described using a suspension model, wherein $c[\eta]$ correlates the η_0 data on a master plot. A concise presentation of the relationship between η_0 , M_η , and c for poly(acrylamide) in water at 25°C has been made (12).

Solutions of poly(acrylamide) that are well in excess of the overlap concentration can display viscoelastic properties. Viscoelasticity of these polymeric fluids can be observed in a variety of ways, including the presence of a normal stress and/or flow irregularities (eg, vortices) in steady-shear flow, stress overshoot during shear flow startup, a measurable storage modulus (G') in oscillatory flow, an apparent shear thickening in flows with an elongational component (eg, porous media flow), a measurable elongational viscosity, or the ability to pull a solution "fiber" (tubeless siphon effect). A simple means for qualitatively assessing the molecular weight of a linear poly(acrylamide) in solution is to see how long a thread one can pull out of a semidilute solution of the polymer using a rod.

Acrylamide Polymerization

Acrylamide [79-06-1] (2-propenamide, C_3H_5ON) readily undergoes free-radical polymerization to high molecular weight poly(acrylamide) [9003-05-8]. The synthetic methods have been reviewed extensively (12). Free-radical initiation can be accomplished using organic peroxides, azo compounds, inorganic peroxides including persulfates, redox pairs, photoinduction, radiation-induction, electroinitiation, or ultrasonication. Several reasons account for the ultrahigh molecular weights achievable. First, preparations of polyacrylamides are usually conducted in water, and the chain transfer constant to monomer and polymer appears to be zero in water (76). Second, the value of $k_p/k_t^{1/2}$, about 4.2, is unusually high (77) and is independent of the pH of the media. The rate of polymerization is proportional to the 1.2–1.5 power of the monomer concentration and to the square root of the initiator concentration (78–80). All this results in a high rate of propagation. Chain termination is primarily by disproportionation (81).

Table 4. Suggested Mark-Houwink-Sakurada Correlations for Polyacrylamides in Solution $[\eta] = K_{\eta} M_{\eta}^a a_{\eta}$ ($[\eta]$ in cm³/g)

Polymer	Solvent	Temp., °C	MW range (10 ⁶ Da)	10 ² K_{η} , cm ³ /g	a_{η}	Reference
Poly(acrylamide)	Water	25	0.038–9	1.00	0.76	68
Poly(acrylamide)	0.5 <i>M</i> NaCl	25	0.5–5.5	0.719	0.77	69
Poly(acrylamide)	1.0 <i>M</i> NaCl	25	1.1–14.6	2.57	0.67	70
Poly(Na acrylate ₂₀ - <i>co</i> -acrylamide ₈₀)	0.5 <i>M</i> NaCl pH 9	25	0.12–3.0	1.40	0.75	61 ^a
Poly(Na acrylate ₂₀ - <i>co</i> -acrylamide ₈₀)	0.5 <i>M</i> NaCl pH 9	25	0.12–3.0	1.09	0.78	61 ^b
Poly(Na acrylate ₃₀ - <i>co</i> -acrylamide ₇₀)	0.5 <i>M</i> NaCl	25	0.77–5.5	1.12	0.79	69
Poly(Na acrylate ₂₀ - <i>co</i> -acrylamide ₈₀)	1.0 <i>M</i> NaCl pH 9	25	0.12–3.0	1.41	0.74	61 ^a
Poly(Na acrylate ₂₀ - <i>co</i> -acrylamide ₈₀)	1.0 <i>M</i> NaCl pH 9	25	0.12–3.0	1.31	0.76	61 ^b
Poly(acrylamide ₇₀ - <i>co</i> -AETAC ₃₀)	1.0 <i>M</i> NaCl + biocide	25	0.5–2.7	1.05	0.73	62

^aUncorrected or polydispersity.

^bCorrected for polydispersity.

The large amount of heat (82.8 kJ/mol) that evolves during polymerization can result in a rapid temperature rise. One way in which this exotherm problem has been addressed in commercial high-solids and high-molecular-weight processes has been through the use of an adiabatic gel process in which the initiation temperature is 0°C. In another approach, controllable-rate redox polymerization of aqueous acrylamide-in-oil emulsions can be carried out at moderate temperatures of 40–60°C in order to accommodate the exotherm and to achieve very high molecular weights. At 70–100°C, a persulfate initiator can give a grafted or branched polymer (82). Additives greatly affect the rate and the kinetics of polymerization (83,84). These additives include metal ions, surfactants, chelating agents, and organic solvents. The high chain-transfer constant of compounds such as 2-propanol, bisulfite ion, or persulfate ion to active polymer has been reported (85). Chain-transfer agents have been used purposely to control molecular weight, minimize insoluble polymer, and control cross-linking and the degree of branching in commercial preparations.

Structural Modifications of Poly(acrylamide)

Poly(acrylamide) is a relatively stable organic polymer. However, poly(acrylamide) can be degraded (eg, molecular weight decreases) under certain conditions. The amide functionality is acidic in nature and is capable of undergoing most of the chemical reactions of primary amides. Consequently, acrylamide polymers can be functionalized by post-polymerization chemical reactions. Examples illustrated in the following constitute the most-used chemical modifications. To obtain anionic derivatives, poly(acrylamide) can be hydrolyzed with caustic. Sulfomethylated poly(acrylamide) can be prepared by reacting poly(acrylamide) with formaldehyde and sodium bisulfite under acidic conditions. Reacting poly(acrylamide) with hydroxylamine under alkaline conditions can yield hydroxamated poly(acrylamide). As an example of a cationic derivative, Mannich-base poly(acrylamide) can be obtained by reacting poly(acrylamide) with formaldehyde and dimethylamine to produce a cationic polymer with a charge that varies with pH. As an example of a nonionic derivative, poly(acrylamide) can be reacted with glyoxal to yield pendent aldehyde functionality. These structurally modified polyacrylamides are successful commercial products.

Degradation. Dry poly(acrylamide) is relatively stable. The onset of dry poly(acrylamide) decomposition occurs at 180°C (86). Inter- or intra-amide condensation (87) to an imide can occur in acidic media at high temperatures (140–160°C). At temperatures above 160°C, thermal degradation, imidization, nitrile formation, and dehydration take place. Polymer stability is very important in actual applications in order to maintain consistent and excellent performance. In most applications, polymer solutions are prepared and used at moderate temperatures; however, there are exceptions such as in the harsh reservoir conditions (high temperature and high salinity) found in some enhanced oil recovery operations. Impurities such as residual persulfate from batch manufacturing can degrade the polymer (88,89). A residual Fe^{2+} EDTA complex in the product can also enhance degradation at both ambient and elevated temperatures (90–92).

Hydroxy radicals, which can form in the presence of oxygen (93,94), can attack the polymer backbone. In the absence of oxygen, anionic polyacrylamide solutions were stable at 90°C for 20 months (95). Polyacrylamide in aqueous solution, in the presence of oxidizing agents such as KMnO_4 , bromine, and AgNO_3 , will degrade. The degraded polymer shows a reduced molecular weight, cross-linking, and chain stiffening (96). Recently, potassium peroxosulfate (97) was also reported to degrade hydrolyzed polyacrylamide. In the presence of ozone, very little degradation was found at low pH. However, random chain scission occurred at pH 10 (98). In the presence of sodium azide, a bactericide, a poly(acrylamide) in solution at room temperature showed no degradation for a long time (60). A combination of both pressure and elevated temperature can enhance polyacrylamide degradation. Polymer degradation can also occur under shear and elongational stresses (93,99). Backbone homolytic cleavage has been confirmed by a free-radical trap technique. Under certain shear conditions one macroradical per 12 monomer units can be formed.

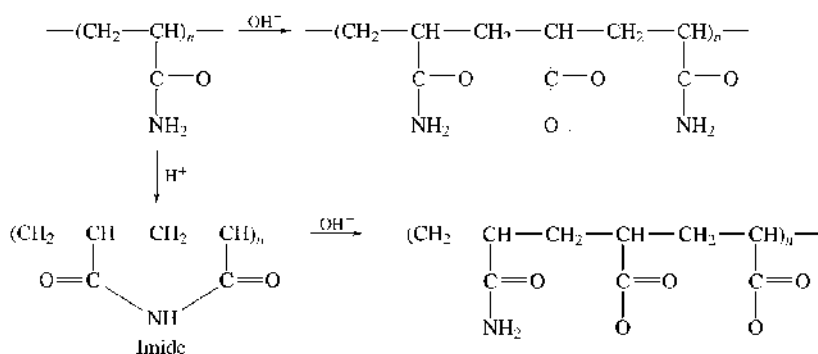
Numerous types of oxygen scavengers are used to inhibit and prevent oxidative degradation. These stabilizers have been reviewed (96) extensively. Effective compounds are thio compounds, hydroquinone, bisulfite, phenolic compounds, hydroxylamine, hydrazine, and others.

The biodegradability of poly(acrylamide) has not been definitively delineated in the literature (96). Recently, however, microorganisms (100), enterobacter agglomerans and azomonas macrocytogenes, were isolated from soil and the molecular weight of poly(acrylamide) in the presence of these microorganisms was found to undergo a 40-fold reduction as a result of chain degradation. The rate of biodegradation was equivalent to 20% of the carbon being consumed each day.

Hydrolyzed Polyacrylamide. Hydrolysis of poly(acrylamide) proceeds smoothly over a wide range of pH. Fundamental studies have been reviewed extensively (13,101–103). At alkaline pH, three reaction kinetics constants have been described, k_0 , k_1 , and k_2 . The subscripts characterize the number of neighboring carboxylate groups next to the amide group being hydrolyzed. The rate constant k_0 is for no carboxylate neighbors, k_1 is for one carboxylate neighbor, and k_2 is for two carboxylate neighbors. Indirect evidence has shown that $k_0 > k_1 > k_2$. Under alkaline conditions, the rate of hydrolysis of poly(acrylamide) decreases with increasing conversion. The electrostatic repulsion from the increasing number of carboxylate groups in the backbone polymer opposes the approaching hydroxyl ion. Consequently, further hydrolysis will be severely retarded. Only about 80% of the amide groups (104) can be hydrolyzed by excess hydroxide ion even at elevated temperatures.

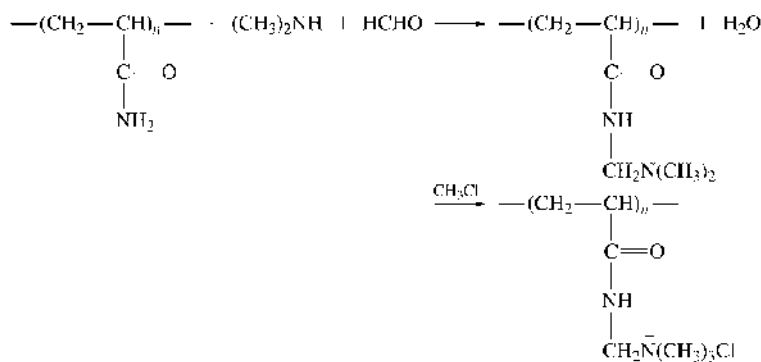
^{13}C nmr studies (105–107) have shown that hydrolysis at high pH results in a nearly random distribution of carboxylate groups. In one industrial process, a polyacrylamide with about 30 mol% hydrolysis is prepared by heating an aqueous poly(acrylamide) solution containing excess sodium carbonate [497-19-8] (108). Polymerization of acrylamide in a water-in-oil emulsion in the presence of sodium hydroxide has also yielded a copolymer with about 30 mol% hydrolysis (109). A method of preparing a hydrolyzed poly(acrylamide) (104) with a viscosity-average molecular weight greater than 30×10^6 Da was achieved in an inverse emulsion, in the presence of caustic, ethoxylated fatty amine, and oil.

Hydrolysis of poly(acrylamide) proceeds slowly under acidic conditions. The undissociated carboxylic acid groups are protonated, neutral species under those conditions. The intramolecular catalysis by means of undissociated—COOH groups at low pH has been proposed as the main mechanism (92). An imide structure has been proposed to be an intermediate in the low pH hydrolysis of poly(acrylamide), yielding short blocks of carboxyl groups distributed along the polymer chain. To date, there has been limited application of these block copolymer structures, and ones with high molecular weight have not been commercialized.



Under neutral conditions, the observed mechanism of hydrolysis cannot be explained by a simple superposition of the retardation kinetics at high pH and intramolecular catalysis at low pH (92).

Cationic Carbamoyl Polymers. Poly(acrylamide) reacts with formaldehyde [50-00-0], CH_2O , and dimethylamine [124-40-3], $\text{C}_2\text{H}_7\text{N}$, to produce aminomethylated polyacrylamide (a Mannich reaction). This reaction has been studied extensively (110–114). A wide range of substitution can be produced in solution or in water-in-oil emulsion. ^{13}C nmr studies (114) have verified that the Mannich substitution reaction follows second-order kinetics. The formation of the formaldehyde–dimethylamine adduct is very rapid. The high rate of Mannich substitution at high pH indicates a fast base-catalyzed condensation mechanism. The Mannich reaction is reversible and pH dependent. At low pH, the rate of substitution is very slow.

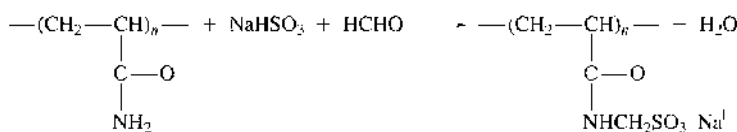


Mannich Reaction

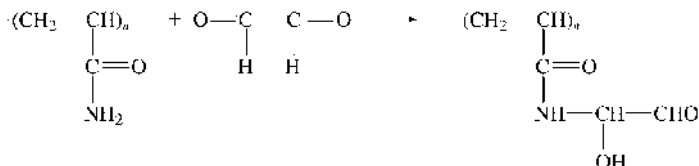
Because of the simplicity of the process, the small capital investment for manufacturing equipment, and the low raw material costs, this group of cationic water-soluble polymers constitutes a substantial percentage of commercially important flocculants. Solution Mannich polyacrylamides are prepared and sold only at 4–6% solids, limited by the large solution viscosities and propensity for cross-linking on standing. The addition of formaldehyde scavengers such as guanidine compounds and dicyandiamide [461-58-5] (115) have improved the shelf stability. Aminomethylation of poly(acrylamide) is a reversible reaction. The reverse reaction can be retarded if the pendent amine groups are protonated by addition of an acid. Mannich base products protonated with organic acids or mineral acids have been patented (116). Low charge-density quaternized aminomethylated products are also sold at polymer solids less than 3% because of very high solution viscosities at higher polymer concentrations.

Several disadvantages of solution Mannich poly(acrylamide)s are the problem of handling high solution viscosities, the added expense of shipping low solids formulations, and the limitations to applications with low pH substrates because of the decrease in cationic charge with increasing pH. Quaternized aminomethylated products in water-in-oil emulsions with greater than 20% solids have been developed. The charges in both high and low charge products were nearly independent of pH (113,117–119). Microemulsion formulations have been developed and now they replace certain polymer macroemulsions. In one such case, poly(acrylamide) was functionalized in a microdroplet (~100 nm in diameter) that contained only a few poly(acrylamide) molecules (120). Products based on this technology have been commercially successful as high performance cationic organic flocculants for municipal and industrial wastewater applications (121,122).

Sulfomethylation. The reaction of formaldehyde and sodium bisulfite [7631-90-5] with polyacrylamide under strongly alkaline conditions at low temperature to produce sulfomethylated polyacrylamides has been reported many times (123–125). A more recent publication (126) suggests, however, that the expected sulfomethyl substitution is not obtained under the previously described strongly alkaline conditions of pH 10–12. This nmr study indicates that hydrolysis of polyacrylamide occurs and the resulting ammonia reacts with the sodium bisulfite and formaldehyde to form sulfomethyl amines and hexamethylenetetramine [100-97-0]. A recent patent describes a high pressure, high temperature process at slightly acid pH for the preparation of sulfomethylated polyacrylamide (127).



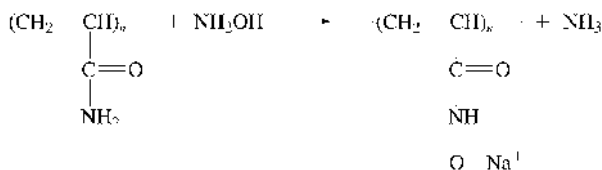
Reaction with Other Aldehydes. Poly(acrylamide) reacts with glyoxal [107-22-2], $\text{C}_2\text{H}_2\text{O}_2$, under mild alkaline conditions to yield a polymer with pendent aldehyde functionality.



The rate of this reaction can be controlled by varying the pH and reaction temperature. Cross-linking is a competing reaction. The reaction rate increases rapidly with increasing pH and with increasing polymer concentration. In a typical commercial preparation, a 10% aqueous solution of a low molecular weight polyacrylamide reacts with glyoxal at pH 8–9 at room temperature. As the reaction proceeds, solution viscosity increases slowly and then more rapidly as the level of functionalization and cross-linking increases. When the desired extent of reaction is achieved, before the gel point, the reaction is acidified to a pH below 6 to slow the reaction down to a negligible rate. These glyoxalated polyacrylamides are used as paper additives for improving wet strength (128).

A similar reaction occurs when poly(acrylamide) is mixed with glyoxylic acid [298-12-4], $\text{C}_2\text{H}_2\text{O}_3$, at pH about 8. This reaction produces a polymer with the $\text{CONHCH}(\text{OH})\text{COOH}$ functionality, which has found application in phosphate ore processing (129).

Transamidation. Poly(acrylamide) reacts with hydroxylamine [7803-49-8], H_2NOH , to form hydroxamated polyacrylamides with loss of ammonia (130).



This hydroxamation reaction occurs under alkaline conditions (131–133). Carboxyl groups can be produced because of the hydrolysis of the amide (131, 132). Acrylamide polymers can also be reacted with primary amines such as 2-aminoethanesulfonic acid (taurine) [107-35-7] at high temperature and acid pH to yield N-substituted copolymers containing sulfoethyl groups (134).

Hofmann Reaction. Polyacrylamide reacts with alkaline sodium hypochlorite [7681-52-9], NaOCl , or calcium hypochlorite [7778-54-3], $\text{Ca}(\text{OCl})_2$, to form a polymer with primary amine groups (135). Optimum conditions for the reaction include addition of a slight molar excess of sodium hypochlorite, followed by addition of concentrated sodium hydroxide at low temperature (136). A two-stage addition of sodium hydroxide minimizes a side reaction between the pendent amine groups and isocyanate groups formed by the Hofmann rearrangement (137). Cross-linking sometimes occurs if the polymer concentration is high. High temperatures can result in chain scission. If long reaction times are used, NaOCl will cause chain scission and molecular weight decline. If very short

reaction times are used at temperatures above 50°C, then polymers with high primary amine content can be obtained (138).

Reaction with Chlorine. Poly(acrylamide) reacts with chlorine under acid conditions or with NaOCl under mild alkaline conditions at low temperature to form reasonably stable *N*-chloropolyacrylamides. The polymers are water soluble and can provide good dry strength, wet strength, and wet web strength in paper (139).

Chemistry of Acrylamide Copolymers

Cationic Copolymers. The largest segment of the acrylamide polymer market has been dominated by cationic copolymers. The copolymers of acrylamide (AMD) and cationic quaternary ammonium monomers are manufactured by various commercial processes, which will be discussed in a later section. The most widely used of these cationic comonomers are cationic quaternary amino derivatives of (meth)acrylic acid esters or (meth)acrylamides, and diallyldimethylammonium chloride.

The quaternary ammonium monomer contents in these copolymers are typically between 5 and 80 mol% for most applications. The composition actually employed depends on cost–performance relationships. Costs are largely dominated by the cationic monomer. Thus, the cationic demand of the substrate for each application has to be optimized. Normally, low- to medium-charge copolymers are used for paper waste applications and medium- to high-charge copolymers are used for sludge dewatering. The molecular weights for flocculants are usually 5×10^6 Da or greater. The higher molecular weight polymers often have the advantage of lower dosages in water treating and better fines capture in paper manufacture. Commercially important cationic comonomers, along with their reactivity ratios with acrylamide, are listed in Table 5.

Copolymers [69418-26-4] of acrylamide and AETAC (see Table 5, footnote *b*) are the most important flocculants because of a uniform sequence distribution of comonomers (140,141). Reactivity ratios obtained under very different free-radical copolymerization conditions can agree very well. For example, in one case, a free-radical copolymerization was initiated using potassium persulfate (KPS) [7727-21-1] in aqueous solution at pH 6.1 (141), while in the other case the copolymerization was initiated using a TBHP/MBS redox pair in an inverse emulsion stabilized with sorbitan monooleate (SMO) at pH 3.5 (140). The surfactant in an inverse emulsion may alter the reactivity of both AMD and AETAC. For example, when SMO is utilized, in formulations made below the azeotropic monomer composition (ie, the copolymer composition is the same as the monomer feed composition, at about 58 mol% AETAC), AETAC is consumed slightly faster than AMD. On the other hand, if a block copolymeric surfactant, poly(ethylene oxide-*b*-12-hydroxyteric acid) (HB246), is utilized (148), then AMD is the faster reacting monomer. The results suggest that in the interfacial region near the discrete aqueous droplets, the AMD concentration is greater in the HB246 case than in the SMO case.

During AMD/MAETAC copolymerizations, MAETAC [5039-78-1] reacts with its own monomer significantly faster than with AMD. Consequently,

Table 5. Acrylamide Monomer (M₁) Reactivity Ratios

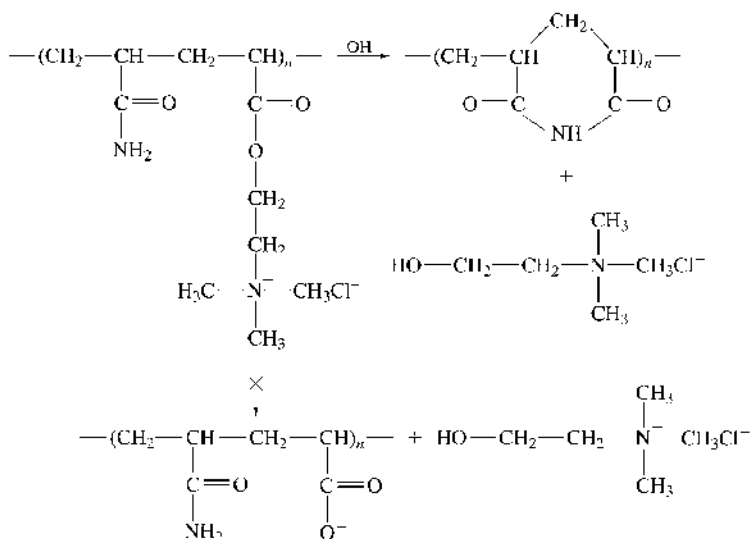
Comonomer M ₂	CAS registry number	Molecular formula	r ₁	r ₂	Initiators ^a	Temp., °C	Reference
Cationic comonomer M^b							
AETAC	[44992-01-0]	C ₈ H ₁₆ NO ₂ Cl	0.61	0.47	TBHP/MBS	40	140
AETAC	[44992-01-0]	C ₈ H ₁₆ NO ₂ Cl	0.61	0.47	KPS	40	141
MAETAC	[5039-78-1]	C ₉ H ₁₈ NO ₂ Cl	0.24	2.47	TBHP/MBS	40	140
MAETAC	[5039-78-1]	C ₉ H ₁₈ NO ₂ Cl	0.25	1.71	KPS	40	141
MAETAC	[5039-78-1]	C ₉ H ₁₈ NO ₂ Cl	0.57	1.11	KPS/NAS	26	142
DMAEAA	[3845-76-9]	C ₆ H ₁₆ N ₂ O	0.47	1.1	KPS	40	141
MAPTAC	[51410-72-1]	C ₁₀ H ₂₁ N ₂ OCl	0.57	1.13	KPS	40	141
DADMAC	[7398-69-8]	C ₈ H ₁₆ NCI	6.4–7.54	0.05–0.58	APS, ACV	20–60	141,143,144
Anionic comonomer M^b							
AA	[79-10-7]	C ₃ H ₄ O ₂	0.25–0.95	0.3–0.95	KPS	30	144,145
AA	[79-10-7]	C ₃ H ₄ O ₂	0.89	0.92	AIBN	45	146
MAA	[79-41-4]	C ₄ H ₆ O ₂	2.8–0.39	0.2–0.51	KPS	30	144
NaAMPS	[5165-97-9]	C ₆ H ₁₂ O ₄ NSNa	0.98	0.49	APS	30	147

^aTBHP: *tert*-Butylhydroperoxide, MBS: sodium metabisulfite, KPS: potassium persulfate, APS: ammonium persulfate, ACV: azocyanovaleic acid, NAS: sodium sulfite, AIBN: 2,2'-azobisisobutyronitrile.

^bAETAC: Acryloyloxyethyltrimethylammonium chloride, CH₂=CHCO₂(CH₂)₂N⁺(CH₃)₃Cl⁻; MAETAC: methacryloyloxyethyltrimethylammonium chloride, CH₂=C(CH₃)CO₂(CH₂)₂N⁺(CH₃)₃Cl⁻; DMAEAA: dimethylaminopropylacrylamide, CH₂=CHCONH(CH₂)₃N(CH₃)₂; MAPTAC: methacrylamidopropylacrylamide, CH₂=C(CH₃)CONH(CH₂)₃N⁺(CH₃)₃Cl⁻; DADMAC: diallyldimethylammonium chloride, (CH₂=CHCH₂)₂N⁺(CH₃)₂Cl⁻; AA: acrylic acid, CH₂=CHCO₂H; MAA: methacrylic acid, CH₂=C(CH₃)CO₂H; NaAMPS: 2-acrylamido-2-methylpropanesulfonic acid, Na salt, CH₂=CHCONH(CH₃)₂CH₂SO₃-Na⁺.

copolymers [35429-19-7] can have severe compositional drift and often poor performance. How the sequence distribution can be improved if copolymerizations of AMD and MAETAC are conducted in water-in-oil microemulsion recipes has been studied (142). $K_2S_2O_8$ - Na_2SO_3 redox initiator and the composite surfactants SMO and octylphenol ethoxylate were used. They found that reactivity ratios for AMD/MAETAC values were $r_{AMD} = 0.57$ and $r_{MAETAC} = 1.11$ (see Table 5).

Quaternary aminoester copolymers are very susceptible to base hydrolysis and are stable under very acidic conditions (140). In both manufacturing and in applications of these products, great care is needed to control the pH in order to prevent hydrolysis. These products should possess sufficient buffering acid to maintain very acidic conditions. The hydrolytic instability of ester copolymers is primarily attributed to a base-catalyzed ester cleavage reaction that forms cyclic imides between neighboring AMD and AETAC groups. The loss in cationic charge is not due to direct ester hydrolysis (149). The chemistry of the six-membered imide ring is shown below (140,150).



The effect of pH on hydrolytic stability of cationic ester-acrylamide copolymers has been long recognized (149). The decrease in viscosity and effectiveness, characteristic of this instability, do not take place in aqueous solutions at pH 2–5. Cationicity loss in AETAC and MAETAC copolymers depends on both pH and composition. For example, in a 43 mol% AETAC copolymer, at least 95% of the ester groups have at least one AMD neighbor. The effect of pH on cationicity loss in this copolymer was minimal at a pH of 2–3 at 90°C for 9 h. Above pH 3, ester loss increased dramatically. Prolonged heating (24 h) resulted in a greater degree of ester loss. It was found that the rate of isolated ester hydrolysis was first order in hydroxide concentration at 60°C at constant buffer pH of 5.5. If there were neighboring acrylamide groups in the chain, then there was a second-order dependence of ester disappearance on hydroxide concentration. This indicated that the imidization reaction was also first order in hydroxide ion concentration.

The percentage of esters cleaved increased as the number of AETAC groups with neighboring AMD groups increased. Polymers with esters and no AMD neighbors such as the homopolymers of AETAC or MAETAC were found to have a low degree of hydrolysis. The rate of hydrolysis of AETAC and MAETAC copolymers were the same only when both had the same number of AMD neighbors.

Cationic copolymers derived from amide monomers, such as MAPTAC [51410-72-1] and APTAC [45021-77-0], are reasonably random and are hydrolytically stable. However, they are more expensive. The molecular weights of high charge AMD/APTAC [75150-29-1] and AMD/MAPTAC [58627-30-8] copolymers typically do not reach the high molecular weights of AMD/AETAC copolymers because of impurities in the APTAC and MAPTAC. However, low charge AMD/MAPTAC copolymers, containing ~3 mol% MAPTAC, are significant commercial products.

Diallyldimethylammonium chloride (DADMAC) [7398-69-8] is the least expensive commercially available cationic monomer. This monomer has been successfully produced by reacting allyl chloride, dimethylamine, and sodium hydroxide in aqueous solution (151,152). Monomer solutions with solids of 60–70% can be achieved and used directly for polymerization without further isolation and purification. DADMAC is a nonconjugated diene monomer that was found to homopolymerize to high molecular weight linear cationic polymer without cross-linking (151,152). Poly(diallyldimethylammonium chloride) (PDADMAC) [26062-79-3] was the first synthetic organic flocculant approved for potable water clarification by the U.S. Public Health Service (154). The polymerization of DADMAC is known as kinetically favorable to give 98% of inter-intra cycloaddition and 2% pendent double bonds (143). The initiator radical attacks the terminal carbon on one allyl group, and the radical formed attacks the internal carbon on the other allyl group in the same molecule to form a five-membered pyrroldinium ring with a cis-to-trans ratio of 6:1 (155).

The rate law for DADMAC polymerization in an aqueous system, when persulfate is used, is not simple: $R_p = (S_2O_8^{2-})^{0.8}(DADMAC)^{2.9}$. A combination of complicated initiation reactions and dimeric DADMAC interactions can account for the unusually high exponent of the DADMAC concentration (156). High monomer concentrations (>1.5 mol/L) used in commercial processes result in greater rates of polymerization and higher molecular weights. PDADMAC with low residual unreacted monomer can be manufactured in water using either persulfate addition or ammonium persulfate with sodium metabisulfite (157). Polymerization of DADMAC has also been studied in water-in-oil emulsion in a continuous stirred tank reactor (158). In that case, the oil-soluble initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), and the surfactants sodium di-2-ethylhexylsulfosuccinate (AOT) and SMO were used. The rate of polymerization was $R_p = k(ADVN)^{0.4}(AOT)^{0.5}(SMO)^{-0.4}(DADMAC)^3$. The negative order of SMO concentration was due to the fact that SMO is a radical scavenger. The influences of partitioning effects and ionic strength contributed to the third order in DADMAC concentration.

The molecular weight of PDADMAC is not as high as for acrylic polymers because of the large chain-transfer constant of allylic radicals. However, a molecular weight of 5×10^5 Da is sufficient for applications such as potable water clarification, color removal, and textile processing. These applications rely on the

very high cationic charge of PDADMAC. This polymer is often used along with a high molecular weight anionic polyacrylamide in process-water clarification in paper deinking mills.

Anionic Copolymers. Anionic acrylamide copolymers such as poly(acrylamide-co-sodium acrylate) [25085-02-3], poly(acrylamide-co-ammonium acrylate) [26100-47-0], poly(acrylamide-co-sodium-2-acrylamido-2-methylpropanesulfonate) (AMD/NaAMPS) [38193-60-1], and poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid) (AMD/AMPS) [40623-73-2] have considerable practical importance. They can be prepared in solution, inverse emulsion (144,145), and inverse microemulsion (146). Comonomer reactivity ratios of AMD with acrylic acid or acrylic acid salts are given in Table 5. Reactivity ratios vary with pH. At high pH the reactivity ratio for AMD is higher, but at low pH the reactivity ratio of acrylic acid is higher. At a pH of about 5, a random copolymer can be obtained. When AMD and sodium acrylate are copolymerized in a microemulsion at pH of about 10, copolymer composition is independent of conversion and the reactivity ratios are equal. The copolymer chain composition conforms to Bernoullian statistics (146). These copolymers are used extensively as industrial flocculants for water treating, mining and paper manufacture, drag reduction agents, and in secondary and tertiary oil recovery. Reasons for their extensive use include their low cost and very high molecular weights. Their limitations include poor solubility at low pH and precipitation of the salt form in the presence of calcium ions.

Comonomer reactivity ratios for AMD and NaAMPS are given in Table 5 (147). AMD/AMPS copolymers and AMD/NaAMPS copolymers maintain their anionic charge at low pH and have a high tolerance to many divalent cations. They are used as flocculants for phosphate slimes, uranium leach residues, and coal refuse. There are also many oilfield applications.

Commercial Processes

There are numerous laboratory methods to prepare polyacrylamides. However, there are only a few viable commercial processes used to manufacture materials that meet the necessary performance standards. There are many requirements for commercial materials: very low to very high molecular weights, low insolubles content, low residual monomer content, fast dissolution rate, ease of handling, minimal dusting (for dry solids), product uniformity, long-term storage stability (to ensure performance consistency), high solids (to reduce shipping costs), and consistent performance characteristics. Several common commercial processes are summarized below.

Solution Polymerization. Commercial production of polyacrylamides by solution polymerization is conducted in aqueous solution, either adiabatically or isothermally. Process development is directed at molecular weight control, exotherm control, producing low levels of residual monomer, and control of the polymer solids to ensure that the final product is fluid and pumpable. A generic example of a solution polymerization follows.

An acrylamide monomer solution (2–30 wt% in water) is typically prepared, and deaerated by sparging it with an inert gas (eg, nitrogen) to reduce the oxygen

content in solution. Stainless steel batch reactors or glass continuous stirred tank reactors are often used for solution polymerizations. A chelating agent is added to complex autopolymerization inhibitors such as copper or other metals, if they are present. The polymerization is then initiated using one of several free-radical initiator systems (azo, peroxy, persulfate, redox, or combinations) at concentrations ranging from 0.001 to 10 wt% on monomer. The rate of polymerization depends on reaction conditions, but it typically depends on the 1.2–1.6 order of monomer concentration and 0.5 order of initiator concentration. The heat evolved during polymerization (82.8 kJ/mol) can be removed by an external cooling system. For adiabatic processes, the temperature rise needs to be estimated and great care needs to be exercised to avoid exceeding the reflux temperature. Chain-transfer agents and inorganic salts can be added to improve processing and to reduce insolubles. Monomer-to-polymer conversions of 99.5% are achievable in 4–6 h of polymerization time. The products can have a molecular weight ranging from one thousand to four million. Polymer solids can be 2–30%. The process can be used in conjunction with thermal drying or precipitation methods in order to obtain products in either powder or granular form. Short residence times in drum drying have been used to avoid chain degradation and formation of insolubles. Precipitation in C_1 – C_4 alcohols can be done to obtain nonsticky rubbery polymer gel that can be further extruded and then dried with hot air. The resulting granules can be milled and sieved to produce a uniform product. Care is taken to avoid very finely divided material that can cause dusting problems.

Some commercial low molecular weight polyacrylamides (LMPAM) are manufactured in solution and sold at 10–50% solids. For example, LMPAM containing DADMAC comonomer is made at 40% solids and can be reacted with glyoxal to produce a strengthening resin for paper. Furthermore, LMPAM hydrolyzed with sodium hydroxide to polyacrylate is manufactured at 30% solids and is used as an antiscalant. High molecular weight poly(acrylamide) is also prepared in solution at 2–6 wt% solids and is often further modified using, for example, the Mannich reaction.

Inverse Emulsion Process. A method of avoiding the high solution viscosities of high molecular weight water-soluble polymers comprises emulsifying the aqueous monomer solution in an oil containing surfactants, homogenizing the mixture to form a water-in-oil (inverse) emulsion, and then polymerizing the monomers in the emulsion. The resulting polymer latex can be inverted in water, releasing the polymer for use. A basic patent (159) illustrated this inverse emulsion process. Processes in which the inverse emulsion polymerization results in finely divided particles that are small enough to retard settling and can be sold without further modification have been developed (160,161). Stability of the inverse emulsion to mechanical shear has recently been improved (162). Commercial production of inverse emulsion polymerization of AMD has been reviewed (163).

Polymerization on Moving Belts. Dry polyacrylamides are sometimes preferred, particularly when transportation distances are long. A variety of continuous processes has been developed for preparing dry polyacrylamides that consist of polymerizing aqueous acrylamide on a moving belt and drying the resulting polymer (164–166). In one such process (167), an aqueous solution of acrylamide and a photosensitizer is pumped onto a moving stainless steel belt,

cooled on the underside by a water spray and covered on the upper side by a humid inert atmosphere. The belt passes under uv lamps that photoinitiate polymerization. The belt speed can be controlled so that the polymerization is complete when the polymer reaches the end of the belt. At the end of the belt the polymer gel that has formed can be sliced into small granules and dried in an oven. The dried polymer is then passed through a grinder to produce the desired particle size for handling and use.

Several recent patents describe improvements in the basic belt process. In one case, a higher solids polymerization is achieved by cooling the starting monomer solution until some monomer crystallizes, and then introducing the resulting monomer slurry onto a belt. The latent heat of fusion of the monomer crystals absorbs some of the heat of polymerization, which otherwise limits the solids content of the polymerization (168). In another patent, a concave belt that flattens near the end is described. This change is said to result in improved release of polymer from the belt (167).

Dry Bead Process. Dry polyacrylamides can also be prepared in the form of dry beads with bead sizes ranging from about 100–2000 μm (169,170). These beads are formed by azeotropically distilling water from inverse suspension polyacrylamides, collecting the beads by filtration, and further drying the beads in a fluid bed drier for short times. The resulting beads can be dissolved in water in a similar manner to other dry polyacrylamides. The size and shape of the beads prepared in the suspension polymerization process are a function of the types and amounts of surfactants and additives employed. Typically, 0.03–0.2 wt% (based on water plus polymer) of an oil-soluble polymeric surfactant is used to obtain the desired bead size. Greater amounts of surfactants lead to smaller beads (169). Certain water-soluble ionic organic compounds are said to be effective in improving the stability of the beads and providing a narrower bead size distribution when used in conjunction with the polymeric stabilizers (169). In the absence of the stabilizer, irregularly shaped, unstable particles can result. The choice of the stabilizer is considered to be dependent on the charge of the polyacrylamide being produced (169).

Microemulsion Polymerization. One inherent problem with water-in-oil emulsions of acrylamide-based polymers is the potential formation of unstable lattices both during production and in finished products. The coagulum that can form in the reactor can result in a time-consuming cleanout (171). Technology has continuously improved reactor configuration, types of agitation, proper cooling (171), and a proper balance of aqueous, oil, and emulsifier ratios (160,161). Microemulsion polymerization (qv) can provide improvements to address these problems (172–182). Monomer microemulsions are thermodynamically stable systems comprising two liquids, insoluble in each other, and a surfactant. They form spontaneously without homogenization. The resulting polymer microlattices are typically nonsettling, transparent, and about 100 nm in diameter. These systems can have high emulsifier levels: more than 8 wt%, which is about 4–5 times more than emulsifier levels in conventional inverse emulsions. Consequently, the cost of producing microemulsions becomes less attractive. However, further refinements to technology lead to the development of cost-effective microemulsified Mannich acrylamide polymers (120–122,183). This technology was used to develop functionalized polyacrylamides (184). In one case, a poly(acrylamide)

microlatex reacted with formaldehyde and dimethylamine (Mannich reaction), and then quaternized with methyl chloride to yield a very highly charged cationic carbamoyl polymer (120–122,185). These commercial products are widely used in many applications for solid–liquid separation. These products have been improved by treating them with buffer acid, a formaldehyde scavenger, and heat to produce a high performance cationic polymer (186).

Environmentally Friendly Polyacrylamides. In recent years, commercial processes that use biodegradable oils to replace petroleum hydrocarbons have received a great deal of attention. Also, there has been a great deal of interest in polymerization in supercritical fluids. These future directions for the manufacture of polyacrylamides are summarized in the following.

Dispersion Polymerization. Water-in-oil emulsions contain at least 30 wt% of a petroleum-based hydrocarbon that is a valuable natural resource. By using such formulations, oils are consumed unnecessarily and can enter the world's waterways as a source of secondary pollution. An aqueous polymer dispersion is one environmentally responsible formulation that contains no oil or surfactant, and near-zero amounts of volatile organic compounds. Dispersion polymerization can be used to prepare cationic, anionic, and nonionic polyacrylamides.

Inverse Emulsions with Biodegradable Oils. Some examples of inverse emulsion polymerization processes employing biodegradable oils include materials with aqueous phase monomer mixtures, such as AMD and AETAC or AMD and MAETAC, dispersed in a biodegradable oil, such as bis-(2-ethylhexyl)adipate (187), containing a polymeric emulsifier that is a copolymer of dimethylaminoethylmethacrylate and mixtures of methacrylates. A buffering acid, such as a dicarboxylic acid, is used to stabilize cationic copolymers. Aliphatic dialkylethers are also used as biodegradable oils (188), in conjunction with SMO as an emulsifier, to produce high-molecular-weight cationic copolymers.

Inverse Emulsion Polymerization Acrylamide in Near-Critical and Supercritical Fluid Conditions. Supercritical fluids exhibit both liquid-like properties (eg, solubilizing power), and gas-like properties (eg, low viscosities). Aqueous AMD has been dispersed and even microemulsified in near-supercritical ethane–propane mixtures using nonionic surfactants such as ethoxylated alcohols (eg, Brij 30 and Brij 52). Emulsion polymerization of AMD was then conducted at 60°C for 5 h and 379 bar, at the near-supercritical condition of certain ethane–propane mixtures (189). 2,2'-Azobis(isobutyronitrile) (AIBN) was used as the initiator. The resulting poly(acrylamide) had a low molecular weight in the range of $(2.7\text{--}5.8) \times 10^5$ Da. The ethane and propane can be easily recovered and recycled in a production plant.

Emulsion polymerization of AMD was also conducted at 60°C for 1 h and 345 bar in near-supercritical CO₂. AIBN was the initiator. An amide end-capped hexafluoropropylene oxide oligomer that has high solubility in the near-supercritical CO₂ was found to stabilize the dispersed particles (190–192). Only a few classes of polymers have good solubility in near-supercritical CO₂. The advantages of using carbon dioxide include very low viscosities during polymerization and ease of recovery.

Applications.

Dewatering. Polyelectrolyte-assisted dewatering constitutes one of the most important application areas of polyacrylamides (3). Solid–liquid separations

in aqueous media can be enhanced by the flocculation of small suspended particles into larger aggregates, which increases separation rates. Floc formation requires a destabilization and adherence of the smaller particles. This is usually accomplished by means of surface charge neutralization, charge-patch formation, and/or polymer bridging (193). Acrylamide-containing polymers make ideal candidates for such flocculants because of the large molecular weights achievable with them. High molecular weight cationic copolymers are typically employed in wastewater treatment. Solid-liquid separations in mining industries often benefit from the use of anionic copolymers, or in some cases dual polymer systems (cationic and anionic in sequence). Various dewatering processes in the paper-making industry regularly make use of cationic, anionic, or dual addition systems (194). Nonionic poly(acrylamide) finds less use in solid-liquid separations, save for some mining applications.

Mineral Processing. Both synthetic and natural hydrophilic polymers are used in the mineral processing industry as flocculants and flotation modifiers. Most synthetic polymers in use are polyacrylamides. Nonionic polymers are effective as flocculants for the insoluble gangue minerals in the acid leaching of copper and uranium (195,196), for thickening of iron ore slimes (197), and for thickening of gold flotation tailings (198). In some uranium leach operations, a cationic polymer with a relatively low charge density is used along with the nonionic polymer to improve supernatant clarity.

Anionic polyacrylamides are extensively used in the mining industry. They are used as flocculants for insoluble residues formed in cyanide leaching of gold (199). Acrylamide-acrylic acid copolymers are used for thickening copper, lead, and zinc concentrates in flotation of sulfide ores. These copolymers, containing from 50 to 100% carboxylate groups, are used to flocculate fine iron oxide particles in the manufacture of alumina from bauxite at high pH (200). Hydroxamated polyacrylamides, prepared by reaction of nonionic polyacrylamide or anionic polyacrylamide with hydroxylamine salts, are also effective in this Bayer process (201). Other uses for hydroxamated polyacrylamides include reduction of titanaceous and siliceous scale in Bayer alumina processes (202) and flocculation of titanium or copper ore tailings in froth flotation processes (203). Copolymers [40623-73-2] of acrylamide and acrylamido-2-methylpropanesulfonic acid [15214-89-8] have been patented as phosphate slime dewatering aids (204).

Low molecular weight polyacrylamide derivatives with mineral specific functionalities have been developed as highly selective depressants for separation of valuable minerals from gangue minerals in froth flotation processes. These depressants have certain ecological advantages over natural depressants such as starches and guar gums. The depressants provide efficient mineral recovery without flocculation. They are often used along with hydrophobic mineral collectors (eg, sodium alkyl xanthates) and froth modifiers. Partially hydrolyzed polyacrylamides with molecular weights of 7,000–85,000 can be used in sylvanite (KCl) recovery (205). Polymers having the functionality $-\text{CONHCH}_2\text{OH}$ are efficient modifiers in hematite-silica separations (206). Polymers containing the $-\text{CONHCH}(\text{OH})\text{COOH}$ functionality provide excellent selectivity in separation of apatite from siliceous gangue in phosphate beneficiation. Valuable sulfide minerals containing copper and nickel can be separated effectively from gangue sulfide minerals such as pyrite in froth flotation processes when

acrylamide–allylthiourea copolymers or acrylamide–allylthiourea–hydroxyethylmethacrylate terpolymers are added to depress the pyrite (207). Acrylamide copolymers can be used as iron ore pellet binders (208). When the ore slurry in water has a pH above 8, anionic polymers are effective. If the ore is acid washed to remove manganese, then a cationic polymer is effective.

Paper Manufacture. Polyacrylamides are used as wet-end additives to promote drainage of water from the cellulose web, to retain white pigments and clay fillers in the sheet, to promote sheet uniformity, and to provide dry tensile strength improvements (209). An important advance in papermaking technology has been the use of microparticle retention aids. Organic microparticles, prepared from acrylamide and anionic comonomers by microemulsion polymerization, provide good sheet formation characteristics and controlled drainage (210,211). Cationic polyacrylamides that have been reacted with glyoxal are used to promote wet strength (212). These wet strength resins have been used in paper towels. Recently, these glyoxalated polymers have been modified so that they can be used in toilet tissue. These polymers provide an initial high wet tensile strength with rapid tensile strength decay in water so that sewers may not become clogged (213,214). Anionic polyacrylamides have been used with alum to increase dry strength (215). Primary amide functionality promotes strong inter-fiber bonds between cellulose fibers. Sometimes paper mills use dry strength additives so that recycled fiber, groundwood, thermomechanical pulp, and other low cost fiber can be used to produce liner board and other paper grades which must meet ICC requirements for burst strength and crush strength. Recently, there has been an increasing demand for writing papers and copy paper that have good print characteristics. Print quality can be improved by use of surface sizes combined with acrylamide polymers. The acrylamide polymer gives the paper sheet better surface strength (216). Details on paper manufacture can be found in Reference (217). All additives used for manufacture of food-grade papers are subject to FDA regulations and are listed in the *Code of Federal Regulations* [paragraphs 176.170, 176.180, 178.3400, and 178.3650] (1998).

Enhanced Oil Recovery. Polymer flooding is a potentially important use for anionic polyacrylamides having molecular weights greater than 5 million and carboxyl contents of about 30%. The ionic groups provide the proper viscosity and mobility ratio for efficient displacement. The anionic charge prevents excessive adsorption onto negatively charged pores in reservoir rock. Viscosity loss is observed in brines particularly when calcium ion is present. A primary advantage of anionic polyacrylamides is low cost (218). Profile modification is a process wherein flooding water is diverted from zones with high permeability to other zones of lower permeability containing oil. Polymeric hydrogels are used for this. Metals such as chromium and aluminum can be injected with anionic polyacrylamides to cross-link the polymers in more permeable reservoir zones prior to the water flood (219,220). The development of new, more environmentally acceptable cross-linking systems has continued. A recent patent claims a composition consisting of hexamethylenetetramine [100-97-0] and 4-aminobenzoic acid [150-13-0] for this purpose (221).

Polyacrylamides are used in many other oilfield applications. These include cement additives for fluid loss control in well-cementing operations (222), viscosity control additives for drilling muds (223) and brines, and for fracturing fluids

(224). Copolymers [40623-73-2] of acrylamide and acrylamidomethylpropane-sulfonic acid do not degrade with the high concentrations of acids used in acid fracturing.

Hydrophobically Associating Polymers. Extensive research in the 1980s and 1990s focused on acrylamide copolymers containing small amounts of hydrophobic side chains. At zero or low shear rates, the apparent viscosity can be very large because of association of the hydrophobic groups between chains. In oil reservoir conditions, the polymers tolerate high salt concentrations while providing proper viscosifying properties (225). These associative thickeners are also used in coatings (226) and in oil spill cleanup (227). Reference (228) gives more information about associative polymers.

Hydrophobically associating acrylamide copolymers can be prepared by micellar polymerization. These copolymers have short blocks of hydrophobic groups randomly distributed in the backbone. A recent paper reviews the major advances in this area (229).

Superabsorbents. Water-swallowable polymers are used extensively in consumer articles and for industrial applications. Most of these polymers are cross-linked acrylic copolymers of metal salts of acrylic acid and acrylamide or other monomers such as 2-acrylamido-2-methylpropanesulfonic acid. These hydrogel-forming systems can have high gel strength, as measured by the shear modulus (230). Sometimes, inorganic water-insoluble powder is blended with the polymer to increase gel strength (231). Patents describe processes for making cross-linked polyurethane foams that contain superabsorbent polymers (232, 233). Recent patents describe grafted copolymers that are highly absorbent to aqueous electrolyte solutions (234).

Analytical Methods. Most of the traditional methods for polymer analysis (235) are applicable to polyacrylamides. We will only point out several special features regarding the use of some of these techniques for the analysis of polyacrylamides.

Oftentimes a preliminary step applied before many analytical methods is the isolation of the polymer. The isolation of polyacrylamides from the other components of the media in which they were prepared (eg, aqueous solution or inverse emulsion, with attendant surfactants and oil) is often readily accomplished by precipitation in short-chain alcohols or acetone. The individual solubilities of formulation components should be tested if there is any doubt. Experience shows that anionic copolymers are often best precipitated in the alcohols, and cationic copolymers in acetone (homopolyaminoesters are soluble in methanol). Since acrylamide is soluble in these organic solvents, it will also be separated from the polymer in this procedure.

Once the polymer is isolated, its chemical composition can be quantified using infrared or nmr spectroscopies (12,236). An nmr study can also give some information about chain architecture in the case of copolymers (237). Elemental analysis can be employed to confirm a composition. Ultraviolet spectroscopy is generally not used for compositional analysis per se; however, polymers containing acrylamide do absorb short-wavelength uv radiation, along with many other materials. A uv detector set around 215 nm is a common choice for measuring polymer concentration in the absence of interfering substances; many surfactants and some salts (eg, NO_3^- , SCN^-) are problematic in this regard. Differential

refractometry is the logical alternative for concentration monitoring when uv-absorbing substances are present.

The extent of conversion during an acrylamide polymerization is most easily followed by determining the disappearance of the monomer. High performance liquid chromatography (hplc) is often found best for this purpose. An hplc method in which poly(acrylamide) inverse emulsions can be used directly has been developed (238). In the case of copolymers, hplc protocols that allow the simultaneous determination of all the unreacted monomers can be used to evaluate compositional drift as a function of conversion.

Global properties of the polymer chains (eg, molecular weight, coil dimensions, branching content) are most often evaluated using scattering, hydrodynamic, or viscometric techniques on dilute polymer solutions. The conventional methods appropriate for soluble polymeric materials typically apply equally well to polyacrylamides. In the case of high molecular weight polyacrylamides, the main difficulties in obtaining accurate information involve preparing a purified polymer solution that is in an equilibrium state, and passing it through the measurement device without substantially altering it in either process.

When using viscometric methods, experiment protocols can be designed to address any effects that instabilities may have on the viscosities of the polyacrylamide solutions, if not to alleviate the instabilities altogether. Mechanical degradation can also occur in high molecular weight polymers. This can happen during sample preparation (eg, mixing), purification (eg, filtration), or during the viscosity measurement itself (especially in elongational flows). In any case, one should estimate these handling effects for any set of protocols.

The presence of colloidal-size contamination ("dust") in polymer solutions can possibly affect either static or dynamic light scattering experiments (239, 240). Neutron scattering is less afflicted by this kind of contamination (241). For high molecular weight polyacrylamides whose coil dimensions are roughly in the same size range as the colloidal contaminants, and which have a natural propensity to adsorb onto suspended materials (after all, many of these polymers are flocculants), any problem of sample purification should not be ignored. If one is simply looking for a clean sample, it is possible to exhaustively filter a solution in a recycle loop (242). Clarification of dilute polymer solutions by centrifugation is another method that can minimize mechanical degradation of the polymers. Centrifuging dilute solutions of high molecular weight linear polyacrylamides from 4 to 8 h in excess of $15,000 \times G$ is satisfactory in many instances. Good light scattering data can be acquired even in the case of a marginally clean polymer solution by attempting to "look through the dust." This is made easier by reducing the scattering volume, slowing (or stopping) the solution flow, and monitoring the scattering volume (either manually or with the aid of a computer algorithm) for periods that are free of point scatterers.

The effects of sample clarification must be gauged when trying to preserve and analyze the polymer in its original form. This includes situations when samples are passed through packed columns, as in HPSEC analysis. A uv-absorbance study can be used to determine polymer loss if there are no interferences in the solution. A method that can monitor the molecular weight distribution (eg, HPSEC or dynamic light scattering), or one that is sensitive to the high

molecular weight component (eg, elongational viscometry), can be used to assay for mechanical degradation.

The double extrapolation of light scattering data to zero polymer concentration and zero scattering angle yields an average property of the macromolecular ensemble: the weight-average molecular weight (M_w) from static light scattering and the z -average hydrodynamic radius ($\langle R_h \rangle_z$) from dynamic light scattering. In some cases, the details of the distribution of these quantities are also of interest. Dynamic light scattering data can be analyzed directly to give a distribution of the hydrodynamic size distribution of a sample. How to derive molecular weight distributions from dynamic light scattering data has been demonstrated (243), but this involves knowing the correlation between the polymer diffusion coefficient and molecular weight, a relationship that is not always available.

Methods involving a physical separation of the components of the distribution, coupled with a method for measuring some feature of the macromolecules across this separated collection, find more use in determining molecular weight (or size) distributions. Size exclusion chromatography (sec) remains a popular way to separate macromolecular populations (244), including polyacrylamides (245). More recently, flow field flow fractionation (ffff) (246) has been shown to have some advantages over sec methods, especially for very high molecular weight polymers, including polyacrylamides. Since the fluid contact surface in ffff is a membrane, as opposed to a packed bed of finely divided particles in sec, there is less opportunity for altering the native distribution by means of polymer adsorption, retention, or mechanical degradation. High molecular weight cationic copolymers of acrylamide can be difficult to pass unaltered through commercial sec columns. Ultracentrifugation (63,247,248) has also been used to separate the components of polyacrylamide samples for subsequent analysis, but this is currently a less popular method than either sec or ffff.

The early approaches to characterizing the molecular weight distributions of samples separated using sec or ffff were based on retention time, requiring a correspondence to be made between the retention time and molecular weight. This was typically done by calibrating the separation device using fractionated (narrowly distributed) standards, which in some cases were only vaguely related chemically to the polymer of interest. More recently the use of in-line light scattering detectors for the purpose of directly determining M_w , R_g (static light scattering photometer), or R_h (dynamic light scattering photometer) for each "slice" of the separated distribution has been an alternative to these approaches (249). This has generally improved one's ability to characterize the details of the molecular weight or size distributions for many acrylamide-containing polymers, for which standards consisting of narrow fractions are not readily available.

Titration methods are mostly applicable to ionic copolymers of acrylamide. Typically, potentiometric titrations are used for high salt concentrations, and conductometric titrations are used for low salt concentrations. This kind of information can be important since ionogenic groups with weak acid or base properties will have both dissociation-dependent and salt-dependent pK_a s when they are in a polymer chain. In addition to titrating ionic acrylamide copolymers with low molecular weight titrants, their titration with other oppositely charged

polyelectrolytes has proven useful (250). For example, poly(potassium vinylsulfonate) can be used to titrate cationic copolymers of acrylamide. This titration gives information about the available charge on the host macromolecule. Usually the macroion titrant is of lower molecular weight than the polymer of interest. In any case, the conditions of the polyelectrolyte–polyelectrolyte complexation reaction must allow for complete 1:1 complex formation. Care must be taken such that the kinetics of the complex formation does not influence the results. The end point can be detected in any one of several ways, including turbidometrically, or using a dye indicator. The color change of the dye at the end point can be determined visually or spectrophotometrically with an “optrode.”

Detecting Polyacrylamides. In order to detect low concentrations of polyacrylamides as part of an analysis scheme (251), to optimize the use of or to monitor the fate of these polymers in a variety of technological applications, an assay method for trace amounts of these polymers that remain in solution is usually needed. One approach, more appropriate for laboratory studies, has been to incorporate fluorescent groups in the polymer either by copolymerization or by post-polymerization derivatization. Acrylamide copolymers containing sodium fluorescein (252), various dyes [phenol red, or brilliant yellow (253)], *N*-2,4-dinitroaniline-acrylamide (254), or a pyrene-labeled monomer (255) have been described. Early methods based on chemical derivatizations describe coupling fluorescein isothiocyanate to amine groups on Hofmann-reacted poly(acrylamide) (256,257). Various other approaches have been developed to add fluorescein (258), dansyl (259), 9-xanthidrol (260), and other fluorescent groups to acrylamide-containing chains (261).

A completely different approach to detecting low levels of high molecular weight polyacrylamides in solution without recourse to prelabeling the polymers has been used in a number of instances. Methods based on the flocculation capacity of these polymers are surprisingly sensitive. Both the turbidity and the settling rate of a suspension can change measurably after exposure to even low concentrations (several ppm) of a flocculant. Such changes were used in the settling rate of kaolin suspensions to assay for low levels of anionic polyacrylamides in runoff water from a soil amendment application involving those polymers (262). They were able to reliably detect residual polymer in the water at the ppm level.

Specifications, Shipping, and Storage. The amount of residual acrylamide is usually determined for commercial polyacrylamides. In one method, the monomer is extracted from the polymer and the acrylamide content is determined by hplc (263). A second method is based on analysis by cationic exchange chromatography (264). For dry products the particle size distribution can be quickly determined by use of a shaker and a series of test sieves. Batches with small particles can present a dust hazard. The percentage of insoluble material is determined in both dry and emulsion products.

Polyacrylamide powders are typically shipped in moisture-resistant bags or fiber packs. Emulsion and solution polymers are sold in drums, tote bins, tank trucks, and tank cars. The transportation of dry and solution products is not regulated in the United States by the Department of Transportation (DOT), but emulsions require a DOT NA 1693 label.

Under normal conditions, dry polymers are stable for 1 year or more. The emulsion and solution products have somewhat shorter shelf lives.

Safety and Health.

Commercial Polyacrylamides. Dry cationic polyacrylamides have been tested in subchronic and developmental toxicity studies in rats. No adverse effects were observed in either study. Chronic studies of polyacrylamides in rats and dogs indicated no chronic toxicity or carcinogenicity. Dry anionic and non-ionic polyacrylamides (265) have acute oral (rat) and dermal (rabbit) LD₅₀ values of greater than 2.5 and greater than 10 g/kg, respectively. Dry cationic polyacrylamides have acute oral (rat) and dermal (rabbit) LD₅₀ values of greater than 5 and greater than 2 g/kg, respectively. Emulsion nonionic, anionic, and cationic polyacrylamides have both acute oral (rat) and dermal (rabbit) LD₅₀ values of greater than 10 g/kg. Dry nonionic and cationic material caused no skin irritation and minimal eye irritation during primary irritation studies with rabbits. Dry anionic polyacrylamide did not produce any eye or skin irritation in laboratory animals. Emulsion nonionic polyacrylamide produced eye irritation in rabbits, while anionic and cationic material produced minimal eye irritation in rabbits. Emulsion nonionic, anionic, and cationic polyacrylamide produced severe, irreversible skin irritation when tested in rabbits that had the test material held in skin contact by a bandage for 24 h. This represents an exaggeration of spilling the product in a boot for several hours. When emulsion nonionic, cationic, and anionic polyacrylamides were tested under conditions representing spilling of product on clothing, only mild skin irritation was noted. Polyacrylamides are used safely for numerous indirect food packaging applications, potable water, and direct food applications.

Experimental Polyacrylamides. It is wise to treat any laboratory-prepared “experimental” polyacrylamide as if it contains substantial amounts of unreacted monomer unless it has been isolated and purified as described above.

Acrylamide is commercially available as a 50% solution in water with a copper salt as a polymerization inhibitor. Polymerization is very exothermic and autopolymerization can occur under certain conditions. In the interest of safety, acrylamide solutions should be stored under the following conditions:

- (1) Maintain the storage temperature below 32°C (90°F) and above the solubility point.
- (2) Keep the solution free of contaminants.
- (3) Maintain the proper level of oxygen and Cu²⁺ inhibitors.
- (4) Maintain the pH at 5.2–6.0.
- (5) Store the solution in a container that is opaque to light.

It is recommended that these solutions be stored for no more than 3 months because of the depletion of the dissolved oxygen. All containers must be dated and no more than 93% full. Packaged acrylamide solutions should be consumed on a first-in, first-out basis.

Economic Aspects. Worldwide, there are many suppliers of polyacrylamides. Some of these are producers and some are repackagers. Suppliers are listed in Table 6. Selling prices for polyacrylamides vary considerably depending on the product form (solution, emulsion, dry), type (anionic, nonionic, cationic), and other factors. Prices on a polymer basis can range from as low as about \$2/kg for simple dry nonionic polyacrylamides to \$8/kg and more for highly charged

Table 6. Suppliers of Polyacrylamides

Region	Companies
United States	Axchem
	Baker-Petrolite Co.
	BetzDearborn, Inc.
	Buckman Laboratories International, Inc.
	Calgon Corp.
	Callaway Chemical Co.
	Chemtall, Inc.
	CIBA Specialty Chemicals Corp. (Allied Colloids, Ltd.)
	Cytec Industries, Inc.
	Delta Chemical Corp.
	The Dow Chemical Co.
	Drew Chemical Corp. (Ashland Chemical, Inc.)
	Exxon Chemical Co.
	Hercules Inc.
	Nalco Chemical Co.
Canada	Polydyne, Inc.
	S.N.F. Floerger SA
	Stockhausen, Inc.
	Cytec Canada, Inc.
	Nalco Canada, Inc.
Mexico	Raisio Chemicals Canada, Inc.
	Rhodia Canada, Inc.
	BASF Mexicana, S.A. de C.V.
	Cytec, Atequiza Jalisco
South America	Nalco, Toluca
	Dispersol San Luis S.A. (Argentina)
	LaForestal Quimica S.A.I.C. (Argentina)
	Henkel Argentina S.A.
	Industrias Quimicas del Valle S.A. (Argentina)
	Proquima Productos Quimicos (Argentina)
	Adesol Produtos Quimicos Ltda. (Brazil)
	Quimicos Nacional Quiminasa S/A (Brazil)
	Cyquim de Columbia
	Quimicos Cyquim, C.A. (Venezuela)
Europe	BASF AG (Germany)
	Ciba Specialty Chemicals PLC (U.K.)
	Cytec Industries BV (Netherlands)
	Cytec Industries U.K. Ltd. (U.K.)
	Deutsche Nalco-Chemie GmbH (Germany)
	Kimira Oyj (Finland)
	Röhm GmbH (Germany)
	S.N.F. Floerger S.A. (France)
	Stockhausen GmbH (Germany)
Japan	Arakawa Chemical Industries, Ltd.
	Dai-Ichi Kogyo Seiyaku Company, Ltd.
	Diafloc Co., Ltd.
	Harima Chemicals, Inc.
	Hymo Corp.

Table 6. (Continued)

Region	Companies
	Kurita Water Industries, Ltd.
	Japan Polyacrylamide Ltd.
	Konan Chemical Industry Co., Ltd.
	Mitsubishi Chemical Industries Co., Ltd.
	Mitsui-Cytec, Ltd.
	Nippon Kayaku Co., Ltd.
	Sankyo Kasei Co., Ltd.
	Sanyo Chemical Industries, Ltd.
	Sumitomo Chemical Co., Ltd.
	Toa Gosei Chemical Industry Co., Ltd.
Republic of Korea	Cytec Korea, Inc.
	E-Yang Chemical Co., Ltd.
	Kolon Industries, Inc.
	Unico (Seoul)
Taiwan	Cytec Taiwan Corp.
	Taiwan Arakawa Chemical Ind., Ltd.
	Young Sun Chemical Works, Ltd.
China	China Petrochemical Corp.
India	Engineer's Poly-Chem
	Kaushal Aromatic Chemicals Pvt. Ltd.
	Somnath Products

cationic polymers. Prices in recent years have dropped because of price erosion and lower manufacturing costs of AETAC and DADMAC cationic monomers. In many applications, such as sludge dewatering in waste treatment, the need for increased performance has lead to increased functionalization (eg, higher cationicity) and increased cost.

In the United States, the major uses for polyacrylamides are in water treating, and paper manufacturing. For water treating, the best growth is expected to be for cationic copolymers because of use in dewatering equipment like belt presses that produce high solids sludge cakes that can be more easily incinerated or disposed of in scarcer landfills. For paper manufacturing, glyoxalated cationic copolymers for paper wet strength, high molecular weight retention aids, and drainage aids are considered to grow in use. Increased use of poly(acrylamide) flocculants in recycled paper mills, particularly in deinking mills where better process water clarification is necessary because of closed water circuits, is also expected. Polyacrylamides are beginning to be used along with surface sizes in paper to improve the control of ink adsorption and print quality. In the mineral process industry in the United States (and Australia), there has been a great increase in the use of hydroxamated polyacrylamides in alumina manufacture. The market for polyacrylamides in enhanced oil recovery has decreased steadily in the United States. In 1985, the total market exceeded 10 million metric tons, but in 1999 the use has been almost none. Total consumption of polyacrylamides is expected to increase about 4% per year during the next few years after 1999 in the United States. In Europe, the use of

Table 7. Consumption of Polyacrylamides^a

Year	Paper, %	Water treating, %	Mining, %	EOR, %	Other, %	Total 10 ³ t
<i>United States</i>						
1989	21.9	59	7.9	6	5.4	68.5
1993	18.3	63	13.6	0	5.1	86.0
1997	25	60	10.8	0	4.2	120.0
<i>Western Europe</i>						
1997	38.4	53.5	5.8	0	2.3	86
<i>Japan</i>						
1985	62	38				42
1989	57.7	42.3				52
1993	51	49				53
1997	52.4	47.6				63

^aFrom Ref. (1).

water-treating chemicals on municipal sludge treatment will increase because of European Union legislation preventing sewage dumping. The treatment of wastewater is intensive, and many waste treatment plants and paper mills have closed circuits because of environmental concerns. The total consumption of poly(acrylamide)s is expected to increase about 3% per year in Europe. In Japan, the major consumption has been in paper manufacture (anionic and nonionic polyacrylamides) and water treatment (cationic and amphoteric copolymers). In municipal sludge treatment, highly cationic polyacrylamides are used for rapid flocculation in high speed centrifuges. The use of cationic copolymers is expected to grow at higher rates. Japan exports a considerable amount of polyacrylamides (and acrylamide monomer) to Asian and other markets. Another potential market will be enhanced oil recovery in China. Table 7 gives an estimated breakdown of polyacrylamide consumption (1).

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ACRYLIC (AND METHACRYLIC) ACID POLYMERS

Introduction

Almost all acrylic polymers produced commercially contain acrylic acid and/or methacrylic acid at some level, which gives them a special property. Content of the acidic monomers ranges from <5 wt% present in many widely used emulsion copolymers to 100 wt% in water-soluble homopolymers. Between these extremes, by the inclusion of a wide variety of comonomers, the copolymers may be water-soluble, soluble only in their neutralized forms, the so-called alkali-soluble polymers, or swollen gels if cross-linkers are present. The less expensive acrylic acid produced by a simpler process is now more commercially available than methacrylic acid and dominates the polymer market especially in nonemulsion areas. This article focuses chiefly on water-soluble, alkali-soluble, and water-swellaible gels, based on homopolymers and copolymers since these are very important commercially and they contain significant levels of the acidic monomers. Acrylic emulsion polymers have low acid content and are widely used in industry and household paint formulations: they are included here in a selected limited fashion because they have been widely studied and the open and patent literatures are so voluminous.

Monomers

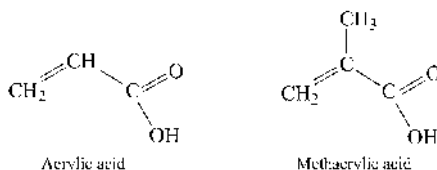
The structures of propenoic acid, commonly called *acrylic acid*, and 2-methylpropenoic acid, commonly called *methacrylic acid*, are shown below:

Table 1. Physical Properties of Acrylic and Methacrylic Acids

Property	Acrylic acid	Methacrylic acid
Formula weight	72.06	86.10
Melting point, °C	13.5	14.0
Boiling point, 101 kPa, ^a °C	141.0	159–163
Vapor pressure, 25°C, kPa ^a	0.57	0.13
Density, 25°C, g/mL	1.045	1.015
Heat of vaporization, J/g ^b	435	418
Heat of polymerization, kJ/g ^b	1.08	0.657
Heat of polymerization, kJ ^b /mol	76.99	56.32
Heat capacity, 25°C, J ^b /(g·°C)	2.1	2.1
Refractive index n_D	1.4185	1.4288
Viscosity, 25°C, mPa·s (=cP)	1.25	1.3
Flash point, tag closed cup, °C	50	67
Flash point, Cleveland open cup, °C	68	77
Surface tension, 25°C, mN/m (=dyn/cm)	–	26.5
Solubility in water	Miscible	Miscible
Autoignition temperature, °C	412	400
Dissociation constants (10 ⁵)	5.5	2.2

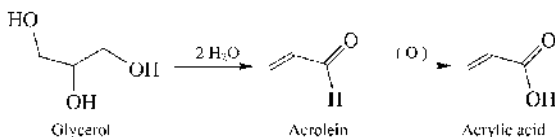
^aTo convert kPa to mm Hg, multiply by 7.5.

^bTo convert J to cal, divide by 4.184.



Acrylic acid and methacrylic acid are selective oxidation products of propylene and isobutylene, respectively. The minor difference in structure between the two acids, the α -methyl substituent of methacrylic acid, results in minimal physical property differences as indicated in Table 1. However, this structural difference distinctly affects polymerization and copolymerization kinetics and the characteristics of the resulting polymers.

Acrylic acid was first reported in 1843 as a product of the air oxidation of acrolein, which is obtained from the high temperature cracking of glycerol (1) (Fig. 1). However, large-scale production of acrylic acid was not introduced until the 1930s when industrial manufacturing processes were developed and safe-handling procedures adopted for this very reactive monomer (2). Since then, commercial growth has been phenomenal and, today, the production and use in

**Fig. 1.** Cracking of glycerol to acrylic acid.

polymerizations greatly predominates over methacrylic acid. This is due to its lower cost and relative ease of preparation by the oxidation of inexpensive propylene, and to a great extent to the global acceptance of superabsorbent acrylic acid-based polymers in diapers and feminine hygiene products.

Frankland and Duma first reported methacrylic acid in 1865 (3). However, like acrylic acid, its commercial development came many years later in 1933 (4). The development required pioneering chemistry on the monomer and its derivatives by Dr. Otto Rohm published in his doctoral thesis in 1901 and its evolution through the formation of the Rohm and Haas Co. in 1909 (5–8). Like the acrylic acid, methacrylic acid and its vinyl derivatives are used mainly in the preparation of polymers. There is little interest in small organic molecules based on the monomers.

Properties. The physical properties of the two acidic monomers are contrasted in Table 1. The major differences to note between the two acidic monomers with regard to polymerization reactions and polymer properties are the higher boiling point of the methacrylic acid and the higher heat of polymerization and higher acidity of acrylic acid.

Both monomers are bifunctional organic compounds, with each having carboxylic acid and conjugated unsaturated double bond functionalities. The carboxyl group undergoes all the reactions expected and readily forms salts and esters using conventional procedures. Caution must be exercised during these reactions because the conjugated unsaturation present in the molecules renders them susceptible to highly exothermic and potentially explosive Michael addition reactions and free-radical polymerizations under uncontrolled conditions. It is this high reactivity of the monomeric double bond that allows rapid carefully controlled polymerization to produce the expected result in polymerization reactions.

Manufacture of Acrylic Acid Monomer. Many synthetic routes to acrylic acid exist and are reported widely in the literature. However, the only currently commercially viable process is based on the direct high temperature gas-phase oxidation of propylene, as indicated schematically in Figure 2. This economical process, based on the availability and low cost of propylene, is expected to predominate commercially for many years. Other once practiced processes based on acrylonitrile, propiolactone, and ethylene cyanohydrin are no longer of importance (2).

The oxidation proceeds by the two-step catalytic process indicated above, without the isolation of the intermediate acrolein. Acrylic acid, obtained in high yield based on propylene, is isolated as an aqueous solution and purified by extraction and distillation. The principal impurities in the commercial monomer, termed glacial acrylic acid, that may affect subsequent polymerization reactions include acetaldehyde, acrolein, furfural, benzaldehyde, and acrylic acid dimer,

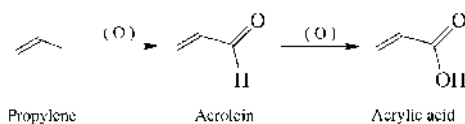


Fig. 2. Acrylic acid by propylene oxidation.

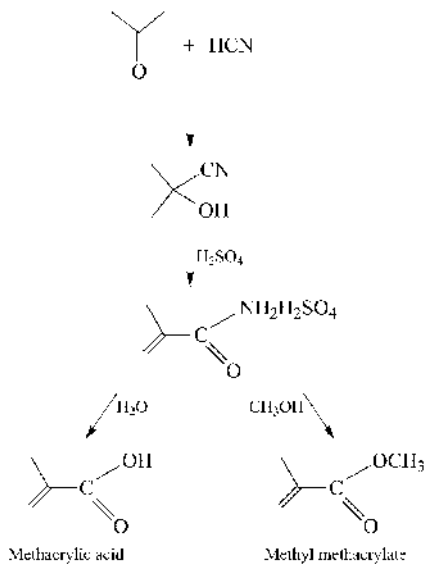


Fig. 3. Processes for methacrylic acid and methyl methacrylate.

3-acryloxypropionic acid. Since these impurities are inhibitory in polymerization, they must be removed to facilitate the production of ultrahigh molecular weight polymers for use in superabsorbent manufacture, for example.

Manufacture of Methacrylic Acid Monomer. The commercial manufacture of methacrylates began in 1933 based on acetone cyanohydrin, which is still the basis for all current production (4). This well-established technology is based on the commercially inexpensive chemical starting compounds, acetone, hydrogen cyanide, and sulfuric acid. The process is represented by the schematic shown in Figure 3. Acetone reacts with hydrogen cyanide to form acetone cyanohydrin, which is readily converted into the methacrylamide sulfate salt in the presence of anhydrous sulfuric acid. This intermediate salt may be directly converted into either methacrylic acid or methyl methacrylate by reaction with water or anhydrous methanol, respectively. In commercial practice, the two steps are generally carried out simultaneously with an aqueous methanol solution to produce an ester rich mixture, since methyl methacrylate is the higher volume commercial product for the production of Plexiglas (Rohm and Haas Co.).

Handling and Storage of Acrylic and Methacrylic Acids. Acrylic acid is available commercially at 98%+ purity and contains a polymerization inhibitor such as hydroquinone (HQ), monomethylhydroquinone (MEHQ), or phenothiazine. Methacrylic acid, on the other hand, is available at 99%+ purity and is stabilized with either HQ or MEHQ. It is not usually necessary to purify the monomers to remove the inhibitors prior to polymerization, as the level of free-radical initiators used readily overwhelms them. However, where ultrahigh molecular weight polymers are required, for example in superabsorbent polymers, the impurities must be removed. The corrosiveness of the monomers toward many metals requires storage to be in stainless steel, glass, or aluminum or suitably lined vessels. Any metals leached from storage vessels could

potentially promote dangerous runaway polymerizations in the presence of oxygen. Obviously, for the same reasons, polymerization reactions must be carried out in similarly constructed equipment.

Since both acids have relatively high freezing points, 13–14°C, they must be prevented from freezing in cold conditions. If freezing occurs, thawing is a hazardous procedure since the distribution of inhibitor between solid and liquid is difficult to control, and runaway uncontrolled and potentially explosive polymerization of the liquid phase is always a threat. To avoid this potential hazard, monomer storage at temperatures in excess of their freezing points is recommended.

Health and Safety. Both acids are moderately toxic compounds when ingested or absorbed through the skin. Severe internal burns result from swallowing. Skin contact causes rapid tissue damage due to the highly corrosive nature of the monomers. The vapor of acrylic acid is more irritating to the eyes than that of methacrylic acid, but both may cause redness on prolonged exposure.

As with all industrial chemicals with similar characteristics, safe handling with suitable protection gear is highly recommended; gloves, facemask, and clothing are all important. These are all listed in the Material Safety Data Sheets (MSDS) that accompany the monomers and these sheets must be thoroughly read and understood before working with either monomer.

Polymerization of Acrylic and Methacrylic Acids

Dependence on pH. The rates of polymerization of both acidic monomers in dilute aqueous solutions are pH-dependent. The rate of polymerization is high at low pH for both monomers; it falls rapidly to a minimum at pH 6–7, and then increases to a maximum at pH 10 for acrylic acid and 12 for methacrylic acid (9–13). At high salt or monomer concentrations, the polymerization rate minimum at the pH range 6–7 becomes less pronounced.

The explanation of the observed rate minimum at pH 6–7 is generally considered to be due to the slower rate of propagation for the anion than for the free acid. However, as pH is increased, the rate of polymerization increases because of the decreased rate of termination of the radical anions promoted by coulombic repulsion (10). An alternative explanation of both the increase of polymerization with pH and the leveling of the rate by added salts at pH 6–7 is postulated to be due to the formation of terminal ion pair radicals with a propagation rate similar to that of the free-acid monomers (9).

Copolymerization. Acrylic and methacrylic acids readily copolymerize free radically with many vinyl monomers. This versatility results from a combination of their highly reactive double bonds and their miscibility with a wide variety of water- and solvent-soluble monomers. Reactivity ratios derived from copolymerizations with many monomers are tabulated in many books on polymerization, for example in Wiley's *Polymer Handbook* (14) (see also Wiley's Database of Polymer Properties). Q and e values are parameters that may be established for a monomer based on a large number of reactivity ratios with other monomers. These parameters are associated with interactions between the monomer and the growing chain via resonance (Q) and polar effects (e).

As mentioned, the rate of copolymerization of acrylic and methacrylic acids is dependent on pH effects and the resulting ionization as well as the comonomers. This conflict makes it difficult to describe the acidic monomers by single Q and e values derived from reactivity ratios. Neutralization changes both Q and e values. Particularly, e values reverse from a positive value to a negative value on neutralization (15). This is expected as e is a measure of electron-donating ability of the monomeric double bond and neutralization may be equated to a change from electron-withdrawing carboxylate group to an electron-donating carboxylate ion.

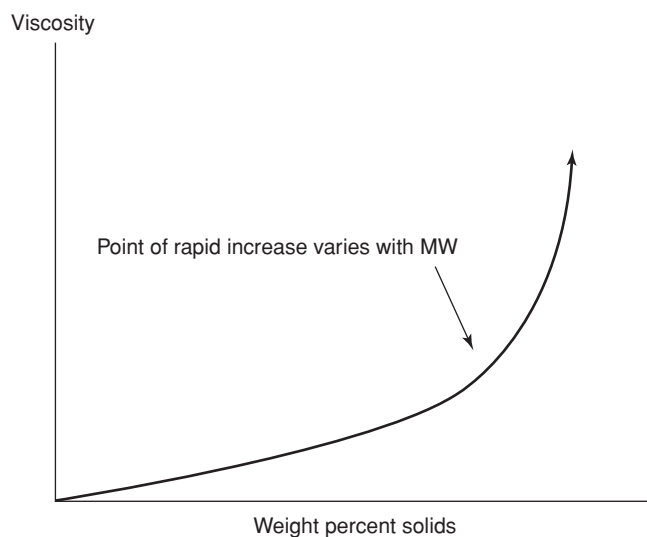
Alternative Synthesis of Acidic Polymers. There are two approaches to homo- and copolymers of acrylic and methacrylic acids. In addition to the conventional use of acrylic acid and methacrylic acid monomers, the main theme of this article, there exists the possibility of converting polymers of the derivatives of these two monomers to acidic polymers. There would obviously have to be very extenuating circumstances to take this route industrially because of cost penalties. However, there are situations where there is a reason to do this. Availability of monomers is a good example. Acrylonitrile was at one time more available than acrylic acid in some parts of the world and simple hydrolysis of the polymer gave poly(acrylic acid). Other potential routes exist from such homo- and copolymers of acrylamide, acrylic and methacrylic esters, and acid chlorides. Although not further discussed here, the reader is reminded that polymer synthesis with acrylic monomers is very versatile and forethought is always necessary before plunging ahead.

Polymerization Processes. A variety of processes are used commercially to homopolymerize and copolymerize acrylic acid and methacrylic acid. On the basis of economics and environmental considerations, water is generally the preferred industrial solvent or polymerization medium. However, the choice of process is usually dictated by the requirements of the polymer to be produced. As already indicated, pH influences the rate of polymerization. Comonomers and molecular weight of the polymer to be produced also have a profound effect on the type of polymerization process that can be used and on the type of product obtained. The contents of Table 2 indicate the change from water-soluble to alkali-soluble emulsions and ultimately emulsion polymers is dependent on the comonomers in copolymers of acrylic and methacrylic acids. This transition from water-soluble polymer to emulsion polymer as the acidic monomer is decreased depends on the hydrophobicity of the comonomer. Introduction of divinyl monomers causes transition to gel materials in all compositions. The gels may vary from highly swollen to tightly bound copolymers, depending on the cross-linker level.

The effect of molecular weight is very pronounced with the water-soluble polymers. The change of viscosity of aqueous solutions is shown schematically in Figure 4. A precipitous increase in viscosity occurs at lower concentrations with higher molecular weights, essentially making it economically impossible to make polymer of greater than about 100,000 Da by aqueous solution polymerization. This can be controlled to some extent by polymerizing the monomers at lower concentration, but this becomes economically undesirable at some point, usually around 30 wt% solids. Hence, new technology is borne. Generally speaking, low molecular weight homopolymers, less than 100,000 Da, may be made in aqueous

Table 2. Comonomer Effects on Acidic Polymers

Comonomer	Polymer
None	Water-soluble
Water-soluble	Water-soluble
Water-insoluble, low level	Water-soluble
Water-insoluble, mid level	Alkali-soluble emulsion
Water-insoluble, high level	Emulsion polymer
Polyvinyl cross-linker	Gel

**Fig. 4.** Water-soluble polymers: viscosity/molecular weight in water.

solution; higher molecular weights require technologies such as suspension and gel polymerization.

Copolymer synthesis suffers the same viscosity restrictions as the homopolymers when the comonomers are sufficiently water-soluble to produce water-soluble copolymers. When water-insoluble comonomers are used it is possible to resort to cosolvents with water or surfactants in micellar polymerizations to effect solubility to a limited degree, but this is only useful at low molecular weight and is undesirable environmentally. Higher molecular weight copolymers are usually made by emulsion, inverse emulsion, or suspension polymerization.

Polymer Characteristics

The polymer types considered here are primarily those that are soluble in water as prepared, soluble after neutralization of emulsion polymerized copolymers, the so-called alkali-soluble polymers, and cross-linked swellable gel polymers. Emulsion polymers are discussed in a limited fashion, as acrylic and methacrylic acids

are used ubiquitously at low levels in almost all acrylic emulsion polymerizations to contribute some special characteristic. For example, the incorporation of acidic monomers contributes to such properties as adhesion, wettability, and emulsion polymer stability.

Emulsion Polymers.

Applications. Acrylic emulsion polymers containing insufficient acrylic or methacrylic acids to solubilize on neutralization are used in a myriad of applications including, coatings, floor polish, inks, dispersants, adhesives, and caulks. These are almost all thin film applications and the acid contributes hydrophilicity, stability, dispersancy, etc. The polymers are balanced by backbone hardness, hydrophobicity/hydrophilicity balance, functionality, all moderated by choice of comonomers and by molecular weight and morphology. Some examples from the literature of the use of emulsion copolymers containing low levels of acidic monomers include autodeposition coatings (16), paper saturants (17), wood coatings (18), corrosion-resistant coatings (19), printing ink binders with core-shell morphology (20), monodispersed particles for liquid toners (21), oil-repellent finishes based on fluoromonomers (22), dilatant dispersants for antistatic coatings (23), water-resistant coatings (24), water-dispersible polymers for building materials (25), surfactant-free emulsions for nonwovens (26), pressure-sensitive adhesives with good mechanical stability (27), water-resistant cosmetics (28), anticorrosion coatings for ferrous metals (29), hair styling shampoos (30), redispersible film-forming coatings (31), core-shell graft polymers for cement modifiers (32), coatings and inks (33), wood coatings (34), acrylic polyester hybrids (35), redispersible powders for cement (36), hair fixatives (37), redispersible core-shell polymers (38), core-shell coatings (39–42), coatings (43), pressure-sensitive adhesives (44), and emulsion paints (45).

Synthesis. The synthesis of emulsions is widely described in the literature, both patent and open. Ingredients are surfactants for setting particle size and stabilization of the emulsion, and initiators for polymerization. Leading reference books are by Blackley; although somewhat dated it is still an excellent book and another is Gilbert's recent publication (46). Other useful synthesis references include some specific interests, pressure-sensitive adhesives (47), styrene emulsion polymerization using alkali-soluble resins as emulsifiers (48), manufacture and use of curable emulsions (49), preparation of concentrated emulsions (50), multistage polymer preparation (51), core-shell vinyl acrylic emulsions (52), acrylic grafted to polyester emulsions (53), aqueous polymer dispersions (54), process for polyacrylate dispersions (55), sterically stabilized acrylic graft copolymers (56), polyacrylate dispersions without colloid protection (57) and with colloid protection (58), low VOC emulsions (59), design of latex polymers (60), random copolymers as emulsifiers (61), multihollow latex particles (62), modeling of acid distribution in lattices (63,64), modeling of microparticles and experimental verification (65), and effect of pH on properties of emulsion polymers (66). Since so many applications of acrylic emulsions are dependent interfacial science, film formation is very important and has received much interest (67–70).

Water-Soluble Polymers.

Synthesis. Water-soluble polymers are prepared by conventional free-radical polymerization methods with molecular weight control through the level of initiator and the use of chain transfer agents. Generally, molecular weights of

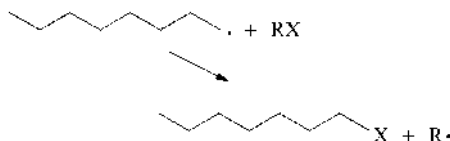


Fig. 5. Chain transfer in free-radical polymerization.

the polymers range from a few thousand to several hundred thousand, which is useful in many applications from dispersants to rheology modifiers to thickeners to flocculants. The lower molecular weights from 1000 to about 30,000 have been most widely worked on. Typical initiators fall into two classes, the thermally activated and the redox types. The thermally activated are persulfates, perphosphates, azos, hydroperoxides, etc, which are used in temperature ranges of 50–100°C. The redox initiators are generally designed for use at lower temperatures and function by using stoichiometric amount of reducing and oxidizing agents in the presence of a metal catalyst. The metal decomposes the peroxy compound to produce radicals for initiating polymerization and is converted to a higher oxidation state in the process; the reducing agent cycles the metal back to the lower oxidation state and the process is repeated.

Molecular weight control by using chain transfer agents (Fig. 5) results in the incorporation of the chain transfer agent at least on the polymer terminus.

RX is a general term for a chain transfer agent. The liberated R· radical then initiates another polymer chain and X, usually hydrogen from chain transfer agents, terminates the current chain. Phosphite chain transfer agents are exemplified in the aqueous preparation of low molecular weight acrylic homo- and copolymers (71,72). A similar utilization was patented by Coatex S. A. (73). Other chain transfer agents that have been used include alcohols such as isopropylalcohol (74), aminothiols (74), mercaptoethanol (75), mercaptoethanol (76), hypophosphorous acid (77), and copper salts that are extremely effective (78–82).

Other interesting polymerizations include the use of metal-activated hydrogen peroxide to deliver low molecular weight polymers (83,84), continuous polymerization of water-soluble monomers in extruders (85), dry polymerization of acrylic acid in super critical carbon dioxide (86,87) and on a powder bed (88), and the use of sodium nitrate mediated aqueous polymerization to allow high solids (89).

Transamidation allows the preparation of unique low molecular weight, water-soluble polymers from acrylic acid–acrylamide copolymers. The advantage is that functional amines such as sulfonic acid salts can be incorporated into pre-formed polymer to create new functional polymers without the need to synthesize new monomers (90–92).

Applications. Water-soluble homopolymers of acrylic and methacrylic acids and their copolymers are widely used in a myriad of applications. Poly(acrylic acid) and copolymers with maleic acid and other monomers are used in large quantities in solid detergents and dishwashing powders (80,93–107). Only minor modifications to composition and/or molecular weight to alter the balance of surface interactions allow use in many different applications. Changing hydrophile/hydrophobe ratio, charge density, introduction of other charged

species, etc, all expand the application range. Scale formation in aqueous systems may be prevented by the presence of sulfonate groups (108–110) and allyloxy functionality (111,112). Cement additives used to reduce water requirements are based on acrylic acid copolymers with poly(ethylene oxide) acrylate monomers (113–116). Copolymers with acrylic alkyl esters are used in textile sizing agents (117). Plant productivity in hydroponic media is reportedly enhanced by the presence of poly(acrylic acid) (118). Dispersing characteristics are imparted by copolymerizing a range of monomers and again they are used widely, for example, in inks (119), for inhibiting barium scale in seawater (120), ceramics (121,122), to disperse acrylic emulsion polymers (123), to disperse dyes (124). Copolymers are also used in oil drilling and recovery (125–129), in corrosion control (130–136), in paper for wet and dry strength (137), boiler water treatment (138–141), specialty cleansers (142–146), eliminating odor from animal excrement (147), reverse osmosis for scale inhibition (148), water clarification (149), soil conditioners (150), and seed coatings (151).

Environmental Issues of Water-Soluble Polymers. Because the water-soluble polymers based on acrylic and methacrylic acids are generally disposed off in the environment, there have been studies to determine their effect on the environment and to monitor their build. Acrylic acid polymers are not biodegradable except at the oligomer molecular weight, that is about 3 to 10 units (152). Elegant monitoring of low concentrations is available by two techniques, immunoassay (153) developed at Rohm and Haas, and fluorescence tagging (154). Tagging is useful both for environmental monitoring and for concentration control in applications.

Alkali-Soluble Polymers. Alkali-soluble polymers are generally emulsion polymers that have insufficient acid content to solubilize in water in the absence of neutralization. In addition to emulsion polymerization, polymerization in partial or complete organic solvents, as suspensions, and inverse emulsions are all reported. However, emulsion polymerization represents the most convenient route to these polymers, with suspension and inverse emulsions being very limited.

Alkali-soluble emulsion polymers were originally developed as thickeners based on copolymers of acrylic acid and methacrylic acid with simple acrylic and methacrylic esters, as exemplified by their preparation in patents to S.C. Johnson (155), BASF (156), and Goodyear (157). However, in the last two decades advanced hydrophobically modified alkali-soluble polymers have emerged as thickeners and rheology modifiers which function by association of their hydrophobic functionalities with themselves or other convenient centers in a formulation containing these polymers. Figure 6 represents this association schematically.

Both types of alkali soluble thickeners generally contain methacrylic acid rather than acrylic acid since this monomer is more readily incorporated into emulsion polymers, as it is more hydrophobic than acrylic acid and less likely to homopolymerize in the aqueous continuous phase. Patents to Dow (158), DeSoto (159), Union Carbide (160), and Rohm and Haas (161) represent the synthesis of hydrophobically modified alkali-soluble emulsion polymers. The hydrophobe may be attached to the acrylic polymer backbone by an ester or urethane linkage (162). The properties of hydrophobic associative thickeners and conventional thickeners in paint-making formulations have been compared (163). Several papers have

appeared on the interactions of similar polymers in paint formulations (164–167) and on general hydrophobic interactions in water (168,169).

There are other less widely used syntheses of associative polymers including acid monomer grafting to poly(ethylene oxide) (170,171), inverse emulsion polymerization (172–174), suspension polymerization (175), micellar polymerization (176,177), and solid-phase extrusion polymerization (178).

Applications. In addition to latex paint applications already mentioned, applications include paper (179), oil spill clean-up (180), flocculants and mineral dewatering (181), emulsion polymerization stabilizers (182), and in mixed associative thickeners in paints (183).

Gel Polymers. Gel polymers based on the acidic monomers are high molecular weight (co)polymers that are cross-linked such that solubilization in water is prevented. The levels of swelling or gel formation are controlled by degree of cross-linking of the polymer. The major outlet for this chemistry is in the development of superabsorbent polymers now ubiquitous in diapers and feminine hygiene products. They have completely revolutionized a way of life for raising infants and caring for incontinent elderly. Hence, it is not surprising that most of the published information is patent literature that relates to manufacturing processes that have been or continue to be used for the preparation of superabsorbents. Some of these processes are referenced herein, but the patent literature is so voluminous that not all are included here.

Synthesis. Gel polymerization of acrylic acid with a polyvinyl cross-linking monomers in water is by far the most prevalent commercial process. Examples of cross-linkers used are triallylamine (184), *N,N'*-methylenebisacrylamide (185), tetraallyloxyethane (186,187), trimethylolpropane triacrylate (188), ethylene diamines (189), trimethylol triacrylate and diacrylate in combination (190), ethylene glycol diglycidyl ether (191), trimethylolpropane tris(3-aziridinylpropionate) (192), and poly(ethylene oxides) diacrylate (193). In an extension of cross-linking one process by Sanyo uses inefficient graft polymerization of acrylic acid onto starch as a source of the cross-linking required to introduce control over gel swelling (194).

Applications. Copolymers of acidic monomers and other water-soluble monomers obtained by gel polymerization for special effects, generally in medical applications, include hydroxyethyl methacrylate (195), hydroxypropyl methacrylate and acrylamide (196), and vinyl saccharides (197).

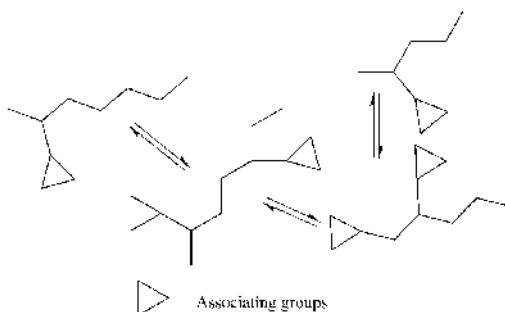


Fig. 6. Association of hydrophobic alkali-soluble polymers.

There has been a move from conventional granular gel materials to foamed (198) and flat plate (199) type superabsorbents based on poly(acrylic acid). In addition to superabsorbents for personal hygiene, the materials have wide ranging applications in many areas from biomedical to cosmetics. Some of these are petroleum recovery and sealing of sewer pipes when cross-linked with metals such as iron salts (200); flocculants in water purification (201); copolymers with acrylamide in textile printing pastes (202); cosmetic gelling agents (203); surgical dressings (204); reversible gels (205); subterranean fault stabilization (206), and controlled release (207).

Block and Graft Polymers

Graft Synthesis. Free-radical-promoted grafting of acrylic and methacrylic acids and other water-soluble comonomers onto synthetic and natural substrates gives unique polymeric structures quite different from the random copolymers obtained in conventional copolymerization. These block and graft polymers bring a unique and different structure/property balance with applications in many areas.

Applications. Poly(ethylene oxides) are readily grafted with acrylic acid to give partially biodegradable detergent polymers (208–210). Grafts onto other substrates include poly(vinyl alcohol) (211), water-soluble maleic anhydride copolymers (212), polycaprolactone (213), and onto emulsion polymers of acrylates and methacrylates (214).

Natural substrates are often starch or cellulose derivatives. Grafts for detergent applications (215,216), thickening dispersions (217), leather tanning (218), water treatment (219), oil recovery (220), water-absorbents (221), and water-absorbents in fibers and sheets (222). More fundamental studies on grafting to polysaccharides have been published (223).

Block Synthesis. Water-soluble block copolymers are formed from the copolymerization of macromonomers of methacrylates with acrylic and methacrylic acid monomers and their solution properties compared with random copolymers of similar composition (224). Diblock and triblock copolymers may be prepared by a number of techniques and are also used on ink-jet inks (225) and scale inhibition in water boilers (226), respectively. Associative properties of block polymers to form micellar structures are well established (227,228). Triblock polyampholyte polymers are also known (229).

Inverse Emulsion Polymerization

Inverse emulsion polymerization is a term used for water in oil (monomer) dispersion polymerization as opposed to conventional emulsion polymerization where the monomer and polymer are largely insoluble and dispersed in water. The advantage is that high molecular weight polymers and copolymers of water-soluble monomers may be prepared without the attendant viscosity build mentioned earlier. The process chemistry is well established as indicated in the patent literature (230–233) but not widely used and likely to be less so as solvents are removed from processing. Spray drying is often used for polymer isolation (234).

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ACRYLIC ELASTOMERS, SURVEY

Introduction

Acrylic elastomers have the ASTM designation ACM (1) for polymers of ethyl acrylate and other acrylates, and ANM for copolymers of ethyl or other acrylates with acrylonitrile. In both cases, the M indicates a polymer having a saturated chain of the polymethylene type. The combination of a saturated backbone with polar side chains results in a class of polymers with very good resistance to heat and oil, including oils containing hypoid additives. Thus, they are used for such applications as automotive transmission seals and rear-axle seals. Acrylic elastomers also have good resistance to sunlight and ozone. Their early history and subsequent development have been described in various review articles (2–16). Ethylene-acrylic elastomers are discussed in a separate section of this article.

Monomers

The first acrylic elastomers were homopolymers of either ethyl acrylate or methyl acrylate. Because these had limited utility, particularly for vulcanized applications, various copolymer modifications were developed to improve performance, and there evolved a division of monomers into two types: *backbone monomers*, which comprise the principal proportion of the monomers and determine the physical and chemical properties of the polymer, and *cure-site monomers*, which are incorporated to the extent of 1–5% to introduce reactive sites for subsequent cross-linking reactions.

Cure-site Monomers and Cure Systems. Although poly(ethyl acrylate) has a saturated backbone, it does contain reactive side groups, namely an ester and an active alpha hydrogen, which are potential sites for cross-linking reactions (6,17–19). Poly(ethyl acrylate) does not respond to peroxide curing agents because of the steric hindrance of the ester group protecting the alpha hydrogen, which, in turn, accounts for the excellent heat resistance of acrylic rubbers (20). In general, cures involving the backbone monomers never achieved any commercial significance, and other methods of facilitating cross-linking were sought. In the development of butyl rubber (21), sites for cross-linking were introduced by copolymerizing a small amount of a second monomer, such as isoprene, with isobutylene. This second monomer is referred to as a functional or cure-site monomer, which can be defined as a monomer that maintains a reactive site after the monomer itself has polymerized (22). Since polyisobutylene, like poly(ethyl acrylate), is soft and flexible at room temperature, it was a logical step to use the same concept for acrylic rubbers. Whereas butyl rubber was the first polymer to which a cure-site monomer was deliberately added, it was not the first to have a cure-site monomer. This distinction goes to polychloroprene, since 1.6% of the chloroprene polymerizes in the 1,2 position to give a pendent allylic group and a tertiary chlorine as a cure site (23).

Unsaturated Cure Sites. Following the approach used with butyl rubber, the first cure-site monomers for acrylic rubbers were the dienes, butadiene and isoprene (2). Although these could be cured in a butyl rubber recipe, there were two disadvantages in the use of these monomers. First, pressure vessels were required for monomer storage and polymerization, and second, the polymers were cross-linked during polymerization. Subsequent work to obtain an unsaturated cure site has resulted in the use of less volatile diene monomers in which the double bond intended for curing is less reactive than the one involved in copolymerization (24,25). Examples of these are acrylate monomers with unsaturated side chains, such as tetrahydrobenzyl acrylate (26) and 3-methyl-2-butenyl acrylate (27). The availability of a range of nonconjugated dienes for EPDM rubber (28,29) led to a flurry of activity to use these monomers in acrylic rubbers, not only by themselves (30–34), but also as derivatives of acrylic acid (35,36). Although these polymers with unsaturated side chains do give good cures in sulfur vulcanized recipes, they suffer from the disadvantage that they also cross-link in the presence of sulfur-bearing oils. The polymers with unsaturated side chains could also be cured with peroxides. However, because of the disadvantages noted above, an attempt was made to prepare saturated polymers that would respond to peroxide cures (37). The only acrylic rubber to be used commercially in peroxide cures was a copolymer of *n*-butyl acrylate and acrylonitrile (38). A study of the kinetics of peroxide cures of various rubbers, including acrylic rubbers, was published in Russian (39).

Chlorine Cure Sites. Most acrylic elastomers used commercially today have a chlorine cure site. The first of this family of acrylic elastomers was Lactoprene EV, a copolymer of ethyl acrylate and chloroethyl vinyl ether (40,41). This was developed by the Eastern Regional Research Laboratory of the USDA and introduced commercially as Hycar PA21 (later as Hycar 4021) by BFGoodrich (42). Although chloroethyl vinyl ether overcomes the problems of using a diene like butadiene (41), it does suffer from two disadvantages: the vinyl group

is not resonance-stabilized, so it does not readily copolymerize with resonance-stabilized monomers such as ethyl acrylate, and the chlorine on the chloroethyl group is only moderately active. This moderate activity meant that the early curatives were liquid polyamines, such as triethylenetetramine, which cause sticking to the rolls during mixing and processing. An improvement in milling behavior came with the use of solid curatives, such as the blocked diamines developed for fluoroelastomers under the trade name of Diak (43). Another development was the discovery that the metal oxide–thiourea cure system developed for neoprene could be modified for chlorine-containing acrylic elastomers if the metal oxide was red lead (44). Whereas the most common thiourea used is ethylene thiourea, the system works with other thioureas (45).

Overcoming the moderate reactivity of the chloroethyl group can be approached in another way. The bond dissociation energy of the carbon–chlorine bond decreases (46), and thus the reactivity of the chlorine increases (23) in the series: aromatic <vinyl <primary <tertiary <benzyl <allylic <tertiary allylic.

The chlorine in chloroethyl vinyl ether is primary and that from the 1,2 addition of chloroprene in neoprene is tertiary allylic (23). A big improvement in the reactivity of the chlorine in acrylic rubbers came with the introduction of vinyl chloroacetate as a cure-site monomer (47). The carbonyl group in the acetate activates like an allylic group. This opened the door for interesting new cure systems, such as ammonium benzoate (48), soap–sulfur (49,50), trithiocyanuric acid (51), and bismaleimide–sulfur (52). Because of the greater reactivity of the chlorine in vinyl chloroacetate, polymers with other chloroacetates were soon introduced, including allyl chloroacetate (53) and chloroacetoxymethyl 1-5-norbornene (54). Polymers made with vinyl chloroacetate give good cures with the red lead–thiourea cure system, but no cure is obtained with polymers made with allyl chloroacetate.

Whereas vinyl chloroacetate overcomes one disadvantage of chloroethyl vinyl ether, namely the reactivity of the chlorine, it does not overcome the other, ie, the sluggish copolymerization with acrylate monomers. Better copolymerization is achieved if the cure-site monomer, like the acrylate monomers, is conjugated, ie, of the form $C = C - C = X$, where X = carbon, oxygen, or nitrogen. A simple example is chloroethyl acrylate, which will readily copolymerize with alkyl acrylates; however, the reactivity of the chlorine is the same as that of chloroethyl vinyl ether. For the best cure-site monomer, therefore, it is necessary to combine the chlorine reactivity of vinyl chloroacetate with the copolymerization reactivity of chloroethyl acrylate. Two types of cure-site monomers have been used to achieve this combination. One set are derivatives of an acrylate or methacrylate with a reactive chlorine, such as 2-(chloroacetoxy)ethyl methacrylate (55) and the reaction product of chloroacetic acid with glycidyl methacrylate (56). The second group are derivatives of styrene, such as chloromethylstyrene (57) and vinylbenzyl chloroacetate (58). Since a primary bromine atom has about the same reactivity as a benzyl chlorine atom (46), a third method can be included, which uses 2,3-dibromopropyl acrylate (59) to obtain the desired balance of reactivity during both polymerization and curing.

Other Cure-Site Monomers. Although chlorine-containing polymers dominate the commercial field, mention should be made of other cure-site monomers. Various patents covering the use of *N*-alkoxy unsaturated amides appeared in the

1960s (60–63) and these have two interesting features: the cure sites interact on heating to give a self-cure, and contrary to standard practice with other acrylic rubbers and with sulfur-cured diene rubbers, the cure is accelerated by acids and retarded by bases. There has been relatively little activity with carboxyl-containing acrylic elastomers despite the relatively low cost of acid-containing monomers such as acrylic acid. An early patent describes cures with polyamines (64), and acrylic elastomers appear in a review on carboxylic elastomers (65). One way to incorporate epoxy groups into a polymer is to use allyl glycidyl ether (66). However, as far as copolymerization with alkyl acrylates is concerned, this is no more active than chloroethyl vinyl ether. Better polymerization reactivity is obtained with glycidyl methacrylate or acrylate (66,67). The epoxy group is a very versatile cure site and responds to a wide variety of cure systems, including polyamines (66), ammonium salts (68), blocked diamines (69), red lead–thiourea, zinc dimethyldithiocarbamate (70), and electron-beam radiation (71). Hydroxyl cure sites can be introduced into acrylic rubber by the use of ethylene glycol monoacrylate (72) or methacrylate (73), and the monovinyl ether of a glycol (74). Cures are somewhat limited and are effected through either an anhydride (72) or hexakis(methoxymethyl)melamine (73). Finally, there is a method which corresponds to the production of brominated butyl rubber (75). A diolefin, such as isoprene, is copolymerized with an alkyl acrylate and the resulting polymer is treated with bromine.

Dual Cure Sites. Although chlorine-containing acrylic elastomers have good cure behavior, a postcure is required to obtain low compression set, as it is with silicone and fluorinated elastomers. Polymers with both a chlorine and carboxyl cure site, which give faster curing polymers and eliminate or reduce the necessity to postcure in certain applications, have been introduced (76–78). A modification of this system replaces the acid with an α -cyanoalkyl acrylate (79). Acrylic rubbers containing both chloromethylstyrene and methacrylic acid can be vulcanized in the presence of phosphonium salts (80). Polymers with vinyl chloroacetate and 2-hydroxypropyl methacrylate are claimed to have very good heat resistance (81). Another form of self-cure is obtained by incorporating an epoxy monomer into the polymer with either an acid monomer (82) or a latent acid monomer (83). A polymer with three cure sites has been proposed (84).

As can be seen from the above, there is a plethora of cure-site monomers for acrylic elastomers. However, only a few have achieved commercial significance and most of these contain a chlorine cure site.

Backbone Monomers. The principal backbone monomer is ethyl acrylate. Whereas this gives polymers with good oil resistance, the glass-transition temperature (T_g) of -15°C may not be low enough for some applications. Therefore, there has been a continuing search to improve the low temperature performance of acrylic elastomers. As the number of carbons in the alkyl group is increased from 1 to 8 in a series of homopolymers of normal alkyl acrylates, the brittle point goes from 3 to -65°C (85). A minimum brittle point is reached with poly(*n*-octyl acrylate); longer chain acrylates give higher values. This is attributed to the higher esters forming crystalline waxes, and the brittle point obtained corresponds to the melting point of the wax (3). Replacing a straight chain acrylate with a branched one gives a higher brittle point (86). For example, replacing

n-butyl acrylate with isobutyl acrylate changes the brittle point from -45°C (85) to -24°C (86). Thus, to obtain better low temperature flexibility, straight-chain acrylates should be used. However, this improvement in low temperature flexibility is obtained at the expense of reduced oil resistance (14). This is not unexpected, since a similar situation exists with nitrile rubbers. Copolymerizing acrylate monomers with a polar monomer such as acrylonitrile does not offer any help.

Thus, it would seem possible only to get points above the low temperature vs oil-resistance curve, eg, by using a branched acrylate, but not below it. However, it was discovered that copolymers with ether functional groups, such as ethoxyethyl acrylate, give points below the curve (87,88). Actually, the first ether acrylate was introduced in 1955 by Monsanto and was called Vyram, a polymer based on cyanoethoxyethyl acrylate (89). Apparently it was not realized at the time that this polymer had an excellent balance of oil resistance and low temperature flexibility. Like many acrylic rubbers that followed, Vyram had a fleeting existence and the trade name was later used for another product. At BFGoodrich, it was discovered that methoxyethyl acrylate gave a better balance of oil resistance and low temperature behavior than that of ethoxyethyl acrylate, and patents were obtained covering the use of this backbone monomer with allyl or vinyl chloroacetate (90), and glycidyl acrylate or methacrylate cure-site monomers (91). Ether acrylates are also used with other cure-site monomers (92,93). Thioether acrylates as well as ether acrylates give a good balance of properties (94). Polymers containing 2-cyanoethyl acrylate (62,95) also have a good balance of oil resistance and low temperature properties, but their heat resistance is only moderate. The main backbone monomers used in acrylic elastomer polymerization are

ethyl acrylate	$\text{CH}_2 = \text{CH}-\text{COOC}_2\text{H}_5$
<i>n</i> -butyl acrylate	$\text{CH}_2 = \text{CH}-\text{COOC}_4\text{H}_9$
2-methoxyethyl acrylate	$\text{CH}_2 = \text{CH}-\text{COOC}_2\text{H}_4\text{OCH}_3$
2-ethoxyethyl acrylate	$\text{CH}_2 = \text{CH}-\text{COOC}_2\text{H}_4\text{OC}_2\text{H}_5$

Their properties are published in the literature (96–98).

Polymerization

acrylic elastomers can be produced by ionic polymerization, but this method, at present, is limited and restricted to the laboratory (99,100). Thus, practically all acrylic elastomers, both commercial and experimental, are produced by free-radical polymerization. Of the processes available, only aqueous emulsion and suspension are used for all commercial products and probably for most experimental ones. Solution polymerization is possible, but the choice of a solvent is important because the solvent chain-transfer constants for acrylates are higher

than corresponding values for less reactive monomers such as styrene (6). The main virtue of solution polymerization is that it can be used with monomers that have appreciable solubility in water (6). A big disadvantage is the high viscosity at high concentrations of polymer.

The free-radical polymerization of acrylate monomers, particularly those from lower molecular-weight alcohols, is extremely exothermic so that bulk polymerization is very hazardous and not recommended. Even with the other methods it is essential that there be efficient heat transfer to remove the heat of reaction quickly. It is recommended that only a portion of the monomer be added initially, then, after this has polymerized, the rest of the monomer can be metered in to control the reaction temperature (3).

Emulsion Polymerization. Emulsion polymerization is the most industrially important method of polymerizing acrylic ester monomers (12). The principal ingredients within this type of polymerization are water, monomer, surfactant, and water-soluble initiator. Because of their film-forming properties at room temperature, most commercial acrylic ester polymers are copolymers of ethyl acrylate and butyl acrylate with methyl methacrylate.

Lower acrylates are capable of polymerizing in water in the presence of an emulsifier and a water-soluble initiator. The polymeric product is typically a milky-white dispersion of polymer in water at a polymer solids content of 30–60%. Particle sizes for these latices fall in the range of 0.1–1.0 μm . Because of the compartmentalized nature of the process (99), high molecular weights are obtained with most emulsion polymerizations without the resulting viscosity build encountered with solution polymerizations. Additionally, the use of water as a dispersion medium provides attractive safety, environmental, and heat removal benefits when compared to other methods of polymerizing acrylic ester monomers. The emulsion polymerization of the higher (relatively water insoluble) acrylates can even be accomplished now through the use of a patented method for catalytically transferring monomer from droplets to the growing polymer particles.

The types of surfactants used in an emulsion polymerization span the entire range of anionic, cationic, and nonionic species. The most commonly used soaps are alkyl sulfates such as sodium lauryl sulfate, alkylaryl sulfates such as sodium dodecyl benzene sulfonate, and alkyl or aryl polyoxyethylene nonionic surfactants. Product stability and particle size control are the driving forces which determine the types of surfactants employed; mixtures of nonionic and anionic surfactants are commonly used to achieve these goals.

Water-soluble peroxides, such as sodium or ammonium persulfate, are commonly used in the industrial arena.

Emulsion polymerization batches on the industrial scale are typically run in either stainless steel or glass-lined steel reactors which can safely handle internal pressures of 446 kPa (65 psi). Agitation within the reactors is controlled by use of a variable speed stirring shaft coupled at times with a baffling system within the reactor to improve mixing. Care must be taken to avoid excessive mixing forces being placed on the latex as coagulum will form under extreme conditions. Temperature control of batches is maintained through the use of either steam or cold waterjacketing. Multiple feed lines are necessary to provide for the addition of multiple streams of reactants such as initiators, monomer emulsions, inhibitors if necessary, and cooling water. Monitoring equipment for batches typically

consists of thermocouples, manometers, sightglasses, as well as an emergency stack with a rupture disk in case of pressure buildup within the reactor.

Suspension Polymerization. Suspension polymers of acrylic esters are industrially used as molding powders and ion-exchange resins. In this type of polymerization, monomers are dispersed as 0.1- to 5-mm droplets in water and are stabilized by protective colloids or suspending agents. In contrast to emulsion polymerization, initiation is accomplished by means of a monomer-soluble agent and occurs within the suspended monomer droplet. Water serves the same dual purpose as in emulsion (heat removal and polymer dispersion). The particle size of the final material is controlled through the control of agitation levels as well as the nature and level of the suspending agent. Once formed, the 0.1- to 5-mm polymer beads can be isolated through centrifugation or filtration.

The most commonly used suspending agents are cellulose derivatives, polyacrylate salts, starch, poly(vinyl alcohol), gelatin, talc, and clay derivatives. The important function these agents must serve is to prevent the coalescence of monomer droplets during the course of the polymerization. Thickeners can also be added to improve suspension quality. Other additives such as lauryl alcohol, stearyl acid or cetyl alcohol lubricants and di- or trivinyl benzene, diallyl esters of dibasic acids, and glycol dimethacrylates cross-linkers are used to improve bead uniformity and bead performance properties.

Unlike emulsion polymerization, the initiators employed in suspension polymerization must not be water-soluble; organic peroxides and azo species are most commonly used. In similar fashion to bulk polymerization, the level of initiator used directly influences the molecular weight of the product. Developments in the method of suspension polymerization have been reviewed in the open literature (100,101).

Polymer Properties

Data on the density, refractive index, and glass-transition temperature of these polymers are given in the literature (98,102). Refractive index and glass-transition data for the homopolymers derived from the four most common backbone monomers are given in Table 1. Dielectric measurements on acrylic polymers show the existence of two peaks (103). The higher temperature peak, called the α -peak, is attributed to backbone motion and correlates with the glass temperature. A lower peak, called the β -peak, is attributed to side-chain motion. Acrylic elastomers are polar and dipole-moments have been determined (104). The solubility parameter of homopolymers of methyl, ethyl, *n*-propyl, and *n*-butyl acrylates are 10.1, 9.4, 9.0, and 8.8, respectively (105). As a result, acrylic elastomers are soluble in ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate and *n*-butyl acetate, alcohols such as methanol, and aromatics such as benzene and toluene (106). It has been found that *n*-propanol is a theta solvent at 39.5°C (107). The viscosity of a solution in acetone decreases as the mastication time on a two-roll mill increases (108).

Acrylic elastomers burn and the products of combustion are gaseous; all that is left is a very minor amount of inorganic ash. Various authors have studied the thermal-oxidative degradation of poly(ethyl acrylate). One study found the

Table 1. Properties of Acrylate Polymers

Properties of homopolymer	Acrylate backbone monomer			
	Ethyl	<i>n</i> -Butyl	2-Methoxyethyl	2-Ethoxyethyl
refractive index, n_D^{20} ^a	1.4688	1.4631	1.463	1.471
T_g , °C, from dta 10°/min	−15	−45.5	−36	−41

^aRef. (98).

products to be carbon dioxide, formic acid, ethanol, and water (109), whereas another found carbon dioxide, ethyl acetate, ethanol, and water (110). In the absence of oxygen, the degradation products are carbon dioxide and ethylene (111).

Raw acrylic elastomers have a specific gravity of 1.10, are off-white in color, and tend to be relatively soft, tacky, and thermoplastic. Shelf life is excellent when they are stored under normal, dry conditions. Current commercial types are manufactured in a 25–60 Mooney (ML-1 + 4/100°C) viscosity range. All are normally supplied in solid slab form, but can be provided in ground crumb form. Special solution grades are also available in both slab and crumb form. Published information on the molecular weight of acrylic rubbers appears to be almost nonexistent. Generally speaking, the higher the Mooney viscosity, the higher the molecular weight.

Acrylic elastomers are used in the raw state for some applications, eg, binders, plastics modification. However, for most applications, they must be compounded and cured to develop useful properties.

Suitably compounded and cured, acrylic elastomers are inherently resistant to temperatures from −40 to 204°C, oils and greases at elevated temperatures oxidation at normal and elevated temperatures, ozone at normal and elevated temperatures, aliphatic hydrocarbons, sunlight (uv) discoloration, and weathering.

Typical vulcanizate properties are as follows (112–115): tensile strength (MPa), 5–16; elongation (%), 100–400; hardness (Duro A), 40–90; and compression set, 70 h/150°C (%), 15–60.

Table 2 provides a comparison of the acrylics (ACM) to other oil-resistant, commercially important, elastomers (116,117). Note that they exhibit superior heat resistance vs chloroprene (CR), nitrile (NBR), chlorosulfonated polyethylene (CSM), and epichlorohydrin (CO–ECO) elastomers, but are less heat resistant than the silicone (MQ), fluorosilicone (FMQ), and fluorocarbon (FKM) types. In addition, conventional acrylics also provide significantly greater oil swell-resistance than the chloroprene, chlorosulfonated polyethylene, ethylene–acrylic (E–A), and silicone elastomers.

In general, ethyl acrylate base polymers provide the best overall balance of processing characteristics, physical properties, heat and oil resistance, but possess limited (−14°C) low temperature resistance. Low temperature versions exhibit some sacrifice in this balance, usually proportional to the glass-transition temperature of the polymer. The basic characteristics of representative, current state-of-the-art types and compound properties are given in the supplier's literature.

Table 2. Comparative Properties of Oil-resistant Specialty Elastomers

Elastomer type	Sp gr	Service temp, max, °C, 70 h/air	Service temp, continuous, °C, 1000 h/air	Service temp, min, °C, flexibility	Oil resistance, 150°C, 70 h/ASTM Oil No. 3
CR	1.25	149	107	−40	fair
NBR	1.00	149	107	−46	excellent
CSM	1.15	163	121	−46	fair
CO-ECO	1.30	163	135	−57	excellent
E-A	0.96	204	163	−34	fair
ACM	1.10	204	177	−40	excellent
FMQ	1.40	260	232	−57	excellent
FKM	1.80	288	260	−34	excellent
MQ	0.95	316	274	−100	fair

Heat Resistance. The high temperature service of acrylic elastomers is rated at 70 h max/190–204°C short term, intermittent and 1000 h max/163–177°C long term, continuous in dry heat, depending on type (118,119). The ultimate mode of heat aging failure is embrittlement. Very short time service above 204°C is also possible. In effect, aging under high circulating air conditions is most severe, eg, air oven vs air test tube.

Oil and Chemical Resistance. Acrylic elastomers exhibit outstanding resistance to automotive transmission fluids and a wide variety of conventional petroleum base and synthetic lubricating oils, including the newer longer-life hydrocarbon and ester-base types (14,120–122). Because of their saturated nature, they are especially resistant to sulfur bearing fluids, such as hypoid extreme pressure (EP) gear lubricants, which normally cause embrittlement of unsaturated elastomers, such as nitrile rubber (NBR) (11).

Although not recommended for continuous service in gasoline, ethylene glycol, water, or steam, acrylic elastomers are capable of withstanding short-term, intermittent contact with these media. More detailed information on the oil and chemical resistance of ethyl acrylate-type elastomers is presented in Table 3 (116,117).

Hot Properties. Acrylic vulcanizates tend to soften and lose strength at elevated temperatures. However, at 177°C, they do retain approximately 35% tensile strength and 80% elongation vs room temperature values (123). Very often, they are compounded to relatively high RT hardness to compensate for the softening effect at service temperatures.

Low Temperature Resistance. Acrylic elastomers are commonly characterized by glass-transition temperatures determined by differential thermal analysis. Conventional ethyl acrylate base polymers exhibit by dta, T_g of -14°C ; the newer improved low temperature types range from -19 to -40°C (123). Certain plasticizers can also be utilized to enhance low temperature resistance. Owing to their relatively low strength, acrylic elastomers provide better low temperature flexibility than impact resistance. Low temperature flexibility test methods such as dta, ASTM D 1053 torsional stiffness, and ASTM D 1329 retraction

Table 3. Oil and Chemical Resistance of Ethyl Acrylate Type Elastomers

Media	Rating ^a	Media	Rating ^a
acids, conc	P	hydraulic fluids	
alcohols	P	petroleum base	E
alkalies, conc	P	phosphate ester	P
ATF	E	silicate ester	G
aliphatic hydrocarbons	E	Hypoid (EP) lubricant	E
aromatic hydrocarbons	F-P		
		kerosene	G
chlorinated hydrocarbons	P	ketones	P
diesel oil	G	mineral oil	G
diester lubricants	G		
		silicone oil	G
engine oil	E	steam	P
ethylene glycol	P		
		water, 100°C	F-P
gasoline	F-P		

^aE = excellent; G = good; F = fair, subject to test; P = poor, not recommended.

are generally considered indicative of low temperature performance characteristics (123).

Flexibility. Acrylic elastomers can be compounded to provide excellent flex life. Cure systems and reinforcing agents that impart low modulus and high elongation characteristics generally contribute to flex resistance. Compounds have been developed that provide 2×10^6 cycles without cracking by ASTM D 813 DeMattia flex test (124,125).

Abrasion Resistance. Acrylic elastomers provide only fair abrasion resistance compared to other types of oil-resistant elastomers, eg, nitrile rubbers (123). However, abrasion resistance can be significantly improved through compound design and the use of reinforcing agents.

Corrosion Resistance. Although most acrylic elastomers contain chlorine-type reactive cure monomers, they are not highly corrosive to steel, either in the raw or vulcanized state. By the General Motors test procedure (126), acrylic vulcanizates generally provide relatively low corrosion ratings in the 1–2.5 range (123).

Electrical Properties. Acrylic elastomers are more conductive than the less polar types, eg, natural rubber, styrene-butadiene, etc. They can be compounded to provide high conductivity with conductive furnace black, eg, N-294 CF, or to give fair insulation resistance, with silica and silicate-type reinforcing agents, or both (127).

Ozone and Uv Light Resistance. Acrylic elastomers possess inherent ozone and uv light resistance. Unprotected vulcanizates have been reported to withstand >168 h exposure to 100 pphm ozone at 49°C under 20% stretch conditions and six mo roof exposure without signs of cracking or significant discoloration (128). However, use in outdoor applications is limited to some degree by their water sensitivity characteristics.

Flame Resistance. Acrylic elastomers are 99% by weight carbon, hydrogen, and oxygen. Oxygen content is relatively high, ranging from 20 to 30%. Characteristically, they ignite and burn quite readily and completely, leaving no residue (129).

Little or no information appears to exist for promoting improved flame resistance. However, on the basis of work with other elastomers (130), it is expected that the use of conventional hydrated alumina, antimony oxide, chlorine, and phosphate-type protective agents would be beneficial.

Resilience. Like other elastomers, the resilience characteristics of acrylic elastomers are temperature-dependent. Degree of resilience is directly related to the difference between the test temperature and glass-transition temperature of the polymer. At room temperature, conventional poly(ethyl acrylate) types (-14°C , T_g) exhibit quite low resilience, whereas the -19 to -40°C T_g low temperature versions provide proportionately higher resilience (123). At 149°C , the resilience of all types increases markedly, to 100–200% of room temperature values.

Radiation Resistance. Acrylic elastomers are not highly radiation-resistant. Upon exposure to a 1.3×10^4 C/kg dosage, an ethyl acrylate type tested lost 60–70% tensile strength and elongation. However, it did not harden excessively and retained a high degree of flexibility. Additional protection may be obtained with the use of certain amine type, radical-terminating antioxidants or antiozonants (131).

Gas Permeability. Tested at ambient temperature, vulcanized ethyl acrylate based compounds were reported to provide fair air permeability resistance (132), but relatively poor nitrogen permeability resistance (133) compared to other elastomers. However, more work is required to fully characterize the gas permeability resistance of acrylic elastomers. In theory, gas permeability resistance is primarily related to polymer structure and polarity, gas polarity, and molecule size and temperature (134). Also, as found with nitrile elastomers (133), the use of small particle size carbon-black reinforcing pigments would be expected to promote improved gas permeability resistance.

Additives

Vulcanization. All current commercial acrylic elastomers contain a small amount, ie, 1–5%, of a reactive cure-site monomer, usually a chlorine type. The reactivity of this site governs cure behavior. The type of cure-site monomer varies in commercial acrylic elastomers, and different cure systems have been developed for specific types. The most popular cure systems for U.S.-produced varieties are summarized in Table 4.

Historically, the development of acrylic cure systems has paralleled advances in polymer technology. The first commercial acrylic elastomer, Hycar 4021 (formerly PA-21), was introduced in 1948. This was a 95% ethyl acrylate, 5% chloroethyl vinyl ether copolymer that had only moderate cure-site activity. Accordingly, relatively potent liquid polyamine cure systems, eg, Trimene Base and triethylenetetramine, were required to achieve satisfactory vulcanizate properties (106). The development of more efficient solid diamine, eg, Diak No. 1 (106) and ethylene thiourea, eg, NA-22, cure systems followed (44).

Table 4. Common Core Systems for U.S.-produced Acrylic Elastomers

Polymer	Cure system	Typical phr	Function	Major advantages	Major disadvantages
Hycar 4050 types	Na stearate	4	curative	nonpostcure type	no significant
	Karnex Diuron ^a	1.5	accelerator	good scorch safety	
Hycar 4050 types	Maglite D ^b	optional	activator	fast cure	lead toxicity
	stearic acid	1	retarder	ultra low compression set	
	Vanchem DMTD ^c	0.6	curative	nonpostcure type	
	Butyl Taaads ^d	2.5	accelerator	relatively fast cure	
	lead stearate	1	activator	high elongation	
	zinc stearate	optional	retarder	low compression set	
Hycar 4050 types	Na stearate	4	curative	low compression set	scorchy
	TMTD ^e	0.7	accelerator		
	MBTS ^f	optional	retarder		
	Dyphos ^g	2.5	activator	high elongation	
Hycar 4050 types	Thiate EF-2 ^h	0.5	curatives	high heat resistance	poor compression set lead, thiourea toxicity high cost
	END-75 ⁱ	0.7	curatives	high flexibility	
	MBTS ^j	0.5	retarder		
	Diak No. 3 ^j	2.5	curative	low compression set, (nonblack only)	
Hycar 4040 types	Maglite D ^b	optional	activator		no significant
	stearic acid	1	retarder		
Hycar 4050 types	Na/K stearate	4	curative	general purpose	
Hycar 4040 types	sulfur	0.4	accelerator	low cost	
Cyanacryl	Maglite D ^b , HVA-2 ^k	optional	activators		
	stearic acid	1	retarder		

Cyanacryl	TCY ⁱ	0.75	curative	nonpostcure type	scorchy
Hycar 4050 types	Ethyl Zimate ^m	1	accelerator	very fast cure	malodorous with PVI
	Santogard PVI ⁿ	optional	retarder	low compression set	

^aN,N-Dimethyl-N'-(3,4-dichlorophenyl)urea, 80% active
^bMagnesium oxide, high activity
^c2,5-Dimercapto-1,3,4-thiadiazole
^dTetrabutylthiuram disulfide
^eTetramethylthiuram disulfide
^fBisbenzothiazolyl disulfide
^gDibasic lead phosphite
^hTrimethylthiourea
ⁱEthylenethiourea, 75% active
^jN,N'-Dicinnamylidene-1,6-hexanediamine
^k*m*-Phenylene-N,N'-dimaleimide
^lTrithiocyanuric acid
^mZinc diethyldithiocarbamate
ⁿN-(Cyclohexylthio)phthalimide

Acrylic elastomers with increased cure reactivity were developed in the 1960s by American Cyanamid Co. (47) and BFGoodrich Chemical Co. (54). These responded to milder, less corrosive cure systems, such as soap (metallic carboxylates) and elemental sulfur (49,50). In a soap-sulfur system, the soap, ie, sodium or potassium stearate, functions as the curative, whereas sulfur acts as an accelerator. In practice, a 10 to 1 soap to sulfur ratio is usually employed. The metal ion of the soap also has a significant effect on cure activity. Potassium stearate is much more active than sodium stearate at temperatures below 177°C (135). Sodium and potassium stearates are quite unique in their curing ability, since practical cures with other metal stearates have not been reported. Sulfur donors, eg, tetramethylthiuram disulfide (Methyl Tuads), can also be effectively utilized in place of elemental sulfur (49). Soap-sulfur cure systems are commonly employed.

Certain other cure systems have also been developed for specific acrylic elastomers. It has been shown that ammonium benzoate (48) is an effective curative, ammonium adipate (49) provides improved compression set resistance, and more recently, that trithiocyanuric acid (51) provides very fast, low compression set cures for their Cyanacryl products. BFGoodrich Chemical has shown that soap-quaternary ammonium salt or tertiary amine accelerated systems provide fast and very low compression set cures for their Hycar 4050 series polymers (78). *N,N*-Dimethyl-*N'*-(3,4-dichlorophenyl)urea, a thermally released secondary amine, has been found to function as an effective accelerator for a soap system (127). Most recently, a 2,5-dimercapto-1,3,4-thiadiazole cure system has been developed that also exhibits fast cure and low compression set characteristics (136).

Since the majority of acrylic cure systems are basic in nature, they are retarded by acids and accelerated by bases. Stearic acid, zinc stearate, mercaptobenzothiazyl disulfide (135), and *N*-(cyclohexylthio)phthalimide (137) function as effective retarders, whereas magnesium oxide and *m*-phenylene-*N,N'*-dimalimide (138) act as supplemental activators for certain cure systems, as shown in Table 4.

Despite significant advances in cure technology, all current acrylic elastomers require a relatively long cure cycle or must be postcured, ie, tempered, usually in a circulating hot air environment, to achieve optimum compression set resistance (14). Future research is required for the development of more highly reactive polymers and cure systems, or both, to completely eliminate the necessity of a postcure. A uv curatives epoxy acrylate has been reported (139). A sub photocuring process via a muhoued addition reaction of an unsaturated product of a multifunctionse acrylate acceptor has been reported (140).

Reinforcing Agents. Acrylic elastomers are noncrystalline, amorphous in nature, and do not yield high cured gum strength. Typical gum vulcanizate properties of an ethyl acrylate elastomer are tensile strength (MPa), 1.52; elongation (%), 300; and hardness (Durometer A), 24. Carbon black or mineral reinforcing agents are required to develop useful properties.

Carbon-black reinforcing agents are used almost exclusively in nonelectrically resistant and noncolor-coded applications, since they tend to provide a better overall balance of vulcanizate properties than the mineral types. As with other elastomers, smaller particle-size blacks provide the highest

reinforcement, whereas higher structure types contribute to processing characteristics. Of the many available grades, medium particle-size ASTM N550 high structure and N539 low structure FEF, ie, fast extruding furnace, types are most popular (135,141).

In general, the use of mineral reinforcing agents is primarily limited to electrically resistant and color-coded applications. Aluminum silicate and the smaller particle-size, higher reinforcing, silica types are typically utilized, either alone or in combination. Of these, Nulok 321, an amino silane-modified aluminum silicate, and Zeolex 23, a sodium silico aluminate, have proven especially useful. Amino silane coupling agents, eg, Silane A-1100, are also sometimes employed as additives to improve vulcanizate properties.

In addition, synthetic graphites are often used in conjunction with carbon black and mineral-type reinforcing agents, or both, to promote improved surface lubricity and abrasion characteristics in, for example, rotary shaft seal applications (142). Neutral to high pH alkaline pigments are specifically recommended, since acidic types tend to retard the basic cure mechanism of most acrylic elastomers.

Plasticizers. Plasticizers are generally used sparingly in acrylic compounds because of volatility considerations. However, relatively low, ie, 5–10 phr, concentrations are sometimes utilized, primarily as process aids or to improve low temperature resistance. Type and amount are dictated by the volatility and extraction characteristics of the plasticizer in postcure conditions and by specification and service requirements, or both.

Some common, useful plasticizers are (135,143):

<i>Plasticizer</i>	<i>Type</i>	<i>Volatility</i>	<i>Extractability</i>	<i>Low temp rating</i>
Thiokol TP-759	ether/ester	moderate	high	good
Plastolein 9720	polyester	low	moderate	fair
Admex 760	polyester	very low	very low	poor

Process Aids. Lubricating agents are required to enhance the release characteristics of acrylic compounds. Stearic acid is universally used, usually in combination with commercial process aids, which are specifically designed to provide both external (release) and internal (viscosity-reducing) lubricating qualities (144). However, excessive lubricant levels may interfere with mold knitting and metal-bonding characteristics. Current representative commercial process aids are TE-80 and Vanfre AP-2 (11,102).

Antioxidants. Acrylic elastomers are, of course, inherently resistant to oxidation. However, certain nonvolatile solid diphenylamine antioxidants, eg, AgeRite Stalite S do provide marginally improved dry heat aging resistance (145). The use of sodium alkyl sulfate (146), along with inorganic and organic phosphites (147,148), have also been reported to be beneficial. Since most antioxidants are extractable, they do not tend to improve oil-aging characteristics significantly.

Processing

Because of their inherent rheological characteristics and different cure mechanism, acrylic elastomers are generally more sensitive to processing and contamination than some other elastomers, eg, nitrile. Because of this, fairly rigid processing procedures must be maintained to ensure mix-to-mix quality and uniformity.

Mixing. Acrylic elastomers do not lend themselves especially well to open mill-mixing because of release-associated problems. Internal, Banbury, mixing is much more efficient and generally utilized by the industry. Typical Banbury and mill-mixing procedures are as follows:

Banbury

start—slow speed, full cooling water

Master

0 min—charge polymer

5 min—bump and sweep

1/2 min—add filler, stearic acid, antioxidant

6 min—dump

3 min—add process aid, plasticizer

dump temperature range, 121–150°C

Mill

dip cool

start—RT rolls, full cooling water

5. add plasticizer

dip cool (optional)

1. band polymer

6. add curatives

2. adjust nip to provide rolling bank

dip cool

3. add filler, stearic acid, antioxidant

mixing time range, 30–60 min

open nip as required to retain rolling bank

Finish

4. add process aid

0 min—charge $\frac{1}{2}$ master, curatives, $\frac{1}{2}$ master

dump at 107°C, max

dump time range, 1–3'

dip cool

A one-pass Banbury mix is also possible on relatively nonscorchy compounds (149). Since acrylic elastomers are somewhat thermoplastic, they tend to lose shear resistance fairly rapidly upon mixing. Therefore, it is essential that reinforcing agents be incorporated very early in the mixing cycle to obtain good dispersion. Foreign contaminants are also to be avoided, eg, other polymers and zinc oxide.

Compound Storage Stability. Acrylic compounds exhibit relatively good shelf-stability characteristics, in the range of one to four weeks, when stored under normal RT, dry conditions (150). Shelf life is primarily dependent on the basic activity of the cure system employed. Storage under refrigerated (4°C), low humidity conditions is also an effective method of extending shelf-life. Generally, aged compounds should be mill-freshened prior to subsequent processing.

Extrusion and Calendering. Most acrylic compounds will extrude and calender well enough for intermediate process, preparative purposes. However, for finished goods, special compounding techniques may be required to obtain

satisfactory size, surface, and release characteristics. In general, the use of high structure reinforcing agents, along with increased concentrations of lubricants and process aids, is usually effective. Compound extension via the use of higher loadings, combined with softening-type plasticizers, is also helpful and sometimes necessary.

Typical conditions are as follows:

<i>Extrusion</i>	<i>Calender</i>
screw or ram type	three-roll type
barrel temp, 60–82°C	top roll, 60–71°C
die temp, 82–107°C	middle roll, 71–82°C
	bottom roll, 82–107°C

These conditions will, of course, vary to some degree, depending on the type of compound and equipment. It is also recommended that all compounds be mill-freshened just prior to extrusion or calendering.

Vulcanization Methods. Acrylic elastomers lend themselves to virtually all conventional cure processes. They are commonly used in compression, transfer, and injection-molded applications, but are open steam-cured as well (151). Historically, compression molding has been most prevalent. Typical cure cycles are: compression mold, 2 min/190°C to 1 min/204°C; transfer mold, 8 min/160°C to 4 min/177°C; injection mold, 90 s/190°C to 45 s/204°C; and open steam cure, 30–60 min/163°C. These cycles can vary, of course, depending on the mass and configuration of the article, or both.

In addition, acrylic elastomers can be hot-air cured (152). Electron-beam cures on thin sections have also been reported (19). Although there are no reports in the literature, acrylic elastomers would be expected to respond to continuous vulcanization (CV) techniques.

Utilization of a postcure is determined by application on the basis of required compression-set resistance. Oven postcure cycles in the range of 4–8 h/177°C are typically employed.

Bonding Characteristics. Acrylic compounds provide excellent bonds to metals and other substrates with a variety of commercially available solventbase, curing-type adhesives (153). Bonding is customarily carried out during vulcanization. Recommended substrate surface preparation and application procedures are usually provided by the manufacturer (154). Water-base adhesives have recently been introduced, but little or no information appears to exist at this time for their use with acrylic elastomers.

Economic Aspects

Acrylic acid and esters are the most versatile series of monomers for producing a wide variety of polymer formulations. Incorporation of varying acrylate monomers permits the production of thousands of formulations for latex copolymers copolymer plastics, and cross-linkable polymer systems. World demand for commodity acrylates is forecast to grow at 3.7%/yr during the 2006–2011 time period (155).

In 2005, of the $2,880 \times 10^6$ lb of acrylic acid produced in the United States, 56% was used to produce acrylate esters. Consumption of the largest volume commodity acrylate ester, *n*-butyl acrylate is expected to grow 2.5%/yr through 2008. Conversion from solvent to water-based adhesives resulted in a 10% growth for 2-ethylhexyl acrylate during the period 1993–2003. However, the conversion is almost complete and growth is expected to be at the rate of 3.5%/yr through 2008 (156).

Standards

In the U.S., test procedures and specifications for acrylic compounds are covered by ASTM–SAE standards (157,158). Under this system, commercial acrylic elastomers are identified as ACM. Compound requirements are designated by D2000–80 DF and DH classification line call outs. Although not exclusively used, ASTM–SAE standards generally serve as a basis for other standards and specifications.

Health and Safety Factors

The monomers used in preparing acrylic elastomers have varying degrees to toxicity so that no polymerizations should be undertaken without first consulting the appropriate material safety data sheets. Free-radical polymerization of acrylate monomers is extremely exothermic, so all reactions, and in particular bulk polymerization, can be very hazardous. Precautions should be taken to control the temperature by adequate removal of the heat of polymerization. Ingredients used in compounding and curing acrylic elastomers may be toxic; therefore, material safety data sheets should be consulted.

For ethyl acrylate, eg, OSHA PEL TWA is 5 ppm, STEL is 25 ppm, ACGIH TWA is 5 ppm, STEL is 15 ppm (159).

Uses

Historically, the acrylics have been strongly associated with the automotive industry. However, because of their wide property range, clarity and resistance to degradation by environmental forces, acrylic polymers are used in a large variety of applications (99). They are used in all type of paints as binder vehicles. The industrial finishing area uses include coatings for factory finished wood, furniture, and can and coil coatings. Hydrophobically modified acrylics are used as thickening agents in paints. Acrylic emulsion polymers find a variety of uses in the textile area, such as binders for fiberfill and nonwoven fabrics, textile binding and laminating, back coating and pigment printing. Polyester, glass, rayon, nonwoven and fiberfill mats have been manufactured using acrylic binders to hold the mats together. Final products include clothing, disposable diapers, towel, filters and roofing. Acrylic emulsion polymers are used in adhesives (160). They possess an excellent balance of tack, peel, and shear properties. In the paper industry, acrylics are used as pigment binders for paper and boards and as paper saturants. Other

industries that use acrylics are the leathering finishing, cement, caulk, sealants, and ceramics manufacturers. The manufacturing process for poly(vinyl chloride) uses acrylics as processing aids. In the agricultural area, thin layers of acrylic emulsions have been applied to citrus leaves and fruit to control leaf-spotting damage.

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ACRYLIC ESTER POLYMERS

Introduction

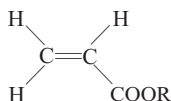
The usage of acrylic esters as building blocks for polymers of industrial importance began in earnest with the research of Otto Röhm (1). The first recorded preparation of the basic building block for acrylic ester polymers, acrylic acid, took place in 1843; this synthesis relied on the air oxidation of acrolein (2,3). The first acrylic acid derivatives to be made were methyl acrylate and ethyl acrylate. Although these two monomers were synthesized in 1873, their utility in the polymer area was not discovered until 1880 when Kahlbaum polymerized methyl acrylate and tested its thermal stability. To his surprise, the polymerized methyl acrylate did not depolymerize at temperatures up to 320°C (4). Despite this finding of incredibly high thermal stability, the industrial production of acrylic ester polymers was not realized for almost another 50 years.

The commercial discovery of acrylic ester polymers took place while Otto Röhm was conducting his doctoral research in 1901. Röhm obtained a U.S. patent in 1912 covering the vulcanization of acrylates with sulfur (5). Commercial

production of acrylic ester polymers by the Rohm and Haas Co. of Darmstadt, Germany, commenced in 1927 (6).

Properties

The structure of acrylic ester monomers is represented by the following:



The R ester groups determine the properties of the polymers formed. This R side-chain group conveys such a wide range of properties that acrylic ester polymers are used in applications varying from paints to adhesives, concrete modifiers and thickeners. The glass-transition range for a polymer describes the temperature range below which segmental pinning takes place and the polymer takes on a stiff, rigid, inflexible nature. This range can vary widely among the acrylic ester polymers from -65°C for 2-ethylhexyl acrylate ($\text{R} = \text{C}_4\text{H}_9$) to 103°C for acrylic acid ($\text{R} = \text{H}$). Film properties are dramatically influenced by this changing of the polymer flexibility.

When copolymerized, the acrylic ester monomers typically randomly incorporate themselves into the polymer chains according to the percentage concentration of each monomer in the reactor initial charge. Alternatively, acrylic ester monomers can be copolymerized with styrene, methacrylic ester monomers, acrylonitrile, and vinyl acetate to produce commercially significant polymers.

Acrylic ester monomers are typically synthesized from the combination of acrylic acid and an alcohol. The properties of the polymers they form are controlled by the nature of the ester side chain as well as the molecular weight of the product. Acrylic ester polymers are similar to others in that they show an improvement in properties as a function of molecular weight until a certain threshold beyond which no further improvement is observed. This threshold is typically reached at a molecular weight value of 100,000–200,000 for acrylic polymers.

Glass-Transition Temperature. The Glass-transition temperature (T_g) describes the approximate temperature below which segmental rigidity (ie, loss of rotational and translational motion) sets in. Although a single value is often cited, in reality a polymer film undergoes the transition over a range of temperatures. The reason for this range of temperatures for the glass transition is that segmental mobility is a function of both the experimental method used [dynamic mechanical analysis (DMA) vs differential scanning calorimetry (DSC)] as well as the experimental conditions. Factors such as hydroplasticization in varying degrees of humidity can alter T_g results. Most polymers experience an increase in the specific volume, coefficient of expansion, compressibility, specific heat, and refractive index. The T_g is typically measured as the midpoint of the range over which the discontinuity of these properties takes place. Care should be taken

Table 1. Physical Properties of Acrylic Polymers

Polymer	Monomer molecular formula	CAS registry number	T_g , °C ^a	Density, g/cm ^{3b}	Refractive index, n_D
Poly(acrylic acid)	C ₃ H ₄ O ₂	[9003-01-4]	106	1.08	1.496
Poly(methyl acrylate)	C ₄ H ₆ O ₂	[9003-21-8]	9	1.22	1.479
Poly(ethyl acrylate)	C ₅ H ₈ O ₂	[9003-32-1]	-24	1.12	1.464
Poly(propyl acrylate)	C ₆ H ₁₀ O ₂	[24979-82-6]	-45		
Poly(isopropyl acrylate)	C ₆ H ₁₀ O ₂	[26124-32-3]	-3	1.08	1.408
Poly(<i>n</i> -butyl acrylate)	C ₇ H ₁₂ O ₂	[9003-49-0]	-54	1.08	1.474
Poly(<i>sec</i> -butyl acrylate)	C ₇ H ₁₂ O ₂	[30347-35-4]	-22		
Poly(isobutyl acrylate)	C ₇ H ₁₂ O ₂	[26335-74-0]	-43		
Poly(<i>tert</i> -butyl acrylate)	C ₇ H ₁₂ O ₂	[25232-27-3]	43		
Poly(hexyl acrylate)	C ₉ H ₁₆ O ₂	[27103-47-5]	-57		
Poly(heptyl acrylate)	C ₁₀ H ₁₈ O ₂	[29500-72-9]	-60		
Poly(2-heptyl acrylate)	C ₁₀ H ₁₈ O ₂	[61634-83-1]	-38		
Poly(benzyl acrylate)	C ₁₀ H ₁₀ O ₂	[2495-35-4]	6	1.05	1.517
Poly(2-ethylbutyl acrylate)	C ₉ H ₁₆ O ₂	[39979-32-3]	-50		
Poly(2-ethylhexyl acrylate)	C ₁₁ H ₂₀ O ₂	[9003-77-4]	-65		1.437
Poly(dodecyl acrylate)	C ₁₅ H ₂₈ O ₂	[26246-92-4]	-30		
Poly(hexadecyl acrylate)	C ₁₉ H ₃₆ O ₂	[25986-78-1]	35		
Poly(2-ethoxyethyl acrylate)	C ₇ H ₁₂ O ₃	[26677-77-0]	-50		
Poly(isobornyl acrylate)	C ₁₃ H ₂₀ O ₂	[30323-87-6]	94		
Poly(cyclohexyl acrylate)	C ₉ H ₁₄ O ₂	[27458-65-7]	16		

^aRefs. (7) and (10).^bRef. (11).

when analyzing T_g data, however, as some experimenters cite the onset of the discontinuity as the T_g value.

The rigidity upon cooling below T_g is observed as an embrittlement of the polymer to the point where films are glass-like and incapable of handling significant mechanical stress without cracking. If, on the other hand, one raises the temperature of a polymer above the glass-transition range, the polymer film becomes stretchable, soft, and elastic. For amorphous acrylic polymers, many physical properties show dramatic changes after passing through the glass-transition temperature range. The physical properties altered are diffusion, chemical reactivity, mechanical and dielectric relaxation, viscous flow, load-bearing capacity, hardness, tack, heat capacity, refractive index, thermal expansivity, creep, and crystallization.

The most common thermal analyses used to determine the glass-transition temperature are DMA and DSC. More information on these techniques and how to interpret the results are contained in References (7–9). The T_g values for the most common homopolymers of acrylic esters are listed in Table 1.

The most common way of tailoring acrylic ester polymer properties is to copolymerize two or more monomers. In this fashion, the balance of hard (high T_g) and soft (low T_g) monomers used to make up the overall composition will determine the overall hardness and softness of the polymer film. An estimate of the T_g , and therefore the film hardness, can be calculated using the Fox equation

(eq. (1)) (12):

$$1/T_g = \sum W(i)/T_g(i) \quad (1)$$

The factor W in this equation refers to the weight, or percent composition, of a given monomer with a given T_g value for the homopolymer.

As can be seen in Table 1, the most common acrylic ester polymers have low T_g values and, therefore, soften films in which they are copolymerized with other vinylic monomers. This effect results in an internal plasticization of the polymer. That is, the plasticization effect from acrylic esters, unlike plasticizer additives which are not covalently bound, will not be removed via volatilization or extraction.

Nondestructive techniques such as torsional modulus analysis can provide a great deal of information on the mechanical properties of viscoelastic materials (8,13–25). For this type of analysis, a higher modulus value is measured for those polymers which are stiffer, harder, or have a higher degree of cross-linking. The regions of elastic behavior are shown in Figure 1 with curve A representing a soft polymer and curve B a harder polymer. A copolymer with a composition between these two homopolymers would fall between the two depicted curves, with the relative distance from each curve determined by the similarity of the copolymer composition to one homopolymer or the other (26–28).

Acrylic ester polymers are susceptible to the covalent bonding of two or more polymer chains to form a cross-link (11,29–38). The above-described thermal analysis techniques are capable of distinguishing not only T_g but also varying degrees of cross-linking between polymers. A higher degree of cross-linking results in an elevation and extension of the rubbery plateau region. After a certain level of cross-linking is obtained, the segmental mobility of the polymer chains is impeded (23,25,28). This loss of mobility is measured as an increase in the T_g of the polymer. Further details on cross-linking within and between polymer chains can be found in References (11) and (29–38).

Molecular Weight. The properties of acrylic ester polymers (and most other types of polymers for that matter) improve as molecular weight increases. Beyond a certain level (100,000–200,000 for acrylic ester polymers) this improvement in polymer properties reaches a plateau. The glass-transition temperature can be described by the equation:

$$T_g = T_{gi} - k/M_n$$

where T_{gi} is the glass-transition temperature for a polymer of infinite molecular weight and M_n is the number average molecular weight. Typical values of k fall in the range of 2×10^5 (39). Reference 40 summarizes the effect of molecular weight on polymer properties.

Mechanical and Thermal Properties. The mechanical and thermal properties of a polymer are strongly dependent on the nature of the ester side-chain groups of its composite monomers. With H as a side chain, poly(acrylic acid) is a brittle material at room temperature, which is capable of absorbing large quantities of water. The first member of the acrylic ester family, poly(methyl

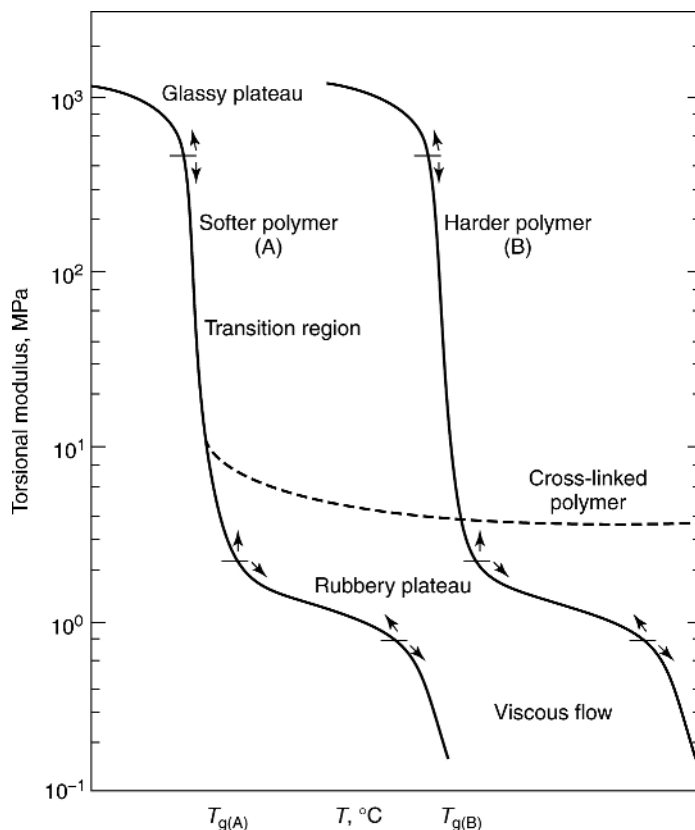


Fig. 1. Modulus–temperature curve of amorphous and cross-linked acrylic polymers. To convert MPa to kg/cm^2 , multiply by 10.

acrylate), is a tough, rubbery, tack-free material at room temperature. The next higher chain length material, poly(ethyl acrylate), is softer, more rubbery, and more extensible. Poly(butyl acrylate) has considerable tack at room temperature and is capable of serving as an adhesive material. Information on these homopolymers is summarized in Table 2 (41). Softness of these polymers increases with increasing chain length until one reaches poly(*n*-nonyl acrylate). Beginning with this chain length, the side chains start to crystallize, which leads to a stiffening of the polymer. This stiffening translates into an embrittlement of the polymer (42); poly(*n*-hexadecyl acrylate), for example, is a hard, waxy material at room temperature. Breaking this crystallinity will be a challenge for longer chain biobased acrylics moving forward as many natural side chain groups (eg dodecyl acrylate) contribute to this embrittlement via Van der Waals interactions via their linearity.

Acrylic ester polymers are quite resilient to extreme conditions. This resilience gives finished products the durability that has earned acrylic polymers their reputation for quality over time. In contrast to polymers of methacrylic esters, acrylic esters are stable when heated to high temperatures. Poly(methyl

Table 2. Mechanical Properties of Acrylic Polymers

Polyacrylate	Elongation, %	Tensile strength, kPa ^a
Methyl	750	6895
Ethyl	1800	228
Butyl	2000	21

^aTo convert kPa to psi, multiply by 0.145.

acrylate) can withstand exposure to 292–399°C in vacuo without generating significant quantities of monomer (43,44). Acrylic ester polymers are also resistant to oxidation. Hydroperoxides can be formed from polymer radicals and oxygen under forcing conditions (45–47), but by and large this is a minor concern.

Solubility. Like most other properties, the side chain of acrylic ester polymers determines their solubility in organic solvents. Shorter side-chain polymers are relatively polar and will dissolve in polar solvents such as ether alcohols, ketones, and esters. With longer side-chain polymers, the solubility of a polymer shifts to the more hydrophobic solvents such as aromatic or aliphatic hydrocarbons. If a polymer is soluble in a given solvent, typically it is soluble in all proportions. Film formation occurs with the evaporation of the solvent, increase in solution viscosity, and the entanglement of the polymer chains. Phase separation and precipitation are not usually observed for solution polymers.

Solubility is determined by the free energy equation (the Flory–Huggins equation) governing the mutual miscibility of polymers (eq. (2)):

$$\Delta G_{\text{Mix}} = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \quad (2)$$

where k is the Boltzmann's constant, T the temperature, N_1 the number of solvent molecules, N_2 the number of polymer molecules, v_1 the volume fraction of the solvent, v_2 the volume fraction of the polymer, and χ_1 the Flory–Huggins interaction parameter.

With this equation, polymer dissolution takes place when the free energy of mixing is negative. A polymer in solution always has a much higher entropy level than undissolved polymer since it is free to move to a far greater extent. This means the change in entropy term will always have a large positive value. Therefore, the factor which determines whether or not a polymer will dissolve in a particular solvent is the enthalpy term. If the difference in the solubility parameters for two substances is small, dissolution will occur since the heat of mixing will be small and the entropy difference will be large (this translates into a negative overall energy of mixing). A polymer will dissolve in a particular solvent if the solubility parameters and the polarities for the polymer and the solvent are comparable (38,48–53). Some relevant solubility parameters are given in Table 3.

Once dissolved, polymer solution viscosity is a function of the polymer molecular weight, concentration in solvent, temperature, polymer composition, and solvent composition (9,54–56).

Chemical Resistance. Acrylic polymers and copolymers are highly resistant to hydrolysis. This property differentiates acrylic polymers from poly(vinyl

Table 3. Solubility Parameters of Acrylic Homopolymers Calculated by Small's Method^a

Polymer	(J/cm ³) ^{1/2b}
Methyl acrylate	4.7
Ethyl acrylate	4.5
<i>n</i> -Butyl acrylate	4.3

^aRefs. (23) and (53).^bTo convert (J/cm³)^{1/2} to (cal/cm³)^{1/2}, divide by 2.05.

acetate) and vinyl acetate copolymers. When exposed to highly extremely acidic or alkaline environments, acrylic ester polymers can hydrolyze to poly(acrylic acid) and the corresponding alcohol. Resistance to hydrolysis decreases in the order butyl acrylate > ethyl acrylate > methyl acrylate. Although it is the least hydrolytically stable, methyl acrylate is still far more resistant to hydrolysis than vinyl acetate (57,58).

Ultraviolet radiation (UV) is the other main stress encountered by polymers in the coatings arena. One hundred percent acrylic polymers are highly resistant to photodegradation because they are transparent to the vast majority of the solar spectrum (59). When UV-absorbing monomers, such as styrene, are incorporated into the polymer backbone, the UV-resistance of the resulting polymer decreases dramatically and a more rapid deterioration in polymer/coating properties is observed. On the other hand, a noncovalently bound UV absorber, such as hydroxybenzophenone [117-99-7], can further improve the uv stability of 100% acrylic polymers (59).

Higher energy radiation such as from gamma ray or electron beam sources results in the scission of both main and side chains (60). The ratio of backbone to side-chain scission is determined by the nature of the side chain (61,62).

Acrylic Ester Monomers

A wide variety of properties are encountered in the acrylic monomers area. This range of properties is made accessible by the variability of the side chain for acrylic monomers. Some of the key physical properties of the most commercially important monomers are included in Table 4. A more complete listing of both monomers and their properties is found in the article Acrylic Acid and Derivatives.

The two most common methods for production of acrylic ester monomers are (1) the semi-catalytic Reppe process which utilizes a highly toxic nickel carbonyl catalyst and (2) the propylene oxidation process which primarily employs molybdenum catalyst. Because of its decreased cost and increased level of safety, the propylene oxidation process accounts for most of the acrylic ester production currently. In this process, acrolein [107-02-8] is formed by the catalytic oxidation of propylene vapor at high temperature in the presence of steam. The acrolein intermediate is then oxidized to acrylic acid [79-10-7].

Table 4. Physical Properties of Acrylic Monomers

Acrylate	CAS registry number	Molecular weight	Bp, °C ^a	d^{25}_4 , g/cm ³	Flash point, °C ^b	Water solubility, g/100 g H ₂ O	Heat of evaporation, J/g ^c	Specific heat, J/g·K ^e
Methyl	[96-33-3]	86	79–81	0.950	10	5	385	2.01
Ethyl	[140-88-5]	100	99–100	0.917	10	1.5	347	1.97
<i>n</i> -Butyl	[141-32-2]	128	144–149	0.894	39	0.2	192	1.92
Isobutyl	[106-63-8]	128	61–63 ^d	0.884	42	0.2	297	1.92
<i>t</i> -Butyl	[1663-39-4]	128	120	0.879	19	0.2		
2-Ethylhexyl	[103-11-7]	184	214–220	0.880	90 ^e	0.01	255	1.92

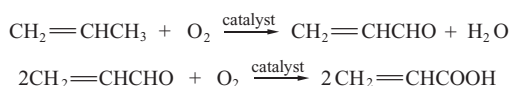
^aAt 101.3 kPa unless otherwise noted.

^bTag open cup unless otherwise noted.

^cTo convert J to cal, divide by 4.184.

^dAt 6.7 kPa = 50 mm Hg.

^eCleveland open cup.



Once the acrylic acid has been formed, the various acrylic ester monomers are synthesized by esterification of acrylic acid with the appropriate alcohol (63–66).

These monomers are then prevented from highly exothermic and hazardous autopolymerization processes during shipping and storage by the addition of a chemical inhibitor. The most common inhibitors currently used are hydroquinone [123-31-9], the methyl ether of hydroquinone (MEHQ) [150-76-5], and 4-hydroxy TEMPO [2226-96-2]. 4-Hydroxy TEMPO, unlike the quinone inhibitors, does not require the presence of oxygen in order to be effective. Chemical inhibitors are only added at the <100 ppm level and are not typically removed prior to their commercial use. Finally, copper and its alloys can also function as initiators and should, therefore, be avoided when constructing a reactor for purposes of producing acrylic ester (co)polymers (67). With no inhibitor added, the monomers must be stored at temperatures below 10°C for no longer than a few weeks. Failure to exercise these precautions can result in violent, uncontrolled, and potentially deadly polymerizations.

Common acrylic ester monomers are combustible liquids. Commercial acrylic monomers are shipped with DOT (Department of Transportation) red labels in bulk quantities, tank cars, or tank trucks. Mild steel is the usual material of choice for the construction of bulk storage facilities for acrylic monomers; moisture is excluded to avoid rusting of the storage tanks and contamination of the monomers.

A variety of methods are available for determining the purity of monomers by the measurement of their saponification equivalent and bromine number, specific gravity, refractive index, and color (68–70). Minor components are determined by iodimetry or colorimetry for hydroquinone or MEHQ, Karl–Fisher method for water content, and turbidimetry for measuring trace levels of polymer. Gas–liquid chromatography is useful in both the general measurement of monomer purity as well as the identification of minor species within a monomer solution.

Although toxicities for acrylic ester monomers range from slight to moderate, they can be handled safely and without difficulty by trained personnel, provided that the proper safety instructions are followed (67,71). Table 5 contains animal toxicity data for common acrylic ester monomers under acute toxicity conditions.

Because of their higher vapor pressures, liquid methyl and ethyl acrylate are the two most potentially harmful acrylic ester monomers. Threshold limit values (TLV) for long-term low level exposures to these monomers in industrial situations have been established by OSHA (Table 5). Local regulations and classifications sometimes apply, however, to these monomers. Ethyl acrylate, for example, has been labeled a known carcinogen by the State of California (71).

Table 5. Toxicities of Acrylic Monomers

Monomer	Acute oral LD ₅₀ (rats), mg/kg	Acute precutaneous LD ₅₀ (rabbits), mg/kg	Inhalation	
			LC ₅₀ (rats), (rats), mg/L	TLV, ppm
Methyl acrylate	277	1243	5.7	2
Ethyl acrylate	800	1800	7.4	5
Butyl acrylate	900	1780	5.3	2

Table 6. Polymerization Data for Acrylic Ester Monomers in Solution^a

Acrylate	Concentration, solvent	<i>k</i> _{sp} , L/mol·h ^b	Heat, kJ/mol ^c	Shrinkage, vol%
Methyl	3 <i>M</i> , Methyl propionate	250	78.7	24.8
Ethyl	3 <i>M</i> , Benzene	313	77.8	20.6
Butyl	1.5 <i>M</i> , Toluene	324	77.4	15.7

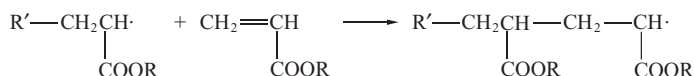
^aRef. (76).^bAt 44.1°C.^cTo convert kJ to kcal, divide by 4.184.

Radical Polymerization

Free-radical initiators such as persulfates, azo compounds, peroxides, or hydroperoxides are commonly used to initiate the polymerization of acrylic ester monomers. Photochemical (72–74) and radiation-initiated (75) polymerization are also possible. At constant temperature, the initial rate of polymerization is first order in monomer and one-half order in initiator. Rate data for the homopolymerization of several common acrylic ester monomers initiated by 2,2'-azobisisobutyronitrile (AIBN) [78-67-1] have been determined and are contained in Table 6. Also included in this table are heats of polymerization and volume shrinkage data (76).

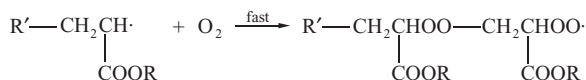
The polymerization of both acrylic and methacrylic ester monomers is accompanied by the release of a large quantity of heat as well as a substantial decrease in sample volume. Commercial processes must account for both these phenomena. Excess heat must be removed from industrial reactors by the use of high surface area heat exchangers. As for the shrinkage issue, the percent shrinkage encountered upon polymerization of the monomer is, in general, inversely proportional to the length of the monomer side chain. Mole for mole, the shrinkage amount is relatively constant (77).

The free-radical polymerization of acrylic monomers takes place through the classical stepwise chain-growth mechanism, which is described as the head-to-tail addition of individual monomer units through attack of the monomer double bond and formation of a single bond between the newly incorporated monomer units.

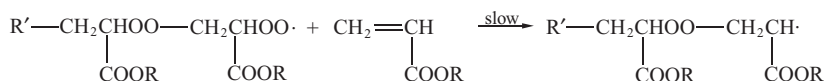


This stepwise growth continues until either termination or chain transfer of the radical chain end takes place. Termination can occur by combination or disproportionation, depending on the conditions of the polymerization (78,79).

The addition step typically takes place as a head-to-tail process although head-to-head addition has been observed as well (80). Oxygen has a strong inhibitory effect on the rate of polymerization of acrylic ester polymers. Oxygen is, therefore, excluded from commercial reactors primarily through the use of positive nitrogen flow. The nature of the oxygen inhibition is known: an alternating copolymer can be formed between oxygen and acrylic ester monomers (81,82).



The stabilized oxygen chain end is relatively unreactive when compared to the acrylic chain end and reduces the overall rate of polymerization. Additionally, the peroxy radical undergoes a faster rate of termination than the standard acrylic-based radical:



One will observe a drop in overall reaction rate, a change in polymer composition and properties, as well as a decrease in polymer molecular weight if oxygen is not excluded from a reactor when polymerizing acrylic ester monomers (83).

The wide variety of acrylic ester monomers dictates that a wide variety of homopolymers with radically different properties are accessible. An even wider variety of polymers can be formed through the copolymerization of two or more acrylic ester monomers (84,85).

Acrylic ester monomers are, in general, readily copolymerized with other acrylic and vinylic monomers. Table 7 presents data for the free-radical copolymerization of a variety of monomers 1:1 with acrylic ester monomers. These numbers are calculated through the use of reactivity ratios:

$$\begin{aligned} r_1 &= k_{11}/k_{12} \\ r_2 &= k_{22}/k_{21} \end{aligned}$$

For a binary copolymer, the smaller reactivity ratio is divided by the larger r value and multiplied by 100. Values greater than 25 indicate that copolymerization proceeds smoothly; low values for the ease of copolymerization can be helped through the adjustment of comonomer composition as well as the monomer addition method (86).

A growing chain with monomer 1 as the chain-end radical has a rate constant for self-addition of k_{11} ; the rate for addition of monomer 2 is k_{12} . The self-addition rate for a terminal monomer 2 radical is given as k_{22} ; the rate for addition of monomer 1 is k_{21} . The reactivity ratios can also be calculated from the Price-Alfrey measures (87) of resonance stabilization (Q) and polarity (e)

Table 7. Relative Ease of Copolymer Formation for 1:1 Ratios of Acrylic and Other Monomers, $\frac{r(\text{smaller})}{r(\text{larger})} \times 100$

Monomer 2	CAS registry number	Monomer 1		
		Methyl acrylate	Ethyl acrylate	Butyl acrylate
Acrylonitrile	[107-13-1]	53	46	74
Butadiene	[106-99-0]	66	4.7	8.1
Methyl methacrylate	[80-62-6]	50.3	30.6	14.6
Styrene	[100-42-5]	21	16	26
Vinyl chloride	[75-01-4]	2.7	2.1	1.6
Vinylidene chloride	[75-35-4]	100	52	55
Vinyl acetate	[108-05-4]	1.1	0.7	0.6

Table 8. *Q* and *e* Values for Acrylic Monomers^a

Monomer	<i>Q</i>	<i>e</i>
Methyl acrylate	0.44	+0.60
Ethyl acrylate	0.41	+0.46
Butyl acrylate	0.30	+0.74
Isobutyl acrylate	0.41	+0.34
2-Ethylhexyl acrylate	0.14	+0.90

^aRef. (88).

which are shown for common acrylic esters in Table 8. NMR can also be used to determine the composition distribution characteristics of acrylic copolymers (88,89).

In addition to the standard side-chain variation discussed above, special functionality can be added to acrylic ester monomers by use of the appropriate functional alcohol. Through the use of small levels of functional monomers, one can allow an acrylic ester polymer to react with metal ions, cross-linkers, or other types of resins. Table 9 contains information on some of the more common functional monomers.

Bulk Polymerization

Bulk polymerizations of acrylic ester monomers are characterized by the rapid formation of an insoluble network of polymers at low conversion with a concomitant rapid increase in reaction viscosity (90,91). These properties are thought to come from the chain transfer of the active radical via hydrogen abstraction from the polymer backbone. When two of these backbone radical sites propagate toward one another and terminate, a crosslink is formed (91).

Table 9. Functional Monomers for Copolymerization with Acrylic Monomers

Monomer	Structure	CAS registry number	Molecular formula
<i>Carboxyl</i>			
Methacrylic acid	$\text{CH}_2=\text{C}(\text{COOH})\text{CH}_3$	[79-41-4]	$\text{C}_4\text{H}_6\text{O}_2$
Acrylic acid	$\text{CH}_2=\text{CHCOOH}$	[79-10-7]	$\text{C}_3\text{H}_4\text{O}_2$
Itaconic acid	$\text{CH}_2=\text{C}(\text{COOH})\text{CH}_2\text{COOH}$	[97-65-4]	$\text{C}_5\text{H}_6\text{O}_4$
<i>Amino</i>			
<i>t</i> -Butylaminoethyl methacrylate	$\text{CH}_2=\text{C}(\text{COO}(\text{CH}_2)_2\text{NHC}(\text{CH}_3)_3)\text{CH}_3$	[24171-27-5]	$\text{C}_{10}\text{H}_{19}\text{NO}_2$
Dimethylaminoethyl methacrylate	$\text{CH}_2=\text{C}(\text{COO}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2)\text{CH}_3$	[2867-47-2]	$\text{C}_8\text{H}_{15}\text{NO}_2$
<i>Hydroxyl</i>			
2-Hydroxyethyl methacrylate	$\text{CH}_2=\text{C}(\text{COOCH}_2\text{CH}_2\text{OH})\text{CH}_3$	[868-77-9]	$\text{C}_6\text{H}_{10}\text{O}_3$
2-Hydroxyethyl acrylate	$\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{OH}$	[818-61-1]	$\text{C}_5\text{H}_8\text{O}_3$
<i>N</i> -Hydroxymethyl acrylamide	$\text{CH}_2=\text{CHCONHCH}_2\text{OH}$	[924-42-5]	$\text{C}_4\text{H}_7\text{NO}_2$
<i>N</i> -Hydroxymethyl methacrylamide	$\text{CH}_2=\text{C}(\text{CONHCH}_2\text{OH})\text{CH}_3$	[923-02-4]	$\text{C}_5\text{H}_9\text{NO}_2$
<i>Oxirane</i>			
Glycidyl methacrylate	$\text{CH}_2=\text{C}(\text{COOCH}_2\text{CH}(\text{O})\text{CH}_2)\text{CH}_3$	[106-91-2]	$\text{C}_7\text{H}_{10}\text{O}_3$
<i>Multifunctional</i>			
1,4-Butylene dimethacrylate	$(\text{CH}_2=\text{C}(\text{COOCH}_2)_2)_2$	[2082-81-7]	$\text{C}_{12}\text{H}_{18}\text{O}_4$

Solution Polymerization

Of far greater commercial value than that of simple bulk polymerizations, solution polymerizations employ a co-solvent to aid in minimizing reaction viscosity as well as controlling polymer molecular weight and architecture. Lower polyacrylates are, in general, soluble in aromatic hydrocarbons, esters, ketones, and chlorohydrocarbons. Solubilities in aliphatic hydrocarbons, ethers, and alcohols are somewhat lower. As one moves to longer alcohol side-chain lengths, acrylics become insoluble in oxygenated organic solvents and soluble in aliphatic and aromatic hydrocarbons and chlorohydrocarbons. Solvent choices for acrylic

Table 10. Chain-Transfer Constants to Common Solvents for Poly(ethyl acrylate)^a

Solvent	$C_s \times 10^5$
Benzene	5.2
Toluene	26.0
Isopropyl alcohol	260
Isobutyl alcohol	46.5
Chloroform	14.9
Carbon tetrachloride	15.5

^aRefs. (79), (92), and (93).

solution polymerizations are made on the basis of cost, toxicity, flammability, volatility, and chain-transfer activity. The chain-transfer constants (C_s) for a variety of solvents in the solution polymerization of poly(ethyl acrylate) are shown in Table 10.

Initiators serve the dual role of beginning the polymerization of an individual chain as well as controlling the molecular weight distribution of a polymer sample. Initiators are chosen based on their solubility, thermal stability (rate of decomposition), and the end use for the polymer. Additionally, initiators can be used to control polymer architecture by crosslinking control; this property also allows initiators to serve a role in the regulation of molecular weight distribution. Levels of usage vary from hundredths of a percent to several percent by weight on the polymer formed. The types of initiators most commonly employed in solution polymerizations are organic peroxides, hydroperoxides, and azo compounds.

Molecular weight control can also be achieved through the use of a chain-transfer agent. The most commonly used species in this class are chlorinated aliphatic compounds and thiols (94). The chain-transfer constants (C_s at 60°C) for some of these compounds in the formation of poly(methyl acrylate) are as follows (87): Carbon tetrabromide, 0.41; Ethanethiol, 1.57; and Butanethiol, 1.69.

Because of the volatile nature of the monomers used and high temperatures often employed, solution polymerizations are typically performed in reactors which can withstand pressures of at least 446 kPa (65 psi). Standard materials of construction include stainless steel (which may be glass-lined) or nickel. Anchor-type agitators are used for solution polymerizations with viscosities up to 1.0 Pa·s (1000 cP), but when viscosity levels move above this range, a slow ribbon-type agitator is used to sweep material away from the reactor walls. Improper agitation can result in the severe fouling of a reactor. Most industrial reactors are jacketed for steam heating and/or water cooling of a batch and contain a rupture disk to relieve pressure buildup. Additionally, there are numerous inlets in a typical industrial reactor as well as a thermocouple for monitoring temperature. A valve is placed in the bottom of the reactor to release polymerized material to storage containers.

Cooling within a reactor is typically provided by a reflux condenser. Since polymerization is a highly exothermic process, temperature control is a safety concern as well as a product integrity issue. Temperature control is primarily obtained through the gradual addition of monomers into the reactor by gravity

from storage containers close to the reactor. In this manner, the rate of monomer addition and reaction can be matched to the cooling capacity of the reactor so that temperatures remain relatively constant throughout the polymerization. If these measures fail to control the temperature of a particular batch, a chemical inhibitor, such as a hydroquinone, can be added to slow the rate of polymerization.

Oxygen can serve as an inhibitor of polymerization. Reactors typically maintain a blanket of nitrogen over the entire reactor kettle. In polymerizations with temperatures below reflux, nitrogen is used to purge the reaction solution; a nitrogen blanket is then placed over the reactor prior to the addition of the initiator. Total cycle times for solution polymerizations run in the range of 24 h (95).

A typical solution polymerization recipe is shown below:

Composition	Parts
Reactor charge	
Ethyl acetate	61.4
Benzoyl peroxide	0.1
Monomer charge	
Ethyl acrylate	36.5
Acrylic acid	2.0

This copolymer has an overall composition of 94.8% ethyl acrylate/5.2% acrylic acid with the monomer charged at a level of 39 wt% in a solution of ethyl acetate. Initially, the solvent and initiator, benzoyl peroxide in this case, are added to the reactor and heated to reflux (80°C). Forty percent of the monomer mixture is added to the reactor in one charge. Then, four equal aliquots of monomer are added 24, 50, 79, and 110 min after the initial charge. Reflux is maintained within the reactor overnight to ensure complete reaction; the product is then cooled and packaged the next morning (96).

Storage and handling equipment are typically made from steel. In order to prevent corrosion and the transfer of rust to product, moisture is typically excluded from solution polymer handling and storage systems (97). Because of the temperature-sensitive nature of the viscosity of solution polymers, the temperature of the storage tanks and transfer lines is regulated either through prudent location of these facilities or through the use of insulation, heating, and cooling equipment.

Emulsion Polymerization

Emulsion polymerization is the most industrially important method of polymerizing acrylic ester monomers (98,99). The principal ingredients within this type of polymerization are water, monomer, surfactant, and water-soluble initiator. Products generated by emulsion polymerization find usage as coatings or binders in paints, paper, adhesives, textile, floor care, and leather goods markets. Because of their film-forming properties at room temperature, most commercial acrylic

ester polymers are copolymers of ethyl acrylate and butyl acrylate with methyl methacrylate.

Lower acrylates are capable of polymerizing in water in the presence of an emulsifier and a water-soluble initiator. The polymeric product is typically a milky-white dispersion of polymer in water at a polymer solids content of 30–60%. Particle sizes for these latices fall in the range of 0.1–1.0 μm . Because of the compartmentalized nature of the process (99), high molecular weights are obtained in most emulsion polymerizations without the resulting viscosity build encountered with solution polymerizations. Additionally, the use of water as a dispersion medium provides attractive safety, environmental, and heat removal benefits when compared to other methods of polymerizing acrylic ester monomers. The emulsion polymerization of the higher (relatively water insoluble) acrylates can even be accomplished now through the use of a novel method for catalytically transferring monomer from droplets to the growing polymer particles (100).

The types of surfactants used in an emulsion polymerization span the entire range of anionic, cationic, and nonionic species. The most commonly used soaps are alkyl sulfates such as sodium lauryl sulfate [151-21-3], alkylaryl sulfates such as sodium dodecyl benzene sulfonate [25155-30-0], and alkyl or aryl polyoxyethylene nonionic surfactants (87,101–104). Product stability and particle size control are the driving forces which determine the type of surfactants employed; mixtures of nonionic and anionic surfactants are commonly used to achieve these goals (105–108).

Water-soluble peroxides, such as sodium or ammonium persulfate, are commonly used in the industrial arena. The thermal dissociation of this initiator (109) results in the formation of sulfate radicals which initiate polymer chains in the aqueous phase. It is possible to use other oxidants, such as hydrogen peroxide [7722-84-1] or persulfates in the presence of reducing agents and/or polyvalent metal ions (87). In this manner, a redox initiator system is formed which allows the experimenter to initiate polymer chains over a much broader range of temperatures (25–90°C) than simple thermal initiation (75–90°C) (110). The primary disadvantage of this initiation method is that a greater level of salt impurities are introduced to the reactor which could, perhaps, adversely influence final polymer properties such as stability.

Emulsion polymerization batches on the industrial scale are typically run in either stainless steel or glass-lined steel reactors which can safely handle internal pressures of 446 kPa (65 psi). Agitation within the reactors is controlled by use of a variable speed stirring shaft coupled at times with a baffling system within the reactor to improve mixing. Care must be taken to avoid excessive mixing forces being placed on the latex as coagulum will form under extreme conditions. Temperature control of batches is maintained through the use of either steam or cold water jacketing. Multiple feed lines are necessary to provide for the addition of multiple streams of reactants such as initiators, monomer emulsions, inhibitors if necessary, and cooling water. Monitoring equipment for batches typically consists of thermocouples, manometers, sightglasses, as well as an emergency stack with a rupture disk in case of pressure buildup within the reactor. A typical industrial emulsion polymerization plant is shown in Figure 2.

There are numerous examples of typical industrial emulsion polymerization recipes available in the open literature (111,112). A process for the

synthesis of a polymer with a 50% methyl methacrylate, 49% butyl acrylate, and 1% methacrylic acid terpolymer at a solids content of 45% is described below:

Charge	Parts
Monomer emulsion charge	
Deionized water	13.65
Sodium lauryl sulfate	0.11
Methyl methacrylate	22.50
Butyl acrylate	22.05
Methacrylic acid	0.45
Initiator charge	
Ammonium persulfate	0.23
Reactor charge	
Deionized water	30.90
Sodium lauryl sulfate	0.11

The monomer emulsion is first formed in a separate agitation tank by combination of the water, soap, and monomer with a proper level of mixing. Care must be taken to avoid excessive levels of agitation in the monomer emulsion tank to avoid incorporating air into the emulsion. The reactor water is heated under a nitrogen blanket to a temperature of at least 75°C prior to the addition of the initiator. Following the addition of the initiator, the monomer emulsion is fed into the reactor over the course of approximately 2.5 h. Temperature control is maintained during this time through both control of the monomer feed rate as well as use of the reactor jacket heating/cooling system. After the monomer emulsion feed is completed, the temperature is held above 75°C for at least 30 min to reduce the level of residual standing monomer within the system. The product is then cooled, filtered, and packaged.

Once packaged, the storage of acrylic latices is a nontrivial matter; problems commonly encountered with these polymer colloids include skinning (surface film formation), sedimentation, grit formation within the latex, formation of coagulum on storage container walls, and sponging (aerogel formation). Exposure of the material to extremes in temperature is avoided through prudent location of these facilities or the use of insulation, heating, and cooling equipment. Acrylic emulsion polymers, like many other types of polymers, are subject to bacterial attack. Proper adjustment of pH, addition of bactericides, and good housekeeping practices (95) can alleviate the problems associated with bacterial growth. Some advances in the industrial application of emulsion polymerization have been described in the open literature (113).

Suspension Polymerization

Suspension polymers of acrylic esters are industrially used as molding powders and ion-exchange resins. In this type of polymerization, monomers are dispersed as 0.1- to 5-mm droplets in water and are stabilized by protective colloids or suspending agents. In contrast to emulsion polymerization, initiation is

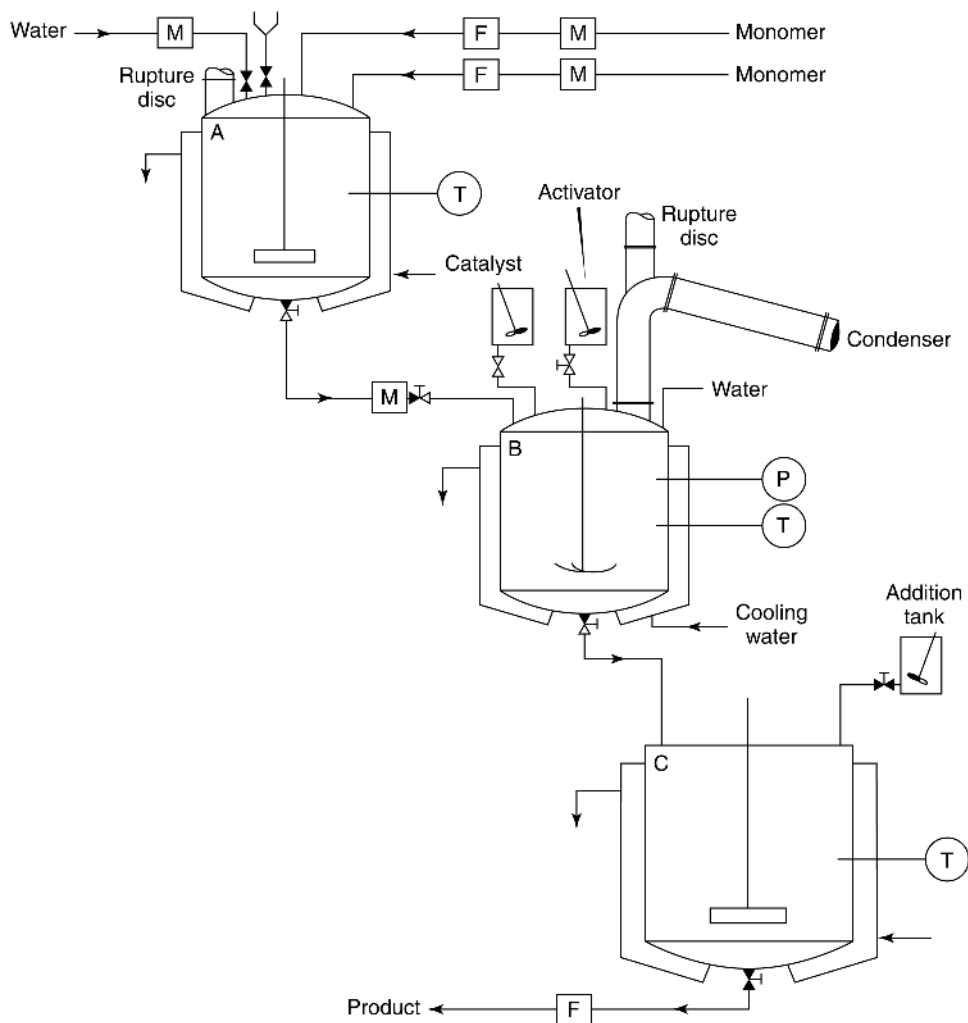


Fig. 2. Emulsion polymerization plant. A, Emulsion feed tank; B, polymerization reactor; C, drumming tank; F, filter; M, meter; P, pressure gauge; T, temperature indication.

accomplished by means of a monomer-soluble agent and occurs within the suspended monomer droplet. Water serves the same dual purpose as in emulsion (heat removal and polymer dispersion). The particle size of the final material is adjusted through the control of agitation levels as well as the nature and level of the suspending agent. Once formed, the 0.1- to 5-mm polymer beads can be isolated through centrifugation or filtration.

The most commonly used suspending agents are cellulose derivatives, polyacrylate salts, starch, poly(vinyl alcohol), gelatin, talc, and clay derivatives (95). The important function these agents must serve is to prevent the coalescence of monomer droplets during the course of the polymerization (114). Thickeners can also be added to improve suspension quality (95). Other additives such as

lauryl alcohol, stearyl acid or cetyl alcohol lubricants and di- or trivinyl benzene, diallyl esters of dibasic acids, and glycol dimethacrylates cross-linkers are used to improve bead uniformity and bead performance properties.

Unlike emulsion polymerization, the initiators employed in suspension polymerization must not be water-soluble; organic peroxides and azo species are most commonly used. In similar fashion to bulk polymerization, the level of initiator used directly influences the molecular weight of the product (95,115,116). Developments in the method of suspension polymerization have been reviewed in the open literature (117,118).

Graft Copolymerization

Polymer chains can be attached to a preexisting polymer backbone of a similar or completely different composition to form what is termed a graft copolymer. Acrylic branches can be added to either synthetic (119,120) or natural (121–124) backbones. Attachment of graft polymer branches to preformed backbones is accomplished by chemical (125–127), photochemical (128,129), radiation (130), and mechanical (131) means. The presence of distinct compositions in this branched geometry often conveys properties which cannot otherwise be attained (132,133).

Living Polymerization

One of the most exciting areas currently in the radical polymerization of acrylic ester monomers is the field of living polymerization. Living polymers are defined in Reference 134 as “polymers that retain their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible.” Because of these properties, exceptional control can be exercised over the topology (ie, linear, comb), composition (ie, block, graft), and functional form (ie, telechelic, macromonomer) of these polymers (135).

Atom-transfer radical polymerization (ATRP), reversible addition fragmentation transfer (RAFT), and nitroxide-mediated (136–138) polymerization show promise in terms of the ability to fine tune polymer architecture using living radical methods. ATRP has been successfully used in the polymerization of methyl acrylate (139,140) as well as functional acrylates containing alcohol (141), epoxide (142), and vinyl groups (143) on the side chain. The main drawbacks to the ATRP method of creating acrylic ester homo- and copolymers are the relatively long reaction times and the high levels of metal-containing initiator required (see LIVING POLYMERIZATION, RADICAL).

Radiation-Induced Polymerization

Coatings can be formed through the application of high energy radiation to either monomer or oligomer mixtures. Ultraviolet curing is the most widely practiced method of radiation-based initiation (144–150); this method finds its main industrial applications in the areas of coatings, printing ink, and photoresists for

computer chip manufacturing. The main disadvantage of the method is that UV radiation is incapable of penetrating highly pigmented systems.

To form a film via this method, a mixture of pigment, monomer, polymer, photoinitiator, and inhibitor are applied to a substrate and polymerized by controlled exposure to UV radiation. Polymers used as co-curing agents often have unsaturated methacrylate functionalities attached; higher order acrylates are often used as the solvent in photocure mixtures.

In order to avoid the problems associated with more highly pigmented systems, electron beam curing is employed (151). This high energy form of radiation is capable of penetrating through the entire coating regardless of the coating's pigment loading level.

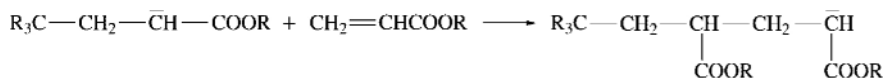
Anionic Polymerization

The anionic polymerization of acrylic ester monomers is accomplished by use of organometallic initiators in organic solvents. The main advantage to the use of anionic polymerization as opposed to other methods is its ability to generate stereoregular or block copolymers. Some examples of this type of polymerization include the anionic formation of poly(*t*-butyl acrylate) (152–155), poly(isopropyl acrylate) (156), and poly(isobutyl acrylate) (157,158). Solvent conditions primarily determine tacticity of the resulting polymer product with nonpolar solvents generating isotactic product and polar solvents resulting in the formation of syndiotactic polymers. The strikingly different physical properties and mechanistic discussions on the formation of these two different types of polymer have been described in the polymer literature (159–162).

The initiation step for anionic polymerizations takes place via a Michael reaction:



A subsequent polymer growth occurs by head-to-tail addition of monomer to the growing polymer chain.



Because of cost constraints and toxicity issues involved with the organometallic initiators, anionic polymerization is of limited commercial significance. Both the living methods described above as well as DuPont's group-transfer polymerization method (163–167) are seen as alternative ways to achieve the same level of control over polymer architecture as that of anionic polymerization. All these methods offer the promise of narrow and controllable molecular weight distributions as well as the ability to form block copolymers through the sequential addition of monomers. Additionally, all the methods suffer from slow overall reaction rates and the difficulty of removing the specialty initiators after polymer formation has created barriers to use.

Analytical Test Methods and Specifications

Emulsion Polymers. Current analytical methods allow for complete characterization of all crucial aspects of an acrylic latex (87). The main properties of interest are an acrylic latex's composition, percent solids content, viscosity, pH, particle size distribution (168,169), glass-transition temperature, minimum film-forming temperature (170), and surfactant type. In addition to these basic properties, the stability of a latex with respect to mechanical shear, freeze-thaw cycles, and sedimentation on standing for long periods of time are of interest in commercial products.

Solution Polymers. A solution polymer's composition, solids content, viscosity, molecular weight distribution, glass-transition temperature, and solvent are of interest. Standard methods allow for all of these properties to be readily determined (171,172).

Environmental Health and Safety Factors

Acrylic polymers are categorized as nontoxic and have been approved for food handling and packaging by the FDA. The main concerns with acrylic polymers deal with the levels of residual monomers and the presence of nonacrylic additives (primarily surfactants) which contribute to the overall toxicity of a material. As a result, some acrylic latex dispersions can be mild skin or eye irritants.

During the manufacture of an acrylic polymer, precautions are taken to maintain temperature control (173). In addition to these measures, polymerizations are run under conditions wherein the reactor is closed to the outside environment to prevent the release of monomer vapor into the local environment. As for final product properties, acrylic latices are classified as nonflammable substances and solution polymers are classified as flammable mixtures.

Uses

Because of their wide property range, clarity, and resistance to degradation by environmental forces, acrylic polymers are used in an astounding variety of applications that span the range from very soft pressure sensitive adhesives to rigid durable items.

Coatings. Acrylic ester latex polymers are used widely as high quality paint binders because of their excellent durability, toughness, optical clarity, UV stability, and color retention. These properties allow acrylics to find use as binder vehicles in all types of paints (76): interior and exterior; flats, semigloss, and gloss; as well as primers to topcoats. Although all-acrylic compositions are most favored in exterior applications because of their excellent durability (174), other types of copolymers such as vinyl-acrylics and styrene-acrylics benefit in terms of performance properties from the acrylic portion of their composition; methods of manufacturing acrylic-based paints have been described previously in the

literature (175). Acrylic emulsion polymers even find use in the protection of structural steel (176) (see COATING METHODS, SURVEY).

The industrial finishing area sees both acrylic emulsions as well as solution polymers utilized in a wide variety of applications including factory finished wood (177,178), metal furniture and containers (179), and can and coil coatings (180). In order to harden acrylic polymers for this type of demanding application, the polymers are often cross-linked with melamines, epoxies, and isocyanates. The coatings are applied via spraying, roll dipping, or curtain coating. Radiation curing using UV radiation or electron beam radiation (181–186), powder coating (187–190), electrode deposition of latices (191–193), and the use of higher solids level emulsions (194) represent newer methods for applying acrylic coatings to form industrial finishes. Excellent reviews on the use of water-based emulsions (195,196) and solution acrylics (197–199) can be found in the open literature (see COATINGS).

Hydrophobically modified acrylics are used extensively as thickening agents in the paints marketplace as well as the area of industrial finishes (200). Flow and leveling improvements are observed when changing a formulation from hydroxyethylcellulose to acrylic-based thickeners. Unlike cellulosic thickeners, the modified acrylics act through an associative thickening mechanism; they stabilize the dispersed polymer phase rather than thickening the aqueous phase of a polymer latex. The main type of modified acrylic of commercial value is termed a HASE (hydrophobically modified alkali-soluble emulsion). These acrylics compete with hydrophobically modified hydroxyethylcellulose and urethane based thickeners in the marketplace (201–203).

Textiles. Because of their durability, soft feel, and resistance to discoloration, acrylic emulsion polymers find a variety of uses in the textiles area including binders for fiberfill and nonwoven fabrics, textile bonding or laminating, flocking, back coating and pigment printing applications. *N*-Methylolacrylamide is often used as a self crosslinker in acrylic textile binders to improve washing and dry cleaning durability as well as overall binder strength (204).

Polyester (205–208), glass (209), and rayon (210) nonwoven and fiberfill mats have been manufactured using acrylic binders to hold the mats together. In this process, the acrylic emulsions are applied to a loose web or mat and are then heated to form a film at the fiber crossover points which maintains the structural integrity of the mat. The final products generated using this technology include quilting, clothing, disposable diapers, towels, filters, and roofing (see NONWOVEN FABRICS).

Acrylic polymers find use in applications that take advantage of their exceptional resistance to environmental assaults such as uv radiation, ozone, heat, water, dry cleaning, and aging (211). Acrylics are often used as the backing material for automotive and furniture upholstery to improve the dimensional handling properties, prevent pattern distortion, prevent unraveling, and minimize seam slippage. Strike-through problems are averted through the use of foamed or frothed acrylic coatings, which also yield a softer fabric and save on energy costs (212). Crushed acrylic latex foam are employed as backing materials for draperies. The foam protects the drapery from sun damage, mechanically stabilizes the fabric, improves drape, and gives a softer hand than conventional backing materials (213). Acrylics are also used as carpet-backings

and to bond fabric-to-fabric, fabric-to-foam, and fabric-to-nonwoven materials (214).

The flocking process begins with the bonding of cut fibers to an adhesive-coated fabric to obtain a decorative and functional material (215). Acrylics can provide the softness and durability that are sought in flocked textiles; they also serve as binders for pigments in the printing of flocked fabrics (35,216,217).

The feel, soil release properties, and permanent-press behavior of a fabric can be finely tuned using acrylic as finishing polymers. Copolymers of acrylics with acrylic or methacrylic acid can be used as thickeners for textile coating formulation.

Adhesives. Acrylic emulsion polymers are used in a wide variety of adhesives. Pressure-sensitive Adhesives, which typically have T_g values less than 20°C, are the main type of acrylic adhesive. Acrylic polymers and copolymers find use as PSAs in tapes, decals, and labels. Along with their aforementioned superior chemical resistance properties, acrylics possess an excellent balance of tack, peel, and shear properties which is crucial in the adhesives market (218,219). Other types of adhesives that employ acrylics include construction formulations and film-to-film laminates.

Paper. Because of their excellent cost-performance balance, acrylic-vinyl acetate copolymer emulsion binders have been used as pigment binders for coated paper and boards. These binders provide higher brightness, opacity, coating solids, and improved adhesion versus styrene-butadiene copolymers (220,221). Acrylics also find usage as paper saturants with properties that compare favorably to natural rubber, butadiene-acrylonitrile, and butadiene-styrene (222). Finally, acrylic emulsion polymers are utilized in starch-latex-pigmented coatings (223) as well as size-press (224) and beater addition (225) applications.

Photoresists. Through the amazing range of acrylic properties made possible through side chain and backbone modification, acrylics and methacrylics find use in the latest generations of positive and negative photoresists for integrated circuit manufacture. The introduction of 157 nm and 193 nm immersion lithography has encouraged the use of fluorinated acrylics and alicyclic acrylates (226,227) while the scission and solubilization properties of methacrylates such as pMMA has resulted in their use for positive electron beam photoresist applications (228).

Other Applications. The leather finishing area is a traditional stronghold of acrylic emulsion polymers. Acrylics are used throughout the entire process of pigskin leather production; the use of acrylics lends uniformity, break improvement, better durability, and surface resistance while preserving the natural appearance of the pigskin (229).

Acrylics are used in the manufacture of aqueous and solvent-based caulks and sealants (230,231). Elastomeric acrylics are used in mastics to prevent uv radiation and chemical damage to the underlying polyurethane foam. Acrylics also impart hailstone resistance as well as flexibility over a broad temperature range (232). The manufacturing process for poly(vinyl chloride) uses acrylics as processing aids and plate-out scavengers in calendered and blown films. Acrylics allow for the manufacture of thick, smooth calendered vinyl sheets through modification of the melt viscosity of the vinyl sheet polymer (233). In the agricultural area, thin layers of acrylic emulsions have been applied to citrus leaves and fruit

to control "Greasy Spot," a disease which causes leaf-spotting and eventually leaf loss (234). Acrylics have found a great deal of use in the floor polish area; a guide to formulating these coatings has been published (235).

Acrylic polymers have been used as alternatives to nitrile rubbers in some hydraulic and gasket applications because of their excellent heat-resistance properties (236,237). Ethylene-acrylate copolymers have been used as transmission seals, vibration dampeners, dust boots, and steering and suspension seals (238).

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ACRYLIC FIBERS

Introduction

The first reported synthesis of acrylonitrile [107-13-1] and polyacrylonitrile (PAN) [25014-41-9] was in the 1890s (1). The polymer received little attention for a number of years, until shortly before World War II, because there were no known solvents and the polymer decomposes before reaching its melting point. The first breakthrough in developing solvents for PAN occurred at I. G. Farben in Germany, where fibers made from the polymer were dissolved in aqueous solutions of quaternary ammonium compounds, such as benzyropyridinium chloride, or of metal salts, such as lithium bromide, ammonium thiocyanate, and zinc chloride (2). In the United States, DuPont discovered an organic solvent for PAN,

N,N-dimethylformamide (DMF) (3,4). The same solvent was discovered independently by I. G. Farben at about the same time (5) (see ACRYLONITRILE AND ACRYLONITRILE POLYMERS).

Using DMF as the spinning solvent, DuPont produced the first commercial acrylic fiber under the trade name Orlon® in 1950. Orlon® was spun using a “dry spinning” process at a plant in Camden SC. Shortly afterward, Chemstrand, a joint venture of Monsanto and American Viscose (now Solutia), introduced Acrilan® acrylic, produced using Monsanto polymer technology and American Viscose wet spinning technology with *N,N*-dimethylacetamide (DMAc) solvent. As is common with new technologies, both products got off to rocky starts, Orlon with poor dyeing performance, Acrilan with fibrillation, but by the late 1950s each had solved the initial problems and established viable markets.

Modacrylic fibers (defined in the United States as those with 35–85% by weight acrylonitrile units) can be dissolved by more conventional solvents, such as acetone, and so were earlier on the market. Union Carbide introduced the first flame-resistant modacrylic fiber in 1948 under the trade names Vinyon N and Dynel. Vinyon N was a continuous filament yarn; Dynel was the staple form. Both were based on 60% vinyl chloride – 40% acrylonitrile copolymer.

During the 1950s, at least 18 companies began production of acrylic fibers. Because acrylic fibers require a spinning solvent, and newly discovered solvents received patent protection, the range of technology used commercially is far greater for acrylics than for any other fiber. The most significant were American Cyanamid’s aqueous sodium thiocyanate wet spinning process, and Asahi’s nitric acid wet spinning process. In the 1950s and 1960s, world production was concentrated in western Europe, Japan, and the United States. By 1960, annual worldwide production had risen to over 100 million kilograms. Once staple processes were developed, acrylic fibers became a significant competitor in markets held primarily by woolen fibers. By 1963 the carpet and sweater markets accounted for almost 50% of the total acrylic production. In the 1970s, the growth rate in the United States and Western Europe decreased sharply. This was due to the maturing of the wool replacement market and loss of market to nylon in carpeting and to polyester in many apparel applications. In the 1970s there was rapid growth of acrylic fiber production capacity in Japan, eastern Europe, and developing countries. By 1981 an estimated overcapacity of approximately 21% had developed. The 1990s saw significant shrinkage of acrylic production in the United States as DuPont and Mann Industries (formerly Badische) exited the business. Significant change has continued into the new century. In 2002, Sterling (formerly Cytec) significantly reduced production of commodity acrylics at their Pace FL plant. These changes have left Solutia as the principal U.S. supplier. In Europe, the changes have been mainly swaps of ownership, with Acordis now having both the Courtaulds and Hoechst businesses, and Fraver, an Italian firm, taking over Bayer’s business. Aksa in Turkey, with the world’s largest acrylic fiber plant, has become an important supplier to Europe. Explosive industry growth has taken place in the Far East, particularly China, where plants based on DuPont and Sterling (Cytec) processes have proliferated. China now has 22% of world capacity, versus 9% 10 years earlier. Japan has reduced capacity, with Asahi Chemical being the latest to announce closure (March 2003) of their business. Modacrylics have all but disappeared from the marketplace, as demand

for flame-retardant textiles have been met by treated cotton or other synthetics at lower cost. A few new markets have emerged, such as carbon-fiber precursors and asbestos replacement fibers, but the volume is small compared to that of the markets lost. For acrylic producers, profit will continue to be sparse.

Physical Properties

Acrylic fibers are sold mainly as staple and tow. Staple lengths may vary from 25 to 150 mm, depending on the end use. Fiber fineness may vary from 1.0 to 22 dtex (0.9–20 dpf; dpf = denier per filament), 2.2 dtex (2.0 dpf), and 1.3 dtex (1.2 dpf) are the most common forms. Tow is sold as a bundle of up to 2.2 million kilotex (2.0 million total denier).

The fiber cross-section under microscopic examination is generally one of three shapes (Fig. 1)—round (wet spun, slow coagulation), bean (wet spun, fast coagulation), or dogbone-shaped (dry spun). It is also possible to produce acrylics with special shapes, such as ribbon or mushroom, by use of shaped or bicomponent spinnerettes. The cross-section may show particles such as TiO_2 added to reduce luster or other pigment to provide coloration. The surface of acrylic fibers is fibrillar, with the fibril size dependent on the spinning process (Fig. 2).

The physical properties of these fibers are compared with those of natural fibers and other synthetic fibers in Table 1.

The elastic properties of these fibers can be characterized as wool-like, with high elongation and elastic recovery. The tensile strength of acrylics and modacrylics is about the same, both considerably lower than that of other synthetics but higher than that of wool, of and about the same as that of cotton. These elastic properties rank acrylics and wool as compliant fibers, yielding fabric with a characteristically soft handle. Acrylics with tenacities as high as 80 cN/tex (9 gf/den) can be produced (8), but these are usually from higher molecular weight polymers, with low comonomer content and higher stretch orientation. Specialty products such as carbon-fiber precursor and cement-reinforcing fiber are produced using this technology.

The mechanical properties of acrylic fiber are deficient under hot-wet conditions. This is primarily due to the fact that the wet T_g of acrylonitrile copolymers is lower than the boiling point of water. Textile wet-processing must be carried out in such a way as to minimize yarn or fabric distortion. Shape retention and maintenance of original bulk under the lower temperatures in home laundering cycles are acceptable. Typical stress-strain curves for acrylic fiber in air and in wet conditions are shown in Figure 3.

Moisture regain, a property that has a great effect on wear comfort, at about 2%, is reasonably good though not as high as that of cotton (7%) or wool (14%). This property can be enhanced by adding hydrophilic comonomers or by generating a porous internal structure in the fiber. Dunova, an acrylic formerly marketed by Bayer, achieved moisture absorption and transport by internal porosity. The adequate regain plus their high compliancy make acrylics competitive in the wear-comfort markets. However, acrylics cannot match the wrinkle resistance and crease retention of polyester.

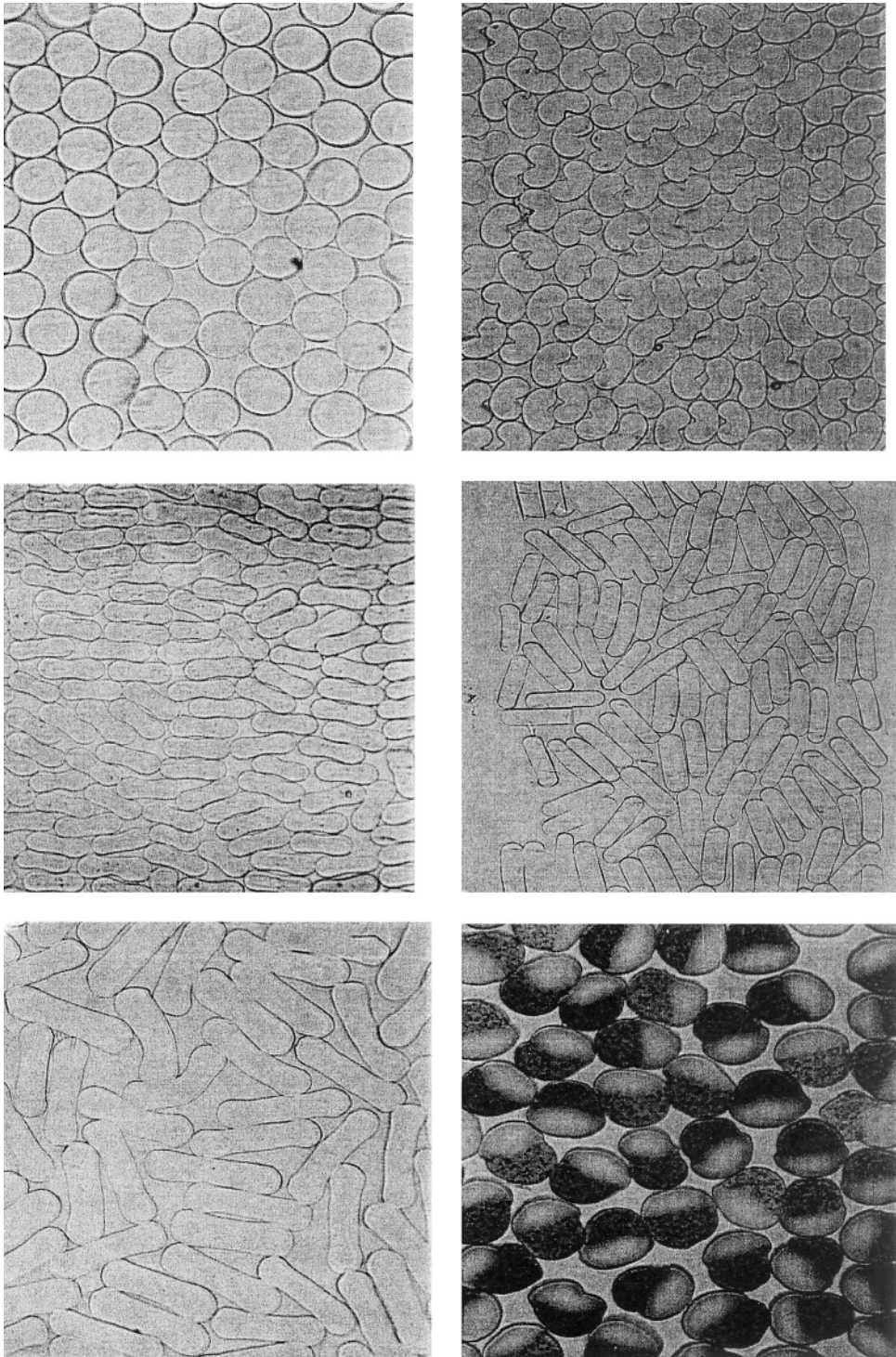
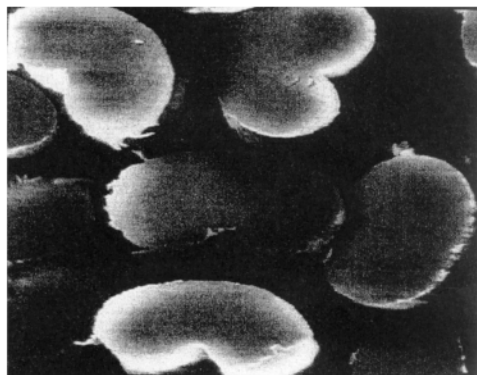
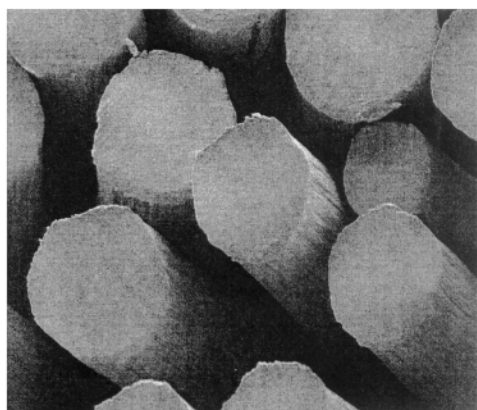
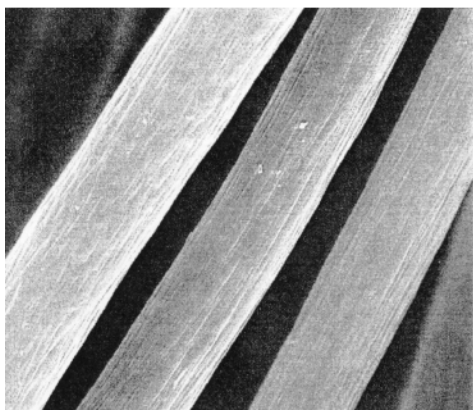


Fig. 1. Acrylic fiber cross sections (Scale: 1 mm = 10 μ m).

Organic solvent wet spun



Salt solvent wet spun



Organic solvent dry spun

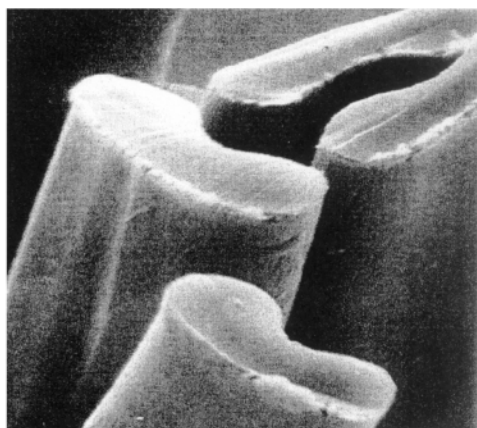
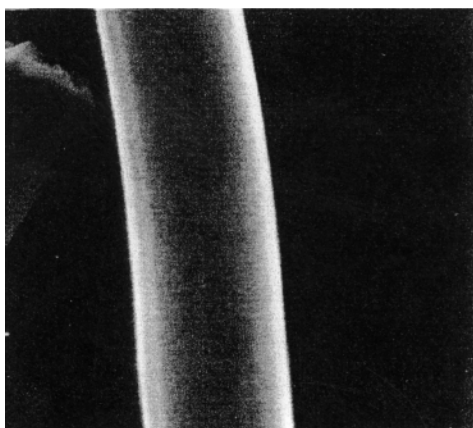


Fig. 2. Acrylic fiber structure comparisons (Scale: 1 mm = 0.5 μ m).

Table 1. Physical Properties of Staple Fibers^a

Property	Acrylic	Modacrylic	Nylon-6,6	Polyester	Polyolefin	Cotton	Wool
Specific gravity	1.14–1.19	1.28–1.37	1.14	1.38	0.90–1.0	1.54	1.28–1.32
Tenacity, N/tex ^b							
Dry	0.09–0.33	0.13–0.25	0.26–0.64	0.31–0.53	0.31–0.40	0.18–0.44	0.09–0.15
Wet	0.14–0.24	0.11–0.23	0.22–0.54	0.31–0.53	0.31–0.40	0.21–0.53	0.07–0.14
Loop/knot tenacity	0.09–0.3	0.11–0.19	0.33–0.52	0.11–0.50	0.27–0.35		
breaking elongation, %							
Dry	35–55	45–60	16–75	18–60	30–150	<10	25–35
Wet	40–60	45–65	18–78	18–60	30–150	25–50	
Average modulus, N/tex ^b	0.44–0.62	0.34	0.88–0.40	0.62–2.75	1.8–2.65		
dry elastic recovery, %							
2% stretch	99	99–100		67–86		74	99
10% stretch		95	99	57–74	96		
20% stretch							65
Electrical resistance	High	High	Very high	High	High	Low	Low
Static buildup	Moderate	Moderate	Very high	High	High	Low	Low
Flammability	Moderate	Low	Self-extinguishing	Moderate	Moderate	Spontaneous ignition at 360° C	Self-extinguishing
Limiting oxygen index	0.18	0.27	0.20	0.21		0.18	0.25
Char/melt	Melts	Melts	Melts, drips	Melts, drips	Melts	Chars	Chars
Resistance to sunlight	Excellent	Excellent	Poor; must be stabilized	Good	Poor; must be stabilized	Fair; degrades	Fair; degrades
Resistance to chemical attack	Excellent	Excellent	Good	Good	Excellent	Attacked by acids	Attacked by alkalis, oxidizing, and reducing agents
Abrasion resistance	Moderate	Moderate	Very good	Very good	Excellent	Good	Moderate
Index of birefringence	0.1		0.6	0.16			0.01
Moisture regain, 65% r.h, 21°C, %	1.5–2.5	1.5–3.5	4–5	0.1–0.2	0	7–8	13–15

^aRef. 7.

^bTo convert N/tex to gf/den, multiply by 11.3.

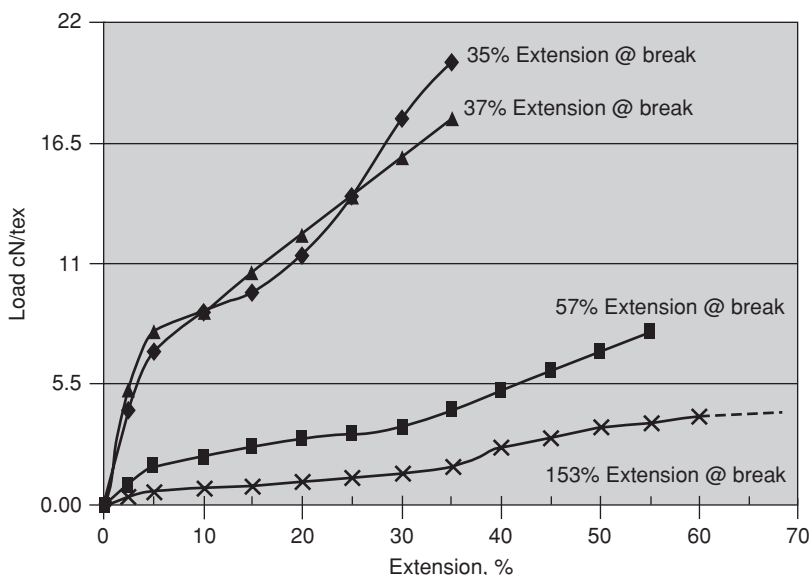


Fig. 3. Acrylic fiber stress-strain behavior at wet and dry conditions. —◆— 30°C dry; —■— 95°C dry; —▲— 25°C wet; —×— 90°C wet. To convert cN/tex to gf/den, multiply by 0.113.

Chemical Properties

Among the outstanding properties of acrylic fibers is their very strong resistance to sunlight. One study (9), found that the acrylic fibers resisted degradation eight times longer than olefin fibers, over five times longer than either cotton or wool, and almost four times longer than nylon. This property makes the acrylics particularly useful for outdoor applications, such as in awnings, tents, and sandbags, as well as for upholstery for autos and outdoor furniture. Pigmented acrylic or modacrylic fibers with lightfast colors are particularly useful for outdoor applications.

Acrylic fibers are also resistant to all biological and most chemical agents. Weak acids or bases, organic solvents, and oxidizing agents affect acrylics very little. They are attacked by strong bases and highly polar organic solvents such as DMAc, DMF, and DMSO (dimethyl sulfoxide). Acrylic fibers tend to be much more susceptible to chemical attack by alkali than by acid. For example, acrylic fibers are stable for up to 24 h at 100°C in 50% sulfuric acid; these same fibers begin degrading with <0.5% sodium hydroxide at the same exposure time and temperature (10).

In resistance of fibers to oxidizing agents, Orlon acrylic (a former DuPont product) was compared to cotton and acetate yarns (10). The acrylic yarn is far superior in strength retention. After 6 h of exposure to bleach, the cotton and acetate yarns had completely deteriorated, whereas the acrylic retained approximately 92% of its original strength.

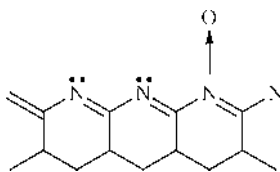


Fig. 4. Structure of air-oxidized PAN.

The excellent chemical resistance of acrylic fiber stems from its laterally bonded structure. Dipole bonds, formed between nitrile groups of adjacent chains, must be broken before chemical attack, melting, or solvation can occur. In addition, the repulsive forces between adjacent nitriles in one chain result in a very stiff polymer backbone, which yields very little entropy gain when the bonds between adjacent chains are broken in solvation or melting. Therefore, relatively high temperatures are required for solvation and melting.

Acrylic fibers discolor and decompose rather than melt when heated. The discoloration process involves formation of a ladder structure containing conjugated $C=N$ double bonds. Some color formation accompanies fiber production; commercial acrylics often contain low levels of blue dye or pigment to mask the yellow tinge. In comparison to polyester, acrylic fiber whiteness stability in sublimation dyeing is deficient; this limits acrylic utility in fleece and sheeting markets. Extensive heating in air leads to a color progression, ending in a black fiber having the structure shown in Figure 4. This product, termed Panox, is useful as a flame-resistant textile. Conversion of acrylic fiber to Panox is the first step in carbon fiber production.

Flammability. Most apparel uses either do not have any flammability standard, or only a modest one which serves to eliminate "torch" fabrics. More rigorous standards are applied for end uses such as carpet, children's sleepwear, drapery, and bedding. Fibers for these applications must be self-extinguishing after removal from the ignition source. Cotton, rayon, and acrylics burn with the formation of a char. The char acts as a wick that feeds additional fuel to the flame. Nylon and polyester meet some flammability tests by melting away from the ignition source. Modacrylics self-extinguish by generation of chlorine radicals, which interfere with the flame-propagation mechanism. This is generally achieved by incorporating vinylidene chloride or vinyl chloride comonomers. Blends of a char-forming fiber with a meltable one require incorporation of an active fire-retardant to meet any stringent flammability test (see FLAMMABILITY; FLAME RETARDANCY).

A measurement used to compare the flammability of textile fibers is the limiting oxygen index (LOI). This quantity describes the minimum oxygen content (%) in nitrogen necessary to sustain candle-like burning. Values of LOI, considered a measure of the intrinsic flammability of a fiber, are listed in Table 2 in order of decreasing flammability.

Table 2. Limiting Oxygen Index of Textile Fibers^a in Order of Decreasing Flammability

Fiber	LOI	Ignition temperature, °C
Cotton	18.0	400
Acrylic	18.2	560
Rayon	19.7	420
Nylon	20.1	530
Polyester	21.0	450
Wool	25.0	600
Modacrylic	27.0	690
Verel modacrylic	33.0	Self-extinguishing
100% PVC	37.0	Self-extinguishing

^aRef. 11.

Polymer Analysis

Many techniques are available for characterizing acrylic and modacrylic materials in order to establish the dyesite content, molecular weight, and chemical composition. The dye-site content of the polymer may be determined by dyeing a polymer suspension with a cationic dye of known molecular weight. The dye attached to the polymer dye sites may be measured directly or by difference. The dye sites themselves, in most acrylics and modacrylics, are sulfonate and sulfate end groups derived from the free-radical initiator used in polymerization. Therefore, the dye site content of the polymer can be measured by potentiometric titration of the strong acid groups or by determining the sulfur content of the polymer. The low levels of sulfur normally required for fiber dyeability can be measured accurately by X-ray fluorescence. Some acrylics have added "dye receptors"—acidic monomers such as sodium *p*-vinylbenzene sulfonate (SSS) or itaconic acid (IA). This sulfonate can be determined directly using ultraviolet spectroscopy. Sulfur analysis will yield a total dye-site value including the end groups and the SSS. Potentiometric titration of a polymer containing IA will yield two breaks, one for the sulfonate/sulfate end groups, and a second for one of the IA carboxyls. Dyeing of polymers containing weak-acid dye receptors such as IA does not give an accurate value for total sites, as the dyeing of the IA is incomplete.

The weight-average molecular weight of the polymer can be measured using gel-permeation chromatography with low-angle-light-scattering detection (see CHROMATOGRAPHY, SIZE EXCLUSION). Solvent systems such as DMF–LiCl are employed to eliminate ionic effects (12). Osmometry may be used to obtain number-average molecular weight (13). These methods are useful to provide absolute values and to determine changes in molecular-weight distribution. However, methods based on solution viscosity are the most popular in commercial practice. The simplest method is to measure the viscosity of a solution of the polymer at a specified concentration and temperature. This may be done using a capillary viscometer. For quality assurance purposes, usually a single point ("specific viscosity") determination is sufficient. The viscosity-average molecular weight may be obtained by extrapolating specific viscosities at several concentrations to zero concentration. The intrinsic viscosity thus derived is then used in the Staudinger

equation (14) or Cleland–Stockmayer equation (15) to give the viscosity-average molecular weight (see MOLECULAR WEIGHT DETERMINATION).

Typical acrylic polymers have number-average molecular weights in the 30,000–40,000 range, or roughly 700 repeat units. The weight-average molecular weight is typically in the range 90,000–120,000, with a polydispersity index (M_w/M_n) between 2.0 and 3.5. Fiber producers favor the lowest molecular weight and broadest distribution that is consistent with acceptable fiber physical properties, as that will result in the highest number of sulfate and sulfonate dye sites.

Analytical methods for identifying and quantifying the chemical composition of acrylic and modacrylic materials are numerous. The usual comonomers found in acrylics—vinyl acetate, methyl acrylate, and methyl methacrylate—can be identified using NMR. They may be quantified using infrared (IR) spectroscopy by the absorbance of the carbonyl group; calibration of the method is sometimes accomplished by preparation of C^{14} tagged polymer standards. Sulfonated monomers, such as SSS or sodium *p*-(sulfophenyl) methallyl ether, can be detected by strong ultraviolet absorbance due to the phenyl group. Halogen monomers can be quantitatively measured by pyrolyzing the polymer and analyzing the pyrolysis products by halide titration. X-ray fluorescence may also be used to determine the concentration of specific halogens. Comonomer content may also be quantified by differential scanning calorimetry of a water–polymer slurry. The mole fraction of comonomer depresses the melting point linearly (16).

Fiber Characterization

To establish whether a fiber or fabric is acrylic or a blend containing acrylic, a portion should be separated into the individual filaments and introduced in a density gradient column [ASTM DI505-8ST (density gradient)]. Acrylic fibers have a density of 1.17 ± 0.01 . An IR scan of a KBr pellet of ground fiber can be used to identify the presence of nitrile groups. It is more difficult to establish the fiber supplier. A library of cross sections, known comonomer type, and other specific information is required. Since many producers now use almost identical technology, it may not be possible to achieve positive identification unless the fiber contains a marker.

In addition to characterizing the properties introduced by the choice of comonomers and the polymerization process itself, further characterization is required to describe the properties imparted by spinning and subsequent downstream processing. These properties relate to the order and microstructure of the fibers, and the resultant performance characteristics, such as crimp retention, abrasion resistance, and mechanical properties. Mechanical testing, to determine breaking elongation, tenacity, and modulus of elasticity, is carried out using devices such as the Instron. Dry-heat shrinkage and shrinkage in boiling water are measured by determining the difference in the length of a section of fiber after treatment at specified conditions. Other properties important to ease of processing or the end use include finish level, crimp frequency and amplitude, whiteness, and dyeing rate.

Acrylonitrile Polymerization

Virtually all acrylic fibers are made from acrylonitrile combined with at least one other monomer. The comonomers most commonly used are neutral comonomers, such as methyl acrylate [96-33-3] and vinyl acetate [108-05-4] to increase the solubility of the polymer in spinning solvents, modify the fiber morphology, and improve the rate of diffusion of dyes into the fiber. Sulfonated monomers, such as sodium *p*-(vinylbenzene)sulfonate [27457-28-9] (SSS), sodium methallyl sulfonate [1561-92-8] (SMAS), and sodium *p*-(sulfophenyl) methallyl ether [1208-67-9] (SPME) are used to provide additional dye sites or to provide a hydrophilic component in water-reversible-crimp bicomponent fibers. Halogenated monomers, usually vinylidene chloride [75-35-4] or vinyl chloride [75-01-4], impart flame resistance to fibers used in the home furnishings, awning, and sleepwear markets.

Polymerization Methods. Acrylonitrile and its comonomers can be polymerized by any free-radical method. Bulk polymerization is the most fundamental of these, but its practical use is limited by its autocatalytic nature. Aqueous dispersion polymerization is the most common commercial method; solution polymerization, where the spin solvent serves as the polymerization medium, is the other commercial process. Emulsion polymerization is used for certain modacrylic compositions.

Aqueous Dispersion Polymerization. By far the most widely used method of polymerization in the acrylic fibers industry is aqueous dispersion (also called suspension). When inorganic compounds such as persulfates, chlorates, or hydrogen peroxide are used as radical generators, the initiation and primary radical growth steps occur mainly in the aqueous phase. Chain growth is limited in the aqueous phase, however, because the monomer concentration is normally low and the polymer is insoluble in water. Nucleation occurs when aqueous chains aggregate or collapse after reaching a threshold molecular weight. If many polymer particles are present, as is the case in commercial continuous polymerizations, the dissolved radicals are likely to be captured on the particle surface by a sorption mechanism. The particle surface is swollen with monomer. Therefore, the polymerization continues in the swollen layer and the sorption becomes irreversible as the chain end grows into the particle.

Since polymer swelling is minimal and the aqueous solubility of acrylonitrile is relatively high, the tendency for radical capture is limited. Consequently, the rate of particle nucleation is high throughout the course of the polymerization, and particle growth occurs predominantly by a process of agglomeration of primary particles. Unlike emulsion particles of a readily swollen polymer, such as polystyrene, the acrylonitrile aqueous dispersion polymer particles are massive agglomerates of primary particles which are approximately 100 nm in diameter.

Redox initiation is normally used in commercial production of polymers for acrylic fibers. This type of initiator can generate free radicals in an aqueous medium efficiently at relatively low temperatures. The most common redox system consists of ammonium or potassium persulfate (oxidizer), sodium bisulfite (reducing agent), and ferric or ferrous ion (catalyst). The mechanism is shown in Figure 5. This redox system works at pH 2.0–3.5, where the bisulfite ion predominates and the ferric ion is soluble. The sulfate and sulfonate ion-radicals react with monomer to initiate rapid chain growth. Termination occurs by radical

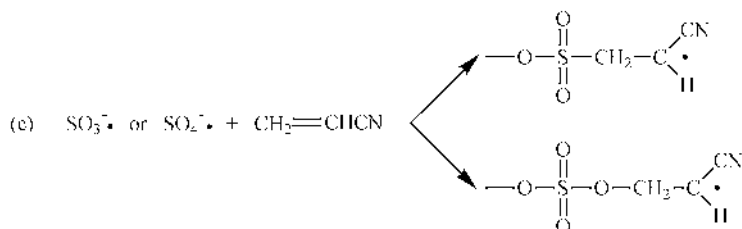
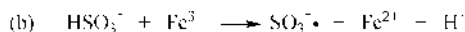
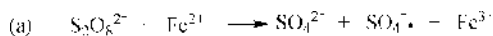


Fig. 5. Persulfate redox initiation mechanism.

recombination or by chain transfer. Bisulfite ion is both a reducing agent, and a chain-transfer agent; it reacts by transferring a hydrogen radical to terminate the chain, thus producing a bisulfite radical to initiate a new chain. The bisulfite concentration has a pronounced effect on polymer molecular weight with virtually no effect on the overall rate of polymerization (17). The ratio of bisulfite to persulfate in the reaction mixture has a strong effect on the dye-site content of the polymer (17,18). Bisulfite chain transfer increases the total dye-site content of the polymer by reducing the polymer molecular weight but at the same time produces chains with just one dyesite. At a given molecular weight the dye-site content of the polymer can, in theory, vary from two per chain at low bisulfite levels to one per chain at very high bisulfite levels.

In commercial practice, excess reducing agent to oxidizing agent ratios are used, for example, molar ratios of bisulfite to persulfate ranging from 5 to 15. These high ratios give narrower molecular weight distributions and, for a given molecular weight, relatively low conversion to polymer. Low conversion is an effective means of minimizing branching and color producing side reactions.

A comprehensive review of aqueous polymerization has been published (19). Many reviews of acrylonitrile polymerization have been published (20–23).

In commercial practice, polymerization is effected in a continuous-stirred-tank reactor (CSTR), a system in which all components are fed continuously and mixed, and the product is continuously discharged. For start-up, the reactor is charged with a certain amount of pH-adjusted water or the reactor is filled with overflow from another reactor already operating at steady state. The reactor feeds are metered in at a constant rate for the entire course of the production run, which normally continues until equipment cleaning or maintenance is needed. A steady state is established by taking an overflow stream at the same mass flow rate as the combined feed streams. The reaction vessel is normally an aluminum alloy; this minimizes scale buildup as the wall provides a sacrificial surface. The reactor is jacketed; steam may be introduced to heat the contents for start-up, but once the polymerization is initiated, water is circulated in the jacket to remove the heat of polymerization and maintain a constant temperature, usually 50–60°C.

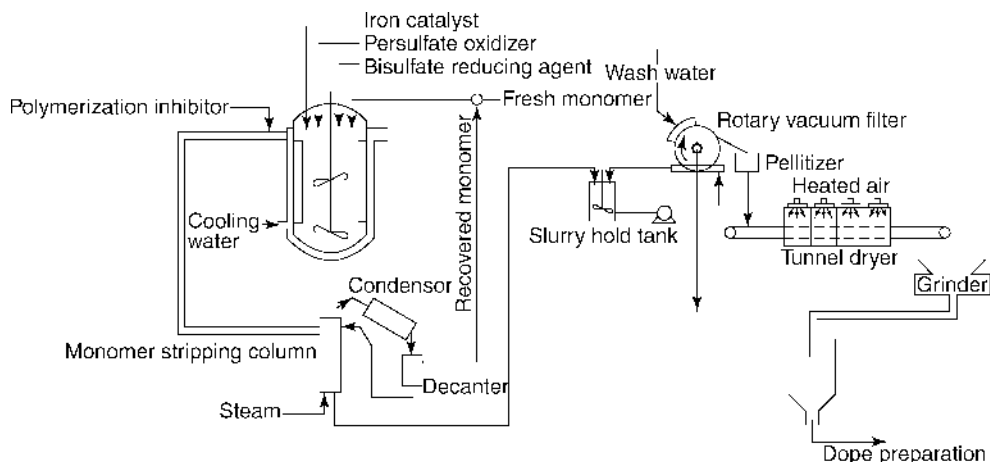


Fig. 6. CSTR Dispersion polymerization process.

An example of a continuous aqueous dispersion process is shown in Figure 6 (24). A monomer mixture composed of acrylonitrile and up to 10% of a neutral comonomer, such as methyl acrylate or vinyl acetate, is fed continuously. Polymerization is initiated by feeding aqueous solutions of potassium persulfate (oxidizer), sulfur dioxide (reducing agent), ferrous iron (promoter), and sodium bicarbonate (buffering agent). Alternately the system may employ a sodium bisulfite/sulfur dioxide or a sodium bisulfite/sulfuric acid buffer. The aqueous and monomer feed streams are fed at rates that give a reactor dwell time of 40–120 min, and a feed ratio of water to monomer in the range 2–5. The reactor overflow, an aqueous slurry of polymer particles, is mixed with an iron chelating agent, or the pH is raised to stop the polymerization. The slurry is then fed to the top section of a baffled monomer-separation column. The separation of unreacted monomer is effected by contacting the slurry with a countercurrent flow of steam introduced at the bottom of the column. Monomer plus water is condensed from the overheads stream and the monomer separated using a decanter, the water phase being returned to the column. The stripped slurry is taken from the column bottoms stream, and the polymer separated using a continuous vacuum filter. After filtration and washing, the polymer is pelletized, dried, ground, and then stored for later spinning.

A less desirable recovery process is to filter or centrifuge the slurry (with washing) to recover the polymer and then pass the filtrate plus wash water through a conventional distillation tower to recover the monomers. Delaying monomer removal may increase operator exposure, results in monomer in drier emissions, and reduces acrylonitrile yield through emissions and a side reaction. The need for monomer recovery may be minimized by using two-stage filtration with the first stage filtrate recycled to the reactor. Nonvolatile monomers, such as SSS, can be partially recovered in this manner. This makes process control more difficult because some reaction by-products can affect the rate of polymerization and the concentration of the recycle stream may vary.

Cost reduction has been a focus of fiber producers since the overall market for acrylic fibers in developed countries has not grown. A significant savings is realized by operating continuous aqueous dispersion processes at very low water-to-monomer ratios. Mitsubishi Rayon, for example, has reported ratios as low as 1.75 (25,26). This compares to ratios of 4–5 widely used in the 1970s. The low water-to-monomer ratios produce a change in the nucleation and particle growth mechanisms that yields denser polymer particles. The dense particles yield a fluid reaction mass, so long as conversion is relatively high. Removal of the heat of polymerization is more difficult in low water-to-monomer polymerizations as there is more heat generated per unit volume. The cost reduction comes in the drying step. While conventional water-to-monomer ratios give wet cake moisture levels of 200% (dry basis), the modified process yields wet cake moisture levels of 100% or less. Thus a savings in drying cost is realized. The low water-to-monomer process has the added advantage of increased reactor productivity.

After monomer removal by slurry distillation, salts are removed from the polymer by washing, either on a rotary vacuum filter or centrifuge. In the case where fiber will be produced from aqueous salt spin solvents such as sodium thiocyanate (NaSCN), the polymer cake may be used without drying to make a spin dope. With organic solvents, a drying step is required. Both belt dryers (with a pretreatment of pelletizing the polymer) and cyclone dryers are used; the former is most common. After drying, the pellets are again reduced to a powder and sent to bin storage. To ensure uniformity, the contents of several bins may be fed to the dope preparation area simultaneously.

Solution Polymerization. Solution polymerization is used by a few producers in the acrylic fiber industry. The reaction is carried out in a homogeneous medium by using a solvent for the polymer. Suitable solvents are aqueous NaSCN used by Acordis and dimethyl sulfoxide [67-68-5] (DMSO) used by Toray. The homogeneous solution polymerization of acrylonitrile follows the conventional kinetic scheme developed for vinyl monomers (27–29) (see BULK AND SOLUTION POLYMERIZATION REACTORS).

Thermally activated initiators such as azobisisobutyronitrile (AIBN), ammonium persulfate, or benzoyl peroxide can be used in solution polymerization, but these initiators are slow acting at temperatures required for fiber-grade polymer processes. Half-lives for this type of initiator are in the range of 10–20 h at 50–60°C (30). Therefore, these initiators are used mainly in batch processes where the reaction is carried out over an extended time. Redox initiators, such as the ammonium persulfate/sodium bisulfite/copper system, have much higher initiation rates and are reported to be employed in the Acordis NaSCN process. A typical continuous solution polymerization equipment diagram is shown in Figure 7.

Chain transfer is an important consideration in solution polymerization. Chain transfer to solvent may reduce the rate of polymerization as well as the molecular weight of the polymer. Other chain-transfer reactions may introduce dye sites, branching, and structural defects which reduce thermal stability. The organic solvents used for acrylonitrile polymerization are active in chain transfer. DMSO and DMF have chain-transfer constants of $(0.1\text{--}0.8) \times 10^{-4}$ and $(2.7\text{--}2.8) \times 10^{-4}$ respectively—high when compared to a value of only 0.05×10^{-4} for acrylonitrile itself and 0.006×10^{-4} for aqueous zinc chloride.

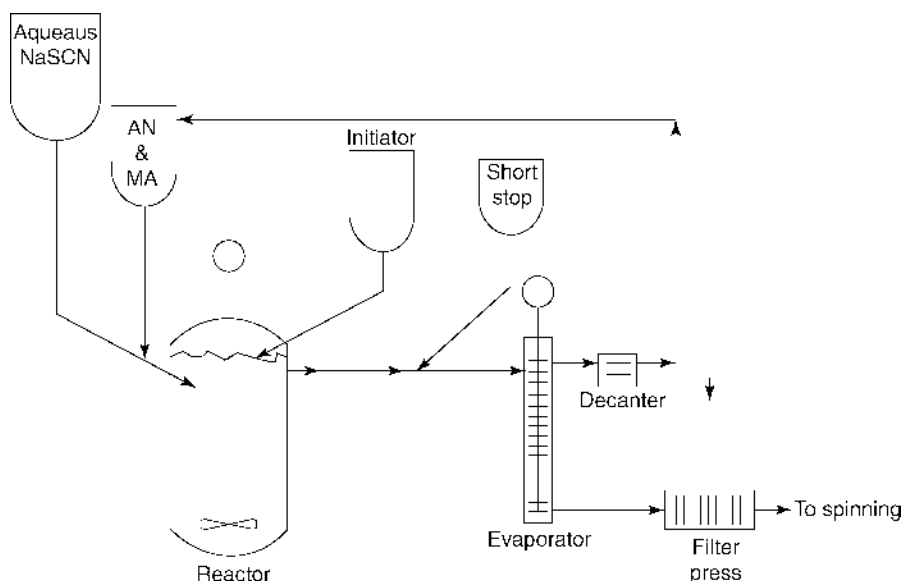


Fig. 7. CSTR NaSCN solution polymerization process. AN = acrylonitrile; MA = methyl acrylate.

Of the two common comonomers incorporated in textile-grade acrylics, methyl acrylate is the least active in chain transfer, whereas vinyl acetate is as active in chain transfer as DMF. Vinyl acetate is also known to participate in the chain transfer-to-polymer reaction (31). This occurs primarily at high conversion, where the concentration of polymer is high and monomer is scarce.

The advantage of solution polymerization is that the polymer solution can be converted directly to spin dope by removing the unreacted monomer. Incorporation of nonvolatile monomers, such as the sulfonated monomers, can be a problem. The sulfonated monomers must be converted to a soluble form such as the amine salt. Nonvolatile monomers are difficult to recover or purge from the reaction medium. Monomer recovery systems based on carbon adsorption have been developed. However, the usual practice is to maximize the single-pass conversion of these monomers.

Subsequent to the polymer reactor, acrylonitrile and volatile comonomers are removed in a thin-film evaporator. Additives such as pigments or stabilizers may be incorporated using a static or active mixer before the dope is transferred to the spinning area.

Bulk Polymerization. The idea of bulk polymerization is attractive, since the polymer would not require water removal and the process would not have the low propagation rates and high chain transfer rates of solution processes (see BULK AND SOLUTION POLYMERIZATION REACTORS). But bulk polymerization of acrylonitrile is complex. Even after many investigations into the kinetics of the polymerization, it is still not completely understood. The complexity arises because the polymer precipitates from the reaction mixture barely swollen by its monomer. The heterogeneity leads to kinetics that deviate from normal.

When initiator is first added, the reaction medium remains clear while particles 10–20 nm in diameter are formed. As the polymerization proceeds, the particle size increases, giving the reaction medium a white milky appearance. When a thermal initiator, such as AIBN or benzoyl peroxide, is used the reaction is autocatalytic. This contrasts sharply with normal homogeneous polymerizations in which the rate of polymerization decreases monotonically with time. With acrylonitrile bulk polymerization, *three* propagation reactions occur simultaneously, accounting for the anomalous autoacceleration (32,33). These are chain growth in the continuous monomer phase, chain growth of radicals that have precipitated from solution onto the particle surface, and chain growth of radicals within the polymer particles (30,34).

Bulk polymerization is not used commercially because the autocatalytic nature of the reaction makes control difficult. This, combined with the fact that the heat generated per unit volume is very high, makes commercial operations difficult to engineer. Last, the viscosity of the medium becomes very high at conversion levels above 40–50%. Therefore, commercial operation at low conversion would require an extensive monomer recovery operation. A bulk process was developed (35) by MEF, which limited conversion to ~50%; it reportedly reached pilot-plant stage but was not commercialized.

Emulsion Polymerization. The use of emulsion polymerization in the acrylic fiber industry is limited to the manufacture of modacrylic compositions. One notable example of an emulsion process was the former Union Carbide process for Dynel (36,37). The mechanism of emulsion polymerization was first developed qualitatively (38) and later quantitatively (39,40) (see HETEROPHASE POLYMERIZATION). It was shown that the emulsifier disperses a small portion of the monomer in aggregates of 50–100 molecules approximately 5 nm in diameter called *micelles*. The majority of the monomer stays suspended in droplet form. These droplets are typically 1000 nm in diameter, much larger than the micelles. Since a water-soluble radical initiator is used, polymerization begins in the aqueous phase. The micelle concentration is normally so high that the aqueous radicals are rapidly captured (41). The micelle is essentially a tiny reservoir of monomer; therefore, polymerization proceeds rapidly, converting the micelle to a polymer particle nucleus. Since the halogen-containing monomers have little water solubility, the micelle promotes their ability to react. The ability of emulsion polymerization to segregate radicals from one another is of great importance commercially. The effect is to minimize the rate of radical recombination, allowing high rates of polymerization to be achieved along with high molecular weight. This is important in modacrylic polymerizations where chain-transfer constants of the halogen monomers are high. Comprehensive reviews of emulsion polymerization technology have been published (42–44), and emulsion polymerization reactor modeling has been reviewed (45). The polymer for Kanekaron modacrylic is reported to be prepared by emulsion polymerization.

Copolymerization.

Homogeneous Copolymerization. Virtually all acrylic fibers are made from acrylonitrile copolymers containing one or more additional monomers that modify the properties of the fiber. Thus copolymerization kinetics is a key technical area in the acrylic fiber industry. When carried out in a homogeneous solution, the copolymerization of acrylonitrile follows the normal kinetic rate laws

of copolymerization. Comprehensive treatments of this general subject have been published (46–50). The more specific subject of acrylonitrile copolymerization has been reviewed (51). The general subject of the reactivity of polymer radicals has been treated in depth (52).

For textile end-use acrylics, the most common comonomer is vinyl acetate, followed by methyl acrylate. The monomer pair acrylonitrile–methyl acrylate is close to being an ideal monomer pair. Both monomers are similar in resonance, polarity, and steric characteristics. The acrylonitrile radical shows approximately equal reactivity with both monomers, and the methyl acrylate radical shows only a slight preference for reacting with acrylonitrile monomer. Many acrylonitrile monomer pairs fall into the nonideal category, for example, acrylonitrile–vinyl acetate. This example is of a nonideality, sometimes referred to as kinetic incompatibility. A third type of monomer pair is that which shows an alternating tendency. This tendency is related to the polarity properties of the monomer substituents (53). Monomers that are dissimilar in polarity tend to form alternating monomer sequences in the polymer chain. An example is the monomer pair acrylonitrile–styrene. Styrene, with its pendent phenyl group, has a relatively electronegative double bond whereas acrylonitrile, with its electron-withdrawing nitrile group, tends to be electropositive.

Copolymer composition can be predicted for copolymerizations with two or more components, such as those employing acrylonitrile plus a neutral monomer and an ionic dye receptor. These equations are derived by assuming that the component reactions involve only the terminal monomer unit of the chain radical. The theory of multicomponent polymerization kinetics has been treated (46,47).

Heterogeneous Copolymerization. When copolymer is prepared in a homogeneous solution, kinetic expressions can be used to predict copolymer composition. Bulk and dispersion polymerization are somewhat different, since the reaction medium is heterogeneous and polymerization occurs simultaneously in separate loci. In bulk polymerization, eg, the monomer-swollen polymer particles support polymerization within the particle core as well as on the particle surface. In aqueous dispersion or emulsion polymerization, the monomer is actually dispersed in two or three distinct phases: a continuous aqueous phase, a monomer droplet phase, and a phase consisting of polymer particles swollen at the surface with monomer. This affects the ultimate polymer composition because the monomers are partitioned such that the monomer mixture in the aqueous phase is richer in the more water-soluble monomers than the two organic phases. Where polymerization occurs predominantly in the organic phases, these relatively water-soluble monomers may get incorporated into the copolymer at lower levels than expected. For example, in studies of the emulsion copolymerization of acrylonitrile and styrene, the copolymer was richer in styrene than copolymer made by bulk polymerization, using the same initial monomer composition (54–56). Analysis of the reaction mixtures (57) showed that nearly all of the styrene was concentrated in the droplet and swollen particle phases. The acrylonitrile, on the other hand, was distributed between both the aqueous and organic phases. The monomer compositions in the droplet and particle phase were found to be essentially the same. The effect of monomer partitioning on copolymer composition is strongest with the ionic monomers, since this type of monomer is usually soluble in water and nearly insoluble in the other monomers. Reviews of emulsion

Table 3. Polymer Concentrations Suitable for Solution Spinning

Solvent	Polymer Concentration, %
Dimethylformamide (DMF)	20–32
Dimethylacetamide (DMAc)	20–27
Dimethyl sulfoxide (DMSO)	20–30
Ethylene carbonate (EC)	15–18
Sodium thiocyanate (NaSCN) 45–55% in water	10–15
Zinc chloride (ZnCl ₂) 55–65% in water	8–12
Nitric acid (HNO ₃) 65–75% in water	8–12

copolymerization kinetics and the effects of reaction heterogeneity on reaction locus have been published (58,59).

In a CSTR dispersion process, the percentage of the less reactive monomer increases until steady state is reached. For example, if a reactor is fed monomer composed of 91% acrylonitrile and 9% vinyl acetate and the process is carried to 75% conversion, the polymer will contain 7.4% vinyl acetate. The unreacted monomer composition will be 86.2% acrylonitrile and 13.8% vinyl acetate.

Solution Spinning

As the acrylic fiber industry has matured, the wide range of spin solvents that were commercialized in the 1950–1960s has narrowed. DMSO and zinc chloride are each limited to one producer; no processes based on ethylene carbonate solvent remain in operation. Most newer plants are based on either DMAc or NaSCN wet spinning. Table 3 shows commercial solvents and the dissolved polymer concentration range for a spin solution.

For dry polymer, the dope-making process may use chilled solvent to form a slurry and wet out the polymer particles before they begin to dissolve, or may use hot solvent so that the solutioning process occurs immediately. Additives such as thermal stabilizers and delusterant (TiO₂) are added at this time. In both cases, active mixing is required. Subsequently, the suspension is pumped through a shell-tube heat exchanger to complete dissolution. The resulting dope is degassed and filtered (plate and frame) before being pumped to the spin area.

Dry Spinning. This was the process first employed commercially by DuPont in 1950. It is shown schematically in Figure 8. For acrylic fibers, the only dry-spinning solvent used commercially is DMF. The DMF spin dope coming from the dope preparation unit is filtered and then heated to approximately 140°C. It is pumped through spinnerettes of up to 2800 holes placed at the top of a solvent removal tower. The DMF is evaporated by circulating an inert gas through the tower at 300–350°C. The tower walls are also heated to prevent any solvent condensation. With such a high boiling solvent (b.p. 153°C) it is not possible (or desirable) to remove all solvent in the tower. Consequently, the fiber from the bottom of the tower contains 10–25% solvent. In discontinuous processes, the fiber exiting the tower is wet with water and combined with the product from other threadlines into a rope; the rope is plaited into a can. The residual DMF

is removed in a second step by passing the rope via roll sets through a series of hot water baths. A more modern process, introduced by Bayer, washes the fiber by sprays while passing on a belt. The as-spun fiber has little orientation, and so it is stretched three- to sixfold either before or concurrent with the washing step. The fiber is crimped to improve bulk and textile processing, then dried by heated air on a moving belt. During drying, the fiber structure collapses to the same density as solid polymer and the length decreases as the structure relaxes. A "finish" comprising an antistatic agent and a lubricant are applied by spray or kiss rolls and the product is either cut to staple or packaged directly as tow. Figure 9 shows the subsequent process steps.

The filament microstructure in dry spinning is derived from gelation exclusively. As evaporation proceeds, the polymer concentration in the filament increases until gelation occurs. This may happen within a few centimeters of the spinneret face. Since no nonsolvent is used, precipitation does not occur during solvent removal. Fiber densities from wet and dry spinning have been compared (60); density of as-spun fiber is much higher in dry-spun fiber. The fiber cross-section shape is typically a "dogbone" (Fig. 2). Very little fibrillar structure, characteristic of wet-spun fibers, is observed in the dry spun filaments. During stretching, however, the dry spun fibers develop a fibrillar network similar to that of the wet spun fibers but finer in diameter. This mode of fiber formation is economical for commodity fibers of 1–5 dtex but has severe limitations for other products:

- (1) Solvent removal is not fast enough to produce fibers of 12–20 dtex suitable for the carpet industry.
- (2) The limitation on the number of holes per spinneret makes production of fine filaments (<1 dtex) expensive as, unlike the wet-spinning process, the number of holes per spinneret is limited.
- (3) The compact structure makes producer dyeing of fiber more difficult.
- (4) The gelation process does not work well to produce special-shaped filaments; the dogbone cross-section is not suitable as a carbon fiber

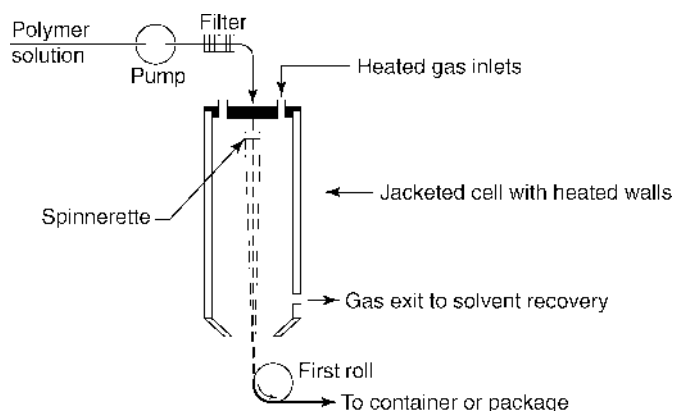


Fig. 8. Schematic of dry-spinning tower.



Fig. 9. Conventional wash-draw-dry-relax fiber process.

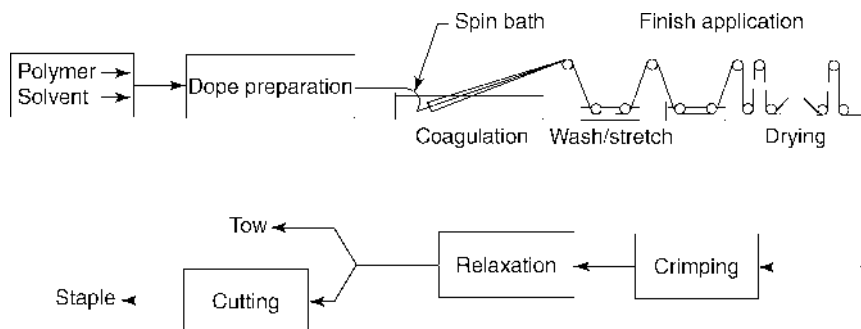


Fig. 10. Wet-spinning organic solvent process.

precursor; and it is not possible to produce a fibrillated product for the asbestos-replacement market.

Wet Spinning. Wet spinning differs from dry spinning primarily in the way solvent is removed from the extruded filaments. Instead of evaporating the solvent in a drying tower, the fiber is spun into a liquid bath containing a solvent/nonsolvent mixture called the coagulant, as shown in Figures 10 and 11. The solvent is the same as the dope solvent and the nonsolvent is usually water. Filament fusion is less of a problem in wet spinning, and so the number of capillaries in wet spinning spinnerettes is much larger than in dry spinning. The spinnerettes in commercial processes may have anywhere from 3000 to 100,000 + capillaries, which may range in diameter from 0.05 to 0.25 mm; it is common to use multiple spinnerettes in a single spinbath.

Because the fiber microstructure is established in the spinbath, the coagulation conditions employed are the result of extensive optimization. The critical part of this process is the transition from a liquid to a solid phase within the filaments. Two liquid-to-solid phase transitions are possible. The first is precipitation of the polymer to form a microporous solid phase. In extreme cases, precipitation produces a structure with macrovoids which must be "healed" in later processing, or the fiber lateral properties will suffer. Precipitation is favored when the solvent is organic and the nonsolvent is water, as the solubility of polymer decreases abruptly with water concentrations of only a few percent. The second and more desirable solid phase is the gel state, characterized by hydrogen and dipole bonding between the polymer and solvent. The gel state is desirable because it gives rise to a finer microstructure once the solvent is removed. Thus, the conditions in the spinbath should be optimized so that gelation of the polymer precedes precipitation. Studies (61) have shown that gelation occurs more rapidly at high dope solids and lower spinbath temperatures.

Low spinbath solvent concentration promotes initial rapid solvent extraction but also produces a thicker filament skin, that ultimately reduces the rate of solvent extraction and may lead to the formation of macrovoids. High spinbath solvent concentration gives a denser microstructure, but solvent extraction is slow and filament-to-filament fusion may occur. Other spinbath conditions that affect coagulation and microstructure are dope solids, spinbath temperature, jet stretch (the ratio of actual filament speed to theoretical speed in the capillary), and immersion time.

The fiber emerging from the spinbath is a highly swollen gel containing both solvent and nonsolvent from the spinbath. The fibers are essentially unoriented except at the fiber skin. The microstructure consists of a fibrillar network. The spaces between fibrils are called microvoids. Depending on the conditions of coagulation, the filaments may also contain large voids radiating out from the center of the fiber. The best combination of tensile properties, abrasion resistance, and fatigue life is realized when the coagulated fiber has a homogeneous, dense structure with small fibrils and no macrovoids (62).

Fiber cross-sectional shape is determined by the coagulation conditions. A thick skin characteristic of most organic solvent-spun fibers will generate a bean-shaped cross-section as the solvent is removed from the interior. The thinner skin characteristic of inorganic solvent-spun fibers can contract with solvent removal and retain the round shape. It is possible, however, to produce the opposite shape in either system. Examples of these shapes were shown in Figure 1. Special cross-sections, such as rectangular or oval, can be made from nonround capillaries by controlling coagulation conditions. Control of die swell is of critical importance. Die swell occurs because most spin dopes are viscoelastic in nature. After undergoing stretching deformation during extrusion through the small spinnerette hole, the dope partially rebounds to a larger, preextrusion diameter. To maintain

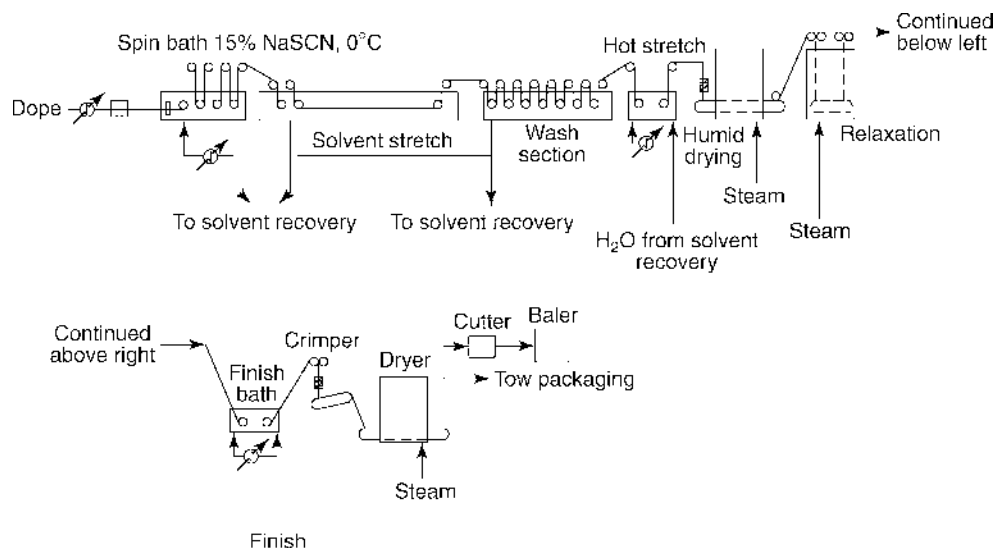


Fig. 11. Wet-spinning NaSCN salt process.

a nonround shape, the tension on the filament at the spinnerette face must be great enough to counterbalance die-swell.

After the spin-bath or spin-tower step, the tow processing is similar for both wet- and dry-spun yarns. Wet-spun tows however, may contain 100–300% of solvent/nonsolvent, while dry-spun tows generally hold only 10–30% solvent. Therefore, the initial washing steps differ in their details. The key wet-spinning steps are washing, stretching, finish application, collapse, drying, crimping, and relaxing. The washing step consists of several countercurrent stages, with the effluent being recycled to a solvent recovery process. Various wash units are employed including baths, sprays, and proprietary devices (63); washing efficiency is a key aspect of cost, as it impacts recovery of solvent from the effluent. The wash step may also be combined with stretching. In one variation of this method, the tow is drawn between sets of godets and passed through a series of solvent extraction baths at the same time.

The washing step may be followed by additional stretching. The porous fibrillar structure of wet-spun fibers increases in density with stretching. In-line dyeing of fiber using cationic dyes is usually carried out after almost all solvent is removed. Because of the open structure of wet-spun fiber, dye penetration and fixation is rapid. An additional wash step removes auxiliaries and unfixed dye. After the fiber is washed, stretched, and optionally dyed, finish may be applied using a bath or similar device. If drying is accomplished on heated rolls (Fig. 10), a predrying finish is required to prevent fiber fusion. In other processes (Fig. 11), finish application may be postponed until the fiber is dried and collapsed.

The collapsing-drying step can be accomplished with the tow held at constant length by contacting the tow on heated rolls or by passing the tow through an in-line oven using a conveyor belt. For fiber that contains a large void structure, roll drying is necessary to effect collapse of the voids. After collapse, boiling water shrinkage is reduced and higher temperatures are required for subsequent relaxation.

After drying/collapsing, the tow is relaxed. Relaxation is essential because it reduces the tendency for fibrillation and increases the dimensional stability of the fiber. Relaxation also increases fiber elongation while reducing strength and increases dye diffusion rate. Relaxation can be done in-line or in batches in an autoclave. For fiber that has been belt dried, relaxation can be accomplished by an atmospheric process (Fig. 11). However, for roll-dried fiber, saturated steam is used because the moisture reduces the process temperatures required. This process can be accomplished in-line, but more commonly it is done batchwise in an autoclave. Fiber shrinkage during relaxation ranges from 10 to 40% depending on the temperature, the polymer composition, and the amount of prior orientation. The amount of relaxation is tailored to the intended application of the product.

Fiber crimping using a stuffer box device may be done before in-line relaxation or before autoclaving. The relaxation process tends to “set” the crimp. In some autoclave processes, a second crimping step is employed subsequent to relaxation. Fiber may be cut to staple at the machine end for in-line relax processes or batchwise for autoclave processes. Tow can be produced from either process type, although large packages of one ton or more are produced more readily from the in-line relax process.

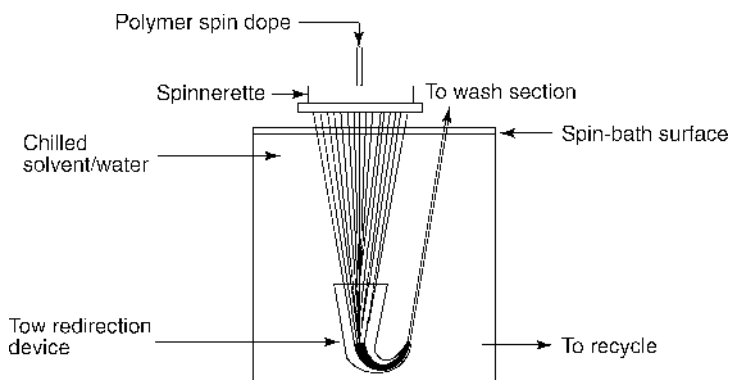


Fig. 12. Air gap coagulation.

Process speeds for wet spinning vary from 55 to 260 m/min. The limitations are the speed at which the fiber can move through the spinbath without filament breakage and the equipment line length required to complete the washing and drying processes. A single machine may have up to 48 spinnerettes (6 rows of 8) with a total productivity of 50 ton/day.

Air-Gap Spinning. This process, also termed dry-jet wet spinning, is used to provide filament yarn either for textile use or as a carbon fiber precursor. It is suitable for producing the small bundles required for these end uses because the filament has been drawn before it enters the bath, and so drag forces are less likely to cause breakage; thus, much higher line speeds can be achieved. In theory, any acrylic solvent can be used in air gap spinning. Commercial examples are known from DMAc, NaSCN, and DMSO.

The dope solids for air-gap spinning are higher than for wet spinning, the intent being to achieve quick gelation on extrusion. The spinnerette is positioned a short distance above the bath, which is a solvent/nonsolvent mixture, typically at low temperature. The fiber is spun vertically into the bath, and then rerouted out via a tube or pulley as shown in Figure 12. Spinnerettes may be less than 1000 holes for a textile product or as many as 4000 for a carbon fiber precursor. The remainder of the process resembles the wet-spinning process, except that there are many small bundles that must be kept separate and the final product is taken up on bobbins. Final line speeds may be up to 500 m/min, but because of the small bundle size, machine productivity may be only 5 ton/day.

Solvent Recovery. Efficient use of solvent and water are key elements in an economic process. With most spinning processes practiced on a large scale, less than 1% solvent is not recycled, based on fiber produced. Since the ratio of solvent to fiber is in the range of 4:1, this means less than 0.25% of the solvent employed is expended per pass. Solvent loss is of several types: (1) solvent remaining in final fiber; (2) solvent lost as vapor; (3) solvent decomposed; (4) solvent lost in reprocessing or maintenance.

The main means of solvent recycling is distillation, either atmospheric or vacuum. With the organic solvents, the water is distilled, perhaps in several steps; then the higher boiling solvent is distilled, leaving behind dissolved salts

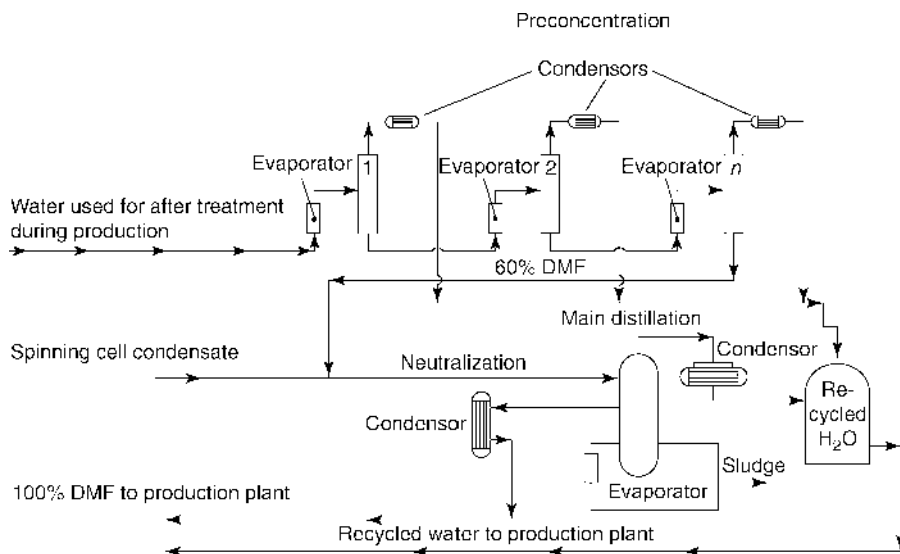


Fig. 13. Diagram of DMF recovery unit.

and low molecular weight polymer. Amide solvents such as DMF and DMAc are subject to hydrolysis and may require a step to remove the acid generated; the recovered water may require removal of dimethylamine before reuse. Figure 13 shows a DMF recovery train (64). Salt solvents such as NaSCN are concentrated by water removal in multieffect evaporators, then may have an ion exchange and/or crystallization step to remove impurities. Recycled water may have the pH adjusted by addition of acid or base to assure neutralization of the fiber in the washing step.

Melt Spinning. Compared to most other synthetic fibers, acrylics have always had the disadvantage of extra process steps and cost incurred because they could not be melt spun. Several approaches to eliminating this limitation have been proposed. Plasticization of the polymer with DMSO was proposed (65) as this lowered the melting point. This only reduced the amount of solvent to be recovered but did not eliminate the washing and solvent recovery steps. A more promising approach was plastization with water (66). This eliminated the process steps, but it was necessary to heat the plasticized mass to 200°C under pressure. The fiber had to be extruded into a chamber also under pressure, or the result would be a foam structure as the water vapor flashed.

A true melt spinning process has been developed by a group at Standard Oil (67). Their approach was to make a polymer containing substantial comonomer content by a process which minimized "blocking" of acrylonitrile groups. The resultant polymer was melt-processible without degradation. Possible limitations of this approach are that the high comonomer content leads to high relaxation shrinkage as well as lower softening and sticking temperatures. These are disadvantages in modern textile processes. No commercial applications of this technology have appeared.

Modifications of Properties.

Reduced Pilling. Staple fabrics, in general, develop small balls of fiber or pills on the fabric surface as a result of abrasive action on the fabric surface. However, the pills build up more on acrylic fabrics than on comparable woolens. Pilling can be reduced by increasing the likelihood that the pills will break or wear off. Thus, the most effective approaches include reducing fiber strength, incorporating defects in the fiber, increasing fiber brittleness, and reducing shear strength. Using the same polymer base, wet-spinning processes can be modified by using low solvent concentration in the spin-bath and high spin-bath temperature to give more brittle fibers with high void content. Other possible approaches are lower draw ratios, which result in low tensile strength, and less complete relaxation, which reduces fiber elongation to break. Commercial examples include Dralon L930 (Fraver), Super Camelon (Mitsubishi Rayon), and Acrilan[®] Pil-Trol[™] (Solutia).

Improved Abrasion Resistance. Abrasion resistance is generally improved by reducing the microvoid size and increasing the initial fiber density. Abrasion-resistant fibers have been produced by incorporating hydrophilic comonomers or comonomers with small molar volumes. Sulfonated monomers, acrylamide derivatives, and *N*-vinylpyrrolidinone are some of the hydrophilic comonomers that can be used to slow coagulation, thus reducing the void content. Vinylidene chloride, with its relatively small molar volume, is effective in increasing fiber density. The spinning process itself has a significant effect on initial fiber density and abrasion resistance. Dry spinning, for example, produces a denser initial fiber structure than conventional wet spinning. Wet-spinning techniques used to improve abrasion resistance generally do so by promoting gelation. Examples include high spinbath that concentration, low spinbath temperature, and additives to the dope or spinbath that slow coagulation. Spinbath additives include nondiffusing nonsolvents, such as poly(ethylene glycol) or high molecular weight alcohols, such as *tert*-butyl alcohol, in place of water.

Commercial Products

The majority of acrylic fiber production is 1.0–5.6 dtex (0.9–5 den) staple and tow furnished, undyed, in either bright or semidull ($\sim 0.5\%$ TiO₂) luster. The principal markets are in apparel and home furnishings. Within the apparel sector these fibers are used in sweaters and in single jersey, double-knit, and warp-knit fabrics for a variety of knitted outerwear garments such as dresses, suits, and children's wear. Other markets for acrylics in the knit goods area are hand-knitting yarns, deep-pile fabrics, circular knits, fleece fabrics, and half-hose. Acrylics also find uses in broadwoven fabric categories such as blankets, drapery, and upholstery. Minor tufted end uses include area rugs and carpets.

Acrylic Tow. A significant proportion of acrylic fiber, perhaps 25% in the United States and more than 50% in Europe, is sold as tow for conversion to yarn through stretch-breaking using the Superba, Seydel, or similar equipment. Tow packages may be as large as 1 ton, with no break in the bundle. The larger the tow package, the higher the tow customer's productivity. Ability to offer a large

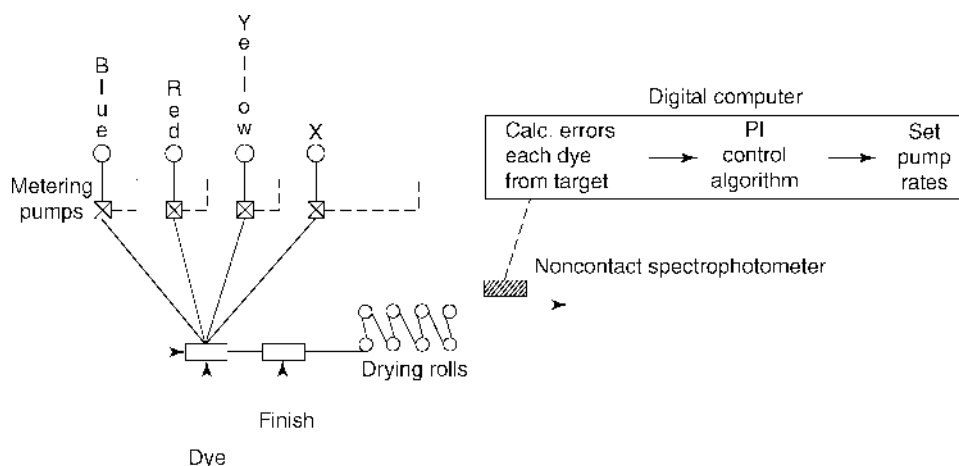


Fig. 14. Color control in a producer-dyed fiber process.

tow package implies that a producer has a highly stable process, as no knots are allowed. Producers with continuous relaxation have no limit on the package size they can offer; the only limits are those arising in package handling. In Europe, many fiber producers convert tow to “tops”—stretch broken product that is ready for yarn spinning.

Acrylic Filament Yarns. Continuous filament acrylic yarns face stiff competition from nylon and polyester. Since they are more costly, acrylics have penetrated only those markets where they have a clear advantage in a critical property. In Japan, continuous filament yarns in very fine deniers are valued as a silk replacement. In this market, the yarn is a premium product used in high fashion dress fabrics, satins, and poplins, or to produce a cloth suitable for surface raising to give a suede or fine velour effect.

Producer-Dyed Fiber. The largest volume “specialty” product offered by acrylic producers is producer-dyed fiber (PDF). Producer dyeing decreases systems cost by elimination of a process step for the customer, but it complicates the inventory. PDF is usually made in an on-line process as shown in Figure 14 (68). The dye is applied using a device which promotes rapid penetration of the fiber mass, as acrylics have a high strike rate and very poor leveling qualities. The process is automated to maintain constant color (shade and depth) by real-time color analysis and correction. Since the final color is influenced by relaxation and crimp, further monitoring and testing may be required. Alternately, the dyes are premixed and a mixed stream is injected into the dyeing device. If the shade is right, then only depth needs adjustment. PDF fiber spun using this dyeing technology is usually sold as “lots,” as color from one production run to the next may not match sufficiently for critical end uses. Dry-spun fibers are difficult to dye in-line as their compact structure makes dyeing too slow to be compatible with the required process speeds. For dry-spun acrylic, the only practical process is dope dyeing. For colors with only a low demand, some producers may use post-production dyeing with a device such as a Serricant Tow-Fix-R. More than 20 producers worldwide offer PDF acrylic.

Pigmented Fiber. Pigmented acrylic and a small amount of modacrylic are used in outdoor applications where outstanding light stability provides a competitive advantage. Pigmentation provides more stable coloration than dyeing through the lifetime of the fabric. End uses include awnings, tents, and lawn furniture. Modacrylic is used where local codes require a flame-retardant fabric. The technology involves mixing of the pigments with the spin dope prior to extrusion. The same feedback mechanism of color control described for PDF may be used with pigmented fiber. About a dozen producers offer pigmented fiber; however, some only sell one color—black. Generally, pigmented fiber commands a higher price than does PDF owing to the high cost of organic pigments. This coupled with the decreased luster of the pigmented products means they do not usually compete in the same end uses.

Fibers with High Bulk and Pile Properties. High-bulk acrylic fibers are commonly made by blending high shrinkage and low shrinkage staple fibers, or by blending relaxed and unrelaxed sliver from tow. The two staple products are made by variation in the fiber stabilization process. When the resulting yarn is allowed to relax, the high shrink component causes the low shrinkage (relaxed) fiber to buckle and add bulk to the yarns.

Another method of producing high bulk yarns is the use of bicomponent fibers. Bicomponent fibers have developed from a desire to match the bulkiness and handle of wool. The three-dimensional crimp of animal fibers in general comes from the presence of two components on the fiber surface. Acrylic bicomponent fibers achieve three-dimensional crimp by spinning two copolymer dopes into a single fiber. If the two streams are present in the same proportion in each spinneret hole, the process is “true” bicomponent; if the proportion varies from filament to filament, then it is a “random” bicomponent. To generate the spiral crimp, the two polymers must have different responses to heat or moisture. For example, if one polymer is more moisture absorbent than the other, a crimp develops when the fiber is dried. The copolymers for this type of bicomponent may be acrylonitrile–vinyl acetate and acrylonitrile–vinyl acetate–sodium *p*-(vinylbenzene) sulfonate. In this combination, the copolymer containing the sulfonate moiety is the more moisture absorbent and therefore shrinks the most on drying. This type of crimp is reversible because it can be renewed by wetting and redrying. Solutia’s A-21 and B-21 are examples of commercial water-reversible-crimp fibers. Crimp can also be imparted by using polymers that react differently to heat. By using copolymers of different compositions, the crimp is imparted permanently when the fiber is heated. The copolymers for this type of bicomponent have a single comonomer, such as vinyl acetate or methyl acrylate, incorporated at two different levels.

True bicomponents require special spinneretters that provide the required dopes to each hole. In random-bicomponent technology, the second component is incorporated through a layering device prior to the spinnerette. This concept is based on the fact that the viscous spinning solutions can be merged without complete mixing (69). When passed through a standard spinnerette, bicomponent fibers are produced ranging in composition from 100% component A to 100% component B. For many years, this was the only bicomponent technology available to wet spinners.

Flame-Resistant Fibers. Acrylics have relatively low flame resistance, comparable to cotton and regenerated cellulose fibers. Additional flame resistance is required for certain end uses, such as children's sleepwear, blankets, carpets, outdoor awnings, and drapery fabrics. The only feasible route is copolymerization of acrylonitrile with halogen-containing monomers such as vinyl chloride, vinyl bromide, or vinylidene chloride. Modacrylics were developed for uses where a high resistance to burning is required. In such fibers, the level of halogen-containing units was up to 60%, as in Dynel, one of the earliest modacrylics. This fiber, no longer produced, was 40–60 acrylonitrile–vinyl chloride copolymer. Tennessee Eastman's Verel, an acrylonitrile–vinylidene chloride copolymer, has also been discontinued. Solutia's SEF modacrylic is the only remaining U.S.-produced modacrylic flame-resistant fiber. It is produced solely in pigmented form as SEF FR for the commercial awning business. Kanekaron, another acrylonitrile–vinyl chloride composition produced in Japan by Kanegafuchi, finds use in wigs, toys, pile, and industrial filter fabrics.

There have been reviews of flammability (70–74), methods that can be used to enhance the flame resistance of acrylic and modacrylic fibers (75), and the mechanism of flame-retardant additives (76).

High Strength Fibers by Conventional Solution Spinning. As a reinforcing material for ambient-cured cement building products, acrylics offer three key properties: high elastic modulus, good adhesion, and good alkali resistance (77). The high modulus requires an unusually high stretch orientation. This can be accomplished by stretching the fiber 8- to 14-fold above its glass-transition temperature, T_g . Normally this is done in boiling water or steam to give moduli of 8.8–13 N/tex (100–150 gf/den) (78,79). Alternatively, the stretch orientation can be achieved by a combination of wet stretch at 100°C and plastic stretch on hot rolls, or in a heat-transfer fluid such as glycerol. This technique is reported to give moduli as high as 17.6 N/tex (200 gf/den) (80,81). Mitsubishi Rayon Co. reported an acrylic asbestos-replacement fiber with a tensile strength of almost 600 MPa (87,000 psi) (82). Many patents have been obtained for acrylic-reinforcing fibers (83–85). The Acordis fiber, marketed under the trade name Dolanit, is offered in several forms (Table 4).

Acrylic fibers such as Dolanit (86) are blended in ambient-cured cement at a rate of 1–3%, compared with 9–15% by weight for asbestos. The flexural strength of cement sheets of acrylic-reinforced cement is equivalent to asbestos-reinforced cement and nearly double that of untreated cement (87). Two factors limiting the rapid development of acrylic asbestos-replacement fibers are a high manufacturing cost (compared to asbestos) and uncertainty as to the long-term stability of the acrylic fiber. Loss of modulus and chemical degradation may be significant over a period of decades. Other studies of acrylic fibers for concrete reinforcement have been carried out (88).

Carbon Fiber. Carbon fibers (qv) are valued for their unique combination of extremely high modulus and strength and low specific gravity. Precursors for carbon fiber can be pitch, rayon, or acrylic fiber. Rayon offers a very low yield of carbon fiber and is no longer used as a precursor. Pitch is useful for generating carbon fiber of exceptionally high modulus, but the predominant precursor is acrylic. Precursors are converted into carbon fibers in a two-stage thermal treatment—a medium temperature “oxidation” stage in air that renders the fiber

Table 4. Properties of Dolanite Asbestos Replacement Fibers^a

	Dolanite Type 10		Dolanite Type 12		
Filament fineness, dtex ^b	1.5	0.7	1.7	2.2	8.2
Staple length, mm	6, 12	40	50	60, 80	80
Tenacity, cN/tex ^c	80–87	65–70	65–70	54–58	43–47
Elongation to break, %	8–12	15–20	15–20	13–16	14–17
Boiling water shrink, %				1.5	
Hot air shrink, % @ 150°C				1–2	
Same, yam form @ 200°C				3–4	
Hydrolysis resistance	Very good—after 350 h @ 130°C—93% tenacity remains				
Resistance to acids	Very good—after 8 weeks @ 20°C in 50% sulfuric acid—85% tenacity remains				
Heat resistance	Good—200 h @ 150°C, 75% tenacity remains		Good—permanent operating temperature up to 125°C, peaks up to 140°C		

^aRef. 7.^bTo convert dtex to den, multiply by 0.9.^cTo convert cN/tex to gf/den, multiply by 0.113.

infusible, and a high temperature “carbonization” treatment in an inert atmosphere, where the fiber is converted into nearly pure carbon. The polymer composition generally has about 98% acrylonitrile and 2% of a weak acid such as itaconic or acrylic acid. The function of the acid is to provide a site to initiate the “ladder” formation in the oxidation step, and thus lower the temperature at which the reaction occurs and reduce the exotherm. Acrylic precursors are usually made by air gap spinning, as it allows higher line speed and the small bundle size is not a serious drawback. One exception is the Courtaulds (now Acordis) process, which uses wet spinning to produce a splittable tow; Toray is reported to use both wet- and air-gap processes to produce precursor. Increased stretch orientation is required to generate the high tenacity and modulus required in a precursor. It has been shown that precursor properties translate directly to carbon fiber properties (89). Precursor fiber is roll dried and not relaxed subsequent to drying. Special attention must be paid to the electrolyte content of the fiber and to drying conditions in order to produce a precursor which will perform well in oxidation and carbonization. The use of PAN as a carbon fiber precursor has been reviewed (90,91).

Other Specialty Fibers.

Microdenier. In the late 1980s, producers of polyester introduced “microdenier” products, that offered softer, more luxuriant handle to fabrics. Some acrylic producers have followed. There are no appreciable technical hurdles to producing a fiber with a denier of 0.6–0.9 (0.66–1.00 dtex), but unless commensurate changes are made in line speed or the number of spinneret holes, productivity will suffer. Acrylic microfibers on the market are all staple products, with Sterling in the United States producing a 0.8 dpf acrylic staple product named MicroSupreme and Solutia a 0.95 dpf product called Ginny. Mitsubishi Rayon offers H-129 (1.0 dtex).

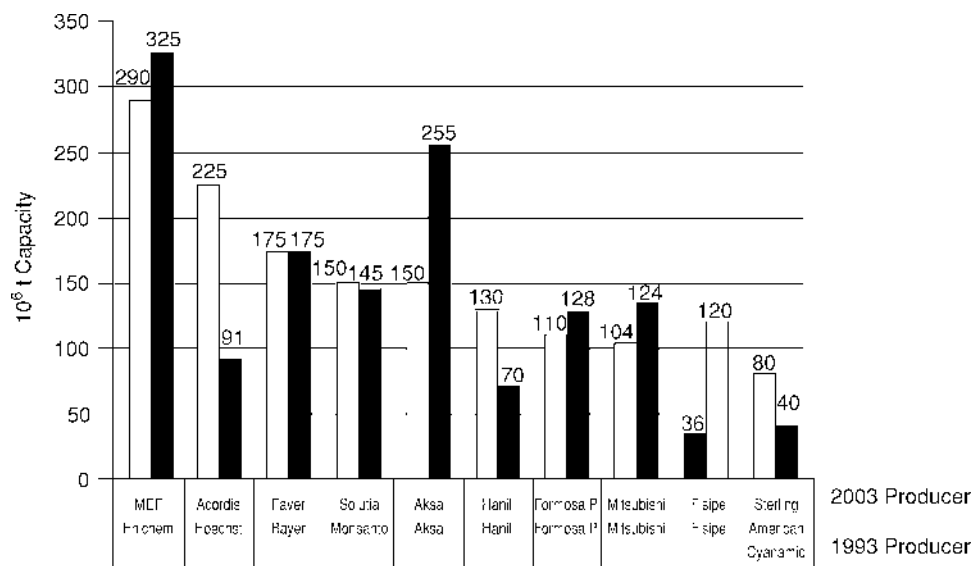


Fig. 15. Leading acrylic producers. □ 1993; ■ 2003.

Antimicrobial. For certain end uses such as half-hose, the ability to inhibit the growth of bacteria and fungi provides a marketing advantage. Several producers offer acrylics which have this characteristic. The antimicrobial effect is achieved by incorporating an additive such as chitosan (from chitan, a polysaccharide from the exoskeleton of crustaceans), metal ions or chlorinated phenols. Commercial examples are New Tafel and Parclean from Mitsubishi Rayon and BioFresh from Sterling.

Fibrillated Fibers. Acrylic fibers are sold in the form of fibrillated pulps for use as highly efficient binders. These fibrillated fibers have a tree-like structure with “limbs” (fibrils) attached to the main “trunk” (fiber). The trunk is 20–50- μ diameter and the limbs range from a few microns to submicron. The product is generated from a special precursor fiber by intense mechanical action. Commercial examples are CCF from Sterling Fibers, Acri-Pulp from Solutia, and Dolanit 10D from Acordis.

Dry pulps are used in dry mix compounding applications such as non-asbestos friction materials. In these applications the product provides green strength for friction material performs. As little as a few percent pulp is required.

Wet pulps are used in specialty paper applications such as speaker cones, filtration, and specialty papers. These pulps have been successfully processed on cylinder, rotoformer, and Fourdrinier paper machines. As little as 15% of a highly fibrillated pulp can interlock other fibers or powders without the need for resin binders.

Conductive Fibers. Acrylic conductive fibers are used in areas where electrostatic discharge is a problem such as electronic device manufacture. Here the applications include dissipative clothing, flooring and work surfaces. Another application is solids/air filtration where discharge has the potential to trigger an explosion. Sterling Fibers manufactures Constructrol, which utilizes a

Table 5. World Acrylic Fiber Production 2003

Country	Company	Location	Process	Capacity, 10 ³ t	Comments
Europe					
Belarus	Novopolosk Polimir	Novopolotskoe	Susp. NaSCN wet	25	10 mod. (acetone)
	Novopolosk Polimir	Novopolotskoe	Sol. DMF wet	35	
Bulgaria	Dimitar Dimov	Burgas	Susp. DMF wet	15	
Germany	Fraver	Dormagen	Susp. DMF dry	115	
		Lingen	Susp. DMAc wet	60	
	Acordis	Kelheim	Susp. DMF wet	11	
	Markische Faser	Premnitz	Susp. DMF wet	Shut	Capacity 48
Hungary	Zoltek	Nyergesujfalu	Susp. DMF wet	35	5 Precursor
Italy	Montefibre	Porto Marghera	Susp. DMAc wet	150	
		Ottana	Susp. DMAc wet	90	
Macedonia	OHIS	Skopje	Sol. NaSCN wet	60	Operates intermittently
Portugal	Fisipe	Lisbon	Susp. DMAc wet	50	
Romania	Melana	Savintsa	Emul acetone wet	46	Modacrylic
Spain	Fisipe	Prat de Liobregat	Sol. NaSCN wet	70	
	Montefibre	Miranda del Ebro	Susp. DMAc wet	85	
Russia	JS Nitron	Saratov	Sol. NaSCN wet	23	
Uzbekistan	Navolazot Production Assn.	Navoi	Sol. NaSCN wet	23	
United Kingdom	Acordis	Grimsby	Sol. NaSCN wet	80	
<i>Total Europe</i>				973	
America					
Argentina	Noy Valesina	Veradero	Sol. DMF wet	20	
Brazil	Sudamericas de Fibras	Camacari	Susp. DMF dry	Shut	Capacity 25
	Crylor Industria	San Jose Dos Campos	Susp. DMF wet	25	
Mexico	CYDSA	El Salto, Jalisco	Susp. DMF wet	100	
	Fibras Sinteticas	Cotaxla, Veracruz	Susp. HNO ₃ wet	28	
	Fibras Nacionales de Acrilica	Altamira, Tamaulipa	Sol. DMF wet	50	
Peru	Fibras Sudamericanas	Lima	Susp. DMF dry	36	

United States	Hexcel	Decatur AL	Susp. NaSCN air	4
	Solutia	Decatur AL	Susp. DMAc wet	145
	Sterling	Pace FL	Susp. NaSCN wet	40
<i>Total America</i>				428
Japan	Asahi	Fuji	Susp. HNO ₃ wet	Shut
	Japan Exlan	Saidaiji	Susp. NaSCN wet	59
	Kanebo	Hofu	Susp. DMF wet	38
	Kanegafuchi	Takasago	Emul acetone wet	55
	Mitsubishi Rayon	Otake	Susp. DMAc wet	119
	Mitsubishi Rayon	Otake	Susp. DMF dry	5
	Toho Rayon	Mishima	Sol. ZnCl ₂ wet	50
	Toray	Ehima	Sol. DMSO wet	44
<i>Total Japan</i>				370
China	Anqing Petrochemical	Anqing, Anhui Prov.	Susp. NaSCN wet	70
	Daqing Petrochem Acry. Fiber	Daqing, Heilongjiang P.	Susp. NaSCN wet	54
	Daqing Petrochem Chem Fiber	Daqing, Heilongjiang P.	Susp. NaSCN wet	10
	Daqing Refin-chem Acry. Fiber	Daqing, Heilongjiang P.	Susp. NaSCN wet	30
	Fushun Petrochem. Acrylic	Fushun, Liaoning Prov.	Susp. DMF dry	30
	Fushun Flame-retard. Acry.	Fushun, Liaoning Prov.	Susp. acetone dry	5
	Gaoglai No. 2 Chemical Plant	Shanghai	Sol. NaSCN wet	7.5
	Jilin Chemical Fiber	Jilin, Jilin Prov.	Susp. DMAc wet	70
	Jinyong Acrylic Fiber Co.	Zhejiang Prov.	Susp. DMF dry	30
	Lanzhou Chemical Fiber Plant	Lanzhou, Gansu Prov.	Susp. NaSCN wet	20
	Maoming Acrylic Fiber	Maoming, Guangdong P	Susp. DMF dry	30
	Qinghuangdao Acrylic Fibre	Qinghuangdao, Hebei P.	Susp. DMF wet	50
	Qilu Petrochem. Acry. Fiber	Zibo, Shandong Prov.	Susp. DMF dry	54
	Shanghai Petrochemical	Shanghai	Susp. DMF dry	120
	Xunyin Chemical Fiber Co.	Zibo, Shandong Prov.	Sol. NaSCN wet	28
<i>Total China</i>				608.5

Table 5. (Continued)

Country	Company	Location	Process	Capacity, 10 ³ t	Comments
Other Asia					
Indonesia	Golden Key	Serang	Susp. DMF dry	Shut	Capacity 40
India	Consolidated Fibres	Haldia W. Bengal	Susp. NaSCN wet	Shut	Capacity 12
	Indian Acrylics	Sangrur Punjab	Susp. DMAc wet	36	
	J. K. Synthetics	Kota Rajasthan	Susp. DMAc wet	Shut	
	Indian Petrochemicals	Baroda Gujarat	Susp. HNO ₃ wet	15	
	Indian Petrochemicals	Baroda Gujarat	Susp. DMF dry	12	
	Pasupati Acrylon	Thakurdwara, Uttar Pradesh	Susp. DMF wet	20	
	Vardhman	Gujarat	Susp. NaSCN wet	17	
Pakistan	Dewan Saiman	Hattar, North-west Frontier		25	
South Korea	Hanil	Masan, Kyongsangnam-do	Susp. HNO ₃ wet	90	
	Tae Kwang Industrial Co.	Ulsan, Kyongsangnam-do	Susp. NaSCN wet	92	
Taiwan	Tong Hwa Synthetic Fiber	Chupel City, Hsinchu Halen	Susp. NaSCN wet	54	
	Formosa Plastic	Jenwu, Kaoshiung Hsien	Susp. HNO ₃ wet	95	
Thailand	Thai Acrylic Fiber	Sara Buri	Susp. NaSCN wet	57	
<i>Total Other Asia</i>				513	15.9%
Middle East					
Iran	Polyacryl Iran	Isfahan	Susp. DMF dry	39	
South Africa	Sasol Industries	Durban	Sol. NaSCN wet	Shut	Capacity 40
Turkey	Aksa	Yalova	Susp. DMAc wet	255	
	Yalova Elyaf	Yalova	Susp. DMF wet	35	
<i>Total Middle East</i>				329	
<i>Total World</i>				3221.5	

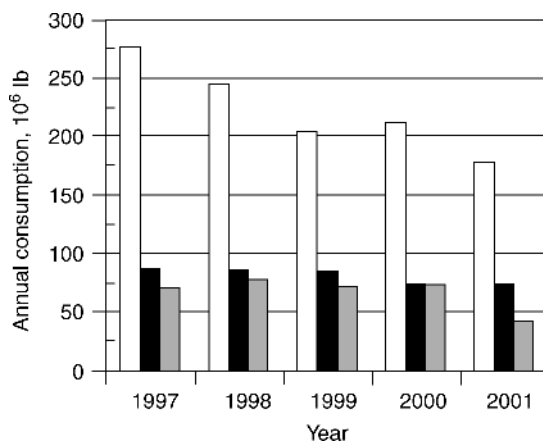


Fig. 16. U.S. acrylic fiber consumption (excluding carbon fibers). □ Apparel; ■ home furnishings; ▒ industrial and nonwovens.

Table 6. U.S. Shipments of Acrylic and Modacrylic for Apparel Markets, 10³ t

Year	Sweaters	Socks	Craft	Pile	Fleece
1995	24.1	9.5	11.8	6.4	28.6
1996	25.0	9.1	11.8	6.4	33.6
1997	30.0	10.0	10.0	8.2	27.3
1998	22.3	10.5	9.1	8.6	21.8
1999	14.1	8.6	9.1	7.7	15.9

combination of conductive carbon in the fiber and a conductive polymer attached to the fiber surface. Tex-Stat markets Thunderon, which uses a chemically bonded copper sulfide technology.

Economic Aspects

As has been mentioned earlier, the focus of acrylic production has moved to Asia which now accounts for 46% of world capacity. The most recent information on world acrylic capacity is listed in Table 5 (92). China leads in building new acrylic capacity with 16 plants as of 2000 and 19% of world capacity versus 8 plants and 9% of world capacity only 7 years earlier (93). Conversely, Europe, which had 38% of capacity in 1993 now has 29%. The changes in capacity and ownership of the major producers are shown graphically in Figure 15.

Markets for acrylic fiber in developed countries have been stagnant or declining as shown in the example for the United States in Figure 16. Many acrylic articles such as sweaters come into the United States as finished goods from Asia. The volumes consumed in U.S. apparel markets are shown in Table 6. All developed countries face a similar situation due to the disparity of labor costs. Losses of volume in western Europe in the late 1990s have been less severe than

Table 7. Western European Consumption of Acrylic Fiber, 10³ t

Year	Weaving	Knitting	Carpet	Others	Total
1995	77	201	12	12	302
1996	76	225	10	12	323
1997	52	280	7	7	346
1998	48	248	7	7	310
1999	48	244	11	7	310
2000	43	245	7	7	301

in the United State, but still ominous as shown in Table 7 (94). The next decade will likely continue the exodus of capacity from the United State, Europe, and Japan.

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ACRYLONITRILE AND ACRYLONITRILE POLYMERS

Introduction

Acrylonitrile (also called acrylic acid nitrile, propylene nitrile, vinyl cyanide, propenoic acid nitrile) is a versatile and reactive monomer (1) which can be polymerized under a wide variety of conditions (2) and copolymerized with an extensive range of other vinyl monomers (3). Since its U.S. commercial debut in 1940, acrylonitrile has been one of the most important building blocks of the polymer industry. This has been demonstrated by the steady production growth of acrylonitrile to more than 4,000,000 t produced worldwide each year. Today, over 90% of the worldwide acrylonitrile production each year uses the Sohio-developed propylene ammoxidation process. Acrylonitrile is among the top 50 chemicals produced

in the United States, as a result of the tremendous growth in its use as a starting material for a wide range of chemicals and polymer products. Acrylic fibers remain the largest user of acrylonitrile. Other significant uses are in styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) resins and nitrile elastomers, and as an intermediate in the production of adiponitrile and acrylamide.

Acrylonitrile Monomer

Physical Properties. Acrylonitrile (C_3H_3N , mol wt = 53.064) is an unsaturated molecule having a carbon-carbon double bond conjugated with a nitrile group. It is a colorless liquid, with the faintly pungent odor of peach pits. Its properties are summarized in Table 1. Acrylonitrile is miscible with most organic solvents, including acetone, benzene, carbon tetrachloride, ether, ethanol, ethyl acetate, ethylene cyanohydrin, liquid carbon dioxide, methanol, petroleum ether, toluene, xylene, and some kerosenes. Table 2 lists the azeotrope compositions of acrylonitrile with some of those solvents. Other important properties are reported in the literature: vapor pressure, solubility in water, and partial vapor pressure over its aqueous solutions (4,5); the partition of acrylonitrile between water and styrene (6); vapor-liquid equilibria and boiling temperatures for acrylonitrile-acetonitrile-water systems (7); high pressure-volume isotherms and temperature-volume isobar (8); electron diffraction and infrared spectral data (4); and Raman and uv spectra (9).

Chemical Properties. The presence of both a double bond and an electron-accepting nitrile group permits acrylonitrile to participate in a large number of addition reactions and polymerizations. The chemical reactions of acrylonitrile have been discussed in great length and detail (10,11). A brief summary follows.

Reactions of the Nitrile Group.

Hydration and Hydrolysis. In concentrated 85% sulfuric acid, partial hydrolysis of the nitrile group produces acrylamide sulfate, which upon neutralization yields acrylamide; this is the basis for acrylamide's commercial production. In dilute acid or alkali, complete hydrolysis occurs to yield acrylic acid.

Alcoholysis. Reactions with primary alcohols, catalyzed by sulfuric acid, convert acrylonitrile to acrylic esters. In the presence of alcohol and anhydrous halides, imido ethers are formed.

Reactions with Olefins and Alcohols. The Ritter reaction occurs with compounds such as olefins and secondary and tertiary alcohols which form carbonium ions in acid, and N-substituted acrylamides are formed.

Reactions with Aldehydes and Methylol Compounds. Catalyzed by sulfuric acid, formaldehyde and acrylonitrile react to form either 1,3,5-triacrylylhexahydro-s-triazine or *N,N'*-methylenebisacrylamide, depending on the conditions. Similarly, in the presence of sulfuric acid, *N*-methylolbenzamide reacts to yield mixed bisamides. *N*-Methylolphthalimide reacts to give *N*-phthalimidomethylacrylamide.

Table 1. Physical Properties of Acrylonitrile Monomer^a

Property	Value
Molecular weight	53.06
Boiling point, °C	
At 101.3 kPa ^b	77.3
At 66.65 kPa	64.7
At 33.33 kPa	45.5
At 13.33 kPa	23.6
At 6.665 kPa	8.7
Critical pressure, kPa	3.535×10^3
Critical temperature, °C	246.0
Cryoscopic constant, mol%/°C	2.7
Density, g/L	
At 20°C	806.0
At 25°C	800.4
At 41°C	783.9
Dielectric constant at 33.5 MHz	38
Dipole moment, C·m ^c	
Liquid	1.171×10^{-29}
Vapor	1.294×10^{-29}
Entropy, vapor at 25°C, 101.3 kPa, J/(mol·K) ^d	273.9
Entropy of polymerization, liquid, 25°C, J/(mol·K)	-109 ^e
Explosive mixture with air at 25°C, vol%	
Lower limit	3.05
Upper limit	17.0 ± 0.5
Flash point (tag open cup), °C	-5
Freezing point, °C	-83.55 ± 0.05
Gibbs energy of formation, vapor at 25°C, kJ/mol	195.4
Heat capacity, specific, liquid, kJ/(kg·K)	2.094
Heat capacity, specific, vapor, kJ/(kg·K)	
At 50°C, 101.3 kPa	1.204
<i>T</i> (K) from 77–1000°C, at 101.3 kPa	$0.53 + 26.23 \times 10^{-4}T$ $-86.03 \times 10^{-8}T^2$
Heat of combustion, liquid at 25°C, kJ/mol	-1.7615×10^3
Heat of formation at 25°C, kJ/mol	
Vapor	189.83
Liquid	151.46
Heat of fusion, kJ/mol	6.635×10^3
Heat of polymerization, kJ/mol	-72.4 ± 2.1
Heat of polymerization at 74.5°C, kJ/mol	-76.5 ^f
Heat of vaporization at 101.3 kPa, kJ/mol	32.65
Ignition temperature, °C	481.0
Molar refraction, D line	15.67
Parachor at 40.6°C	151.1
Polarizability at 25°C	266
Refractive index	
n_D^{20}	1.3911–1.39142
n_D^{25}	1.3888
t from 10–35°C	$n_D^t = 1.4022 - 0.000539t$
n_C^{20}	1.38836
n_F^{20}	1.39890

Table 1. (Continued)

Property	Value
n_{D}^{20}	1.4078
Solubility parameter, (J/mL) ^{1/2}	21.48
Surface tension at 24°C, mN/m (=dyn/cm)	27.3
Surface tension of aqueous solution, c from 0–6 wt%, d , mN/m (=dyn/cm)	$c = 0.223d - 0.0018d^2 + 0.00013d^3$
Vapor density, relative	1.83 (air = 1.0)
Viscosity at 25°C, mPa·s (=cP)	$\log p = 6.6428 - 1.6447 \times 10^3/T$ (K) 0.34

^aRefs. 4, 13, and 14.^bTo convert kPa to mm Hg, multiply by 7.5.^cTo convert C·m to debyes, multiply by 2.997×10^{29} .^dTo convert J to cal, divide by 4.184.^eRef. 15.^fRef. 16.

Reactions of the Double Bond.

Diels-Alder Reactions. Acrylonitrile acts as a dienophile with conjugated carbon–carbon double bonds to form cyclic compounds. On the other hand, acrylonitrile can act as a diene. For example, with tetrafluoroethylene 2,2,3,3-tetrafluorocyclobutanecarbonitrile forms; and with itself, dimers of *cis*- and *trans*-cyclobutanedicarbonitriles form at high temperatures and pressure. The activation energy for acrylonitrile cyclodimerization has been reported to be 90.4 kJ/mol (12).

Hydrogenation. With metal catalysts, an excellent yield of propionitrile is attained, which can be further hydrogenated to propylamine.

Halogenation. At low temperatures, halogenation proceeds slowly to produce 2,3-dihalopropionitriles. In the presence of pyridine, addition of chlorine forms 2,3-dichloropropionitrile quantitatively. At elevated temperatures, without uv light, 2,2,3-trihalopropionitrile is obtained; with uv light, both 2,2,3- and 2,3,3-isomers are formed. Simultaneous chlorination and alcoholysis occur to give 2,3-dichloropropionic acid esters.

Hydroformylation. In a process also known as the oxo-synthesis, acrylonitrile reacts with a mixture of hydrogen and carbon monoxide, catalyzed by cobalt octacarbonyl, to give β -cyanopropionaldehyde. This reacts with hydrogen cyanide

Table 2. Azeotrope Compositions of Acrylonitrile^a

Other component	Boiling point, °C	Acrylonitrile, wt%
Benzene	73.3	47
Carbon tetrachloride	66.2	21
Chlorotrimethylsilane	57	7
Methanol	61.4	39
2-Propanol	71.7	56
Tetrachlorosilane	51.2	11
Water	71	88

^aRef. 4.

and ammonia, and then hydrolysis produces glutamic acid on a large commercial scale.

Hydrodimerization. The reductive dimerization of acrylonitrile can be done either chemically or electrochemically to form adiponitrile. Hydrodimerization with its derivatives also takes place.

Reactions with Azo Compounds. Meerwein reactions of diazonium halides with acrylonitrile take place at low temperatures, catalyzed by cupric chloride, to yield 2-halo-3-arypropionitriles. Reactions with diazomethane compounds lead to pyrazolines and finally cyclopropanes. Reactions with 9-diazofluorene produce a cyanocyclopropane derivative, with the generation of nitrogen. Phenyl azide reacts with acrylonitrile to yield a heterocyclic nitrile at room temperature or an open-chain nitrile at elevated temperatures.

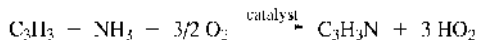
Reactions of Both Functional Groups. Hydrolysis of acrylonitrile catalyzed by hydrochloric acid yields 3-chloropropionic acid. Alcoholysis and chlorination occur simultaneously in the presence of sulfuric acid. Similarly, alcoholysis and hydrochlorination also occur. Addition of both ammonia and hydrogen produces both trimethylenediamine and propylamine. Treatment of acrylonitrile with hydrogen peroxide at neutral to slightly alkaline pH, yields glycidamide. Similarly, treatment with water, containing ammonium sulfide or a weak base, forms bis(2-carboxamidoethyl)sulfide or poly(β -alanine).

Cyanoethylation Reactions (Michael-Type Additions). Most compounds with a labile hydrogen atom can add on the double bond of acrylonitrile to form cyanoethyl groups; that is, the primary products are 3-substituted propionitriles.



A large number of useful reactions fall into this category. Examples of these reactions are carbon cyanoethylation in which aldehydes, ketones, esters, nitriles, nitro compounds, sulfones, aliphatic and aromatic hydrocarbons, or haloforms add to acrylonitrile; nitrogen cyanoethylation where amines, ammonia, anilines, or amides add; oxygen cyanoethylation where alcohols, phenols, water, hydroperoxides, oximes, or hydrogen peroxide react; sulfur cyanoethylation in which sulfides, bisulfides, or sulphydryl compounds add; hydrogen halide cyanoethylphosphonates, boranes, silanes, or tin hydrides. In addition, many natural and synthetic polymers possessing labile hydrogen atoms, such as cotton, jute, gums, lignin, proteins, modified cellulose, poly(vinyl alcohol) (PVC), and acetone-formaldehyde and methyl ethyl ketone-formaldehyde condensates, react with acrylonitrile to yield cyanoethyl derivatives.

Manufacture of Acrylonitrile. Acrylonitrile is produced in commercial quantities almost exclusively by the vapor-phase catalytic propylene ammoxidation process developed by Sohio (now BP Chemicals) (17).



A schematic diagram of the commercial process is shown in Figure 1. The commercial process uses a fluid-bed reactor in which propylene, ammonia, and air contact a solid catalyst at 400–510°C and 49–196 kPa (0.5–2.0 kg/cm²) gage.

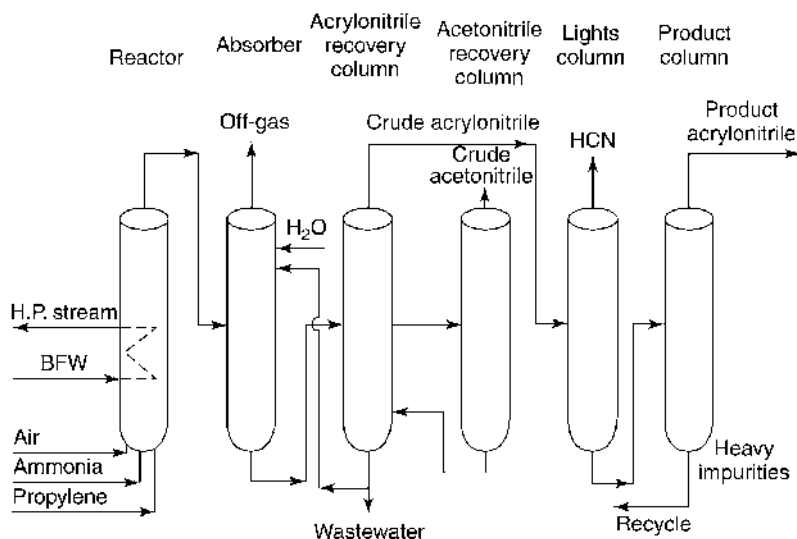


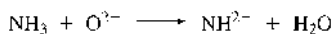
Fig. 1. Process flow diagram of the commercial propylene ammoxidation process for acrylonitrile. BFW is boiler feed water.

It is a single-pass process with about 98% conversion of propylene, and uses about 1.1 kg of propylene per kg of acrylonitrile produced. Useful by-products from the process are HCN (about 0.1 kg per kg of acrylonitrile), which is used primarily in the manufacture of methyl methacrylate, and acetonitrile (about 0.03 kg per kg of acrylonitrile), a common industrial solvent. In the commercial operation the hot reactor effluent is quenched with water in a countercurrent absorber and any unreacted ammonia is neutralized with sulfuric acid. The resulting ammonium sulfate can be recovered and used as a fertilizer. The absorber off-gas containing primarily N₂, CO, CO₂, and unreacted hydrocarbon is either vented directly or first passed through an incinerator to combust the hydrocarbons and CO. The acrylonitrile-containing solution from the absorber is passed to a recovery column that produces a crude acrylonitrile stream overhead that also contains HCN. The column bottoms are passed to a second recovery column to remove water and produce a crude acetonitrile mixture. The crude acetonitrile is either incinerated or further treated to produce solvent quality acetonitrile. Acrylic fiber quality (99.2% minimum) acrylonitrile is obtained by fractionation of the crude acrylonitrile mixture to remove HCN, water, light ends, and high boiling impurities. Disposal of the process impurities has become an increasingly important aspect of the overall process, with significant attention being given to developing cost-effective and environmentally acceptable methods for treatment of the process waste streams. Current methods include deep-well disposal, wet air oxidation, ammonium sulfate separation, biological treatment, and incineration (18).

Although the manufacture of acrylonitrile from propylene and ammonia was first patented in 1949 (19), it was not until 1959 when Sohio developed a catalyst capable of producing acrylonitrile with high selectivity, that commercial manufacture from propylene became economically viable (20). Production

improvements over the past 30 years have stemmed largely from development of several generations of increasingly more efficient catalysts. These catalysts are multicomponent-mixed metal oxides mostly based on bismuth-molybdenum oxide. Other types of catalysts that have been used commercially are based on iron-antimony oxide, uranium-antimony oxide, and tellurium-molybdenum oxide.

Fundamental understanding of these complex catalysts and the surface-reaction mechanism of propylene ammoxidation has advanced substantially since the first commercial plant began operation. Mechanisms for selective ammoxidation of propylene over bismuth molybdate and antimonate catalysts have been published (21). The rate-determining step is the abstraction of an α -hydrogen of propylene by oxygen in the catalyst to form a π -allyl complex on the surface (21–23). Lattice oxygens from the catalyst participate in further hydrogen abstraction, followed by oxygen insertion to produce acrolein in the absence of ammonia or nitrogen insertion to form acrylonitrile in the presence of ammonia (24–27). The oxygens removed from the catalyst in these steps are replenished by gas-phase oxygen, which is incorporated into the catalyst structure at a surface site separate from the site of propylene reaction. In the ammoxidation reaction, ammonia is activated by an exchange with O^{2-} ions to form isoelectronic NH_2^- moieties according to the following:



These are the species inserted into the allyl intermediate to produce acrylonitrile.

The active site on the surface of selective propylene ammoxidation catalyst contains three critical functionalities associated with the specific metal components of the catalyst (28–30): an α -H abstraction component such as Bi^{3+} , Sb^{3+} , or Te^{4+} ; an olefin chemisorption and oxygen or nitrogen insertion component such as Mo^{6+} or Sb^{5+} ; and a redox couple such as Fe^{2+}/Fe^{3+} or Ce^{3+}/Ce^{4+} to enhance transfer of lattice oxygen between the bulk and the surface of the catalyst. The surface and solid-state mechanisms of propylene ammoxidation catalysis have been determined using Raman spectroscopy (31,32), neutron diffraction (33–35), x-ray absorption spectroscopy (36,37), x-ray diffraction (38–40), pulse kinetic studies (26,27), and probe molecule investigations (41).

Other Acrylonitrile Processes. Processes rendered obsolete by the propylene ammoxidation process (42) include the ethylene cyanohydrin process (43–45) practiced commercially by American Cyanamid and Union Carbide in the United States and by I. G. Farben in Germany. The process involves the production of ethylene cyanohydrin by the base-catalyzed addition of HCN to ethylene oxide in the liquid phase at about 60°C, and subsequent dehydration.

A second commercial route to acrylonitrile used by DuPont, American Cyanamid, and Monsanto was the catalytic addition of HCN to acetylene (46). The reaction occurs by passing HCN and a 10:1 excess of acetylene into dilute HCl at 80°C in the presence of cuprous chloride as the catalyst. These processes use expensive C_2 hydrocarbons as feedstocks and thus have higher overall acrylonitrile production costs compared to the propylene-based process technology. The last commercial plants using these process technologies were shutdown by 1970.

Table 3. Worldwide Acrylonitrile Production,^a 10³ t

Region	1997	1998 (Estimated)
Western Europe	1073	1112
Eastern Europe	189	182
United States	1483	1324
Japan	729	730
Far East/Asia	779	841
African/Middle East	147	152
Latin America/Mexico	232	246
<i>Total production</i>	<i>4642</i>	<i>4587</i>

^aRef. 62.

Other routes to acrylonitrile, none of which achieved large-scale commercial application, are acetaldehyde and HCN (47), propionitrile dehydrogenation (48, 49), and propylene and nitric oxide (50,51).

Numerous patents have been issued disclosing catalysts and process schemes for the manufacture of acrylonitrile from propane. These include the direct heterogeneously catalyzed ammoxidation of propane to acrylonitrile, using mixed metal oxide catalysts (52–55).

A two-step process involving conventional nonoxidative dehydrogenation of propane to propylene in the presence of steam, followed by the catalytic ammoxidation to acrylonitrile of the propylene in the effluent stream without separation, is also disclosed (56).

Because of the large price differential between propane and propylene, which has ranged from \$155/t to \$355/t between 1987 and 1989, a propane-based process may have the economic potential to displace propylene ammoxidation technology eventually. Methane, ethane, and butane, which are also less expensive than propylene, and acetonitrile have been disclosed as starting materials for acrylonitrile synthesis in several catalytic process schemes (57,58).

Economic Aspects (Monomer). The propylene-based process developed by Sohio was able to displace almost all other commercial production technologies because of its substantial advantage in overall production costs, primarily due to lower raw material costs. Raw material costs, less by-product credits, account for about 60% of the total acrylonitrile production cost for a world-scale plant. The process has remained economically advantaged over other process technologies since the first commercial plant in 1960 because of the higher acrylonitrile yields, resulting from the introduction of improved commercial catalysts. Reported per-pass conversions of propylene to acrylonitrile have increased from about 65 to over 80% (17,59–61).

More than half of the worldwide acrylonitrile production is situated in Western Europe and the United States (Table 3). In the United States, production is dominated by BP Chemicals with the Sohio Process, with more than a third of the domestic capacity (Table 4). Nearly one-half of the U.S. production was exported in 1997 (Table 5), with most going to Far East Asia.

Far East Asian producers, especially in the People's Republic of China (PRC), have not been able to satisfy their increasing domestic demand in

Table 4. U.S. Acrylonitrile Producers^a

Company	Approximate capacity, ^b 10 ³ t/year
BP Chemicals	640
Solutia, Inc.	260
Sterling Chemicals	360
E. I. du Pont de Nemours & Co., Inc.	185
Cytec Industries	220
<i>Total production</i>	<i>1665</i>

^aRef. 62.^bAs of 1997.**Table 5. U.S. Acrylonitrile Exports,^a 10³ t**

Destination	1997	1996
Far East/Asia	334	378
Japan	92	107
Western Europe	91	57
Canada	7	6
Latin America/Mexico	82	50
Middle East/Africa	91	57
<i>Total export</i>	<i>697</i>	<i>655</i>

^aRef. 62.**Table 6. World Acrylonitrile Demand, 10³ t/year**

Region	1998 (Estimated)	1997	1995	1990	1986
Western Europe	1109	1116	1045	1136	1187
Eastern Europe	141	150	171	311	262
Japan	726	723	674	664	640
North America	781	800	756	641	638
Far East/Asia	1297	1264	1025	646	462
Africa/Middle East	261	257	223	135	142
Latin America/Mexico	302	281	244	206	213
<i>Total demand</i>	<i>4617</i>	<i>4591</i>	<i>4138</i>	<i>3739</i>	<i>3543</i>

recent years. Consequently, the percentage of U.S. production exported grew from around 10% in the mid-1970s to approximately 42% in 1997.

In addition, the higher propylene costs relative to the United States generally makes it more economical to import acrylonitrile from the United States than to install new domestic production. Nevertheless, additions to Far East Asian acrylonitrile production capacity have been made in the 1990s, notably in South Korea. Table 6 provides a breakdown of worldwide demand between 1986 and 1998. Growth in demand has averaged about 3% per year.

Analytical and Test Methods. Numerous instrumental and chemical techniques are available for the determination of acrylonitrile. The method of choice is directed by the concentration and the medium involved. For direct assay of acrylonitrile, titrimetric procedures are frequently used. Dodecyl mercaptan

reacts with acrylonitrile under base catalysis; excess mercaptan is then back-titrated with an acid bromate-iodide solution (63), or alternatively, for colored solutions, with silver nitrate (64). Hydrolysis of the nitrile with strong base generates ammonia, which can then be determined by Nessler's reagent (65).

For dilute solutions, both gas chromatography (66) and polarography (67) are rapid, sensitive, and precise. Small amounts of acrylonitrile can be separated from other components by azeotropic distillation with alcohols, followed by polarographic (67,68) or chromatographic (69,70) analysis.

For monitoring of acrylonitrile in ambient air, a measured quantity of an air sample is drawn through a charcoal tube, followed by quantitative extraction with a carbon disulfide-acetone (98:2) mixture for gas chromatographic analysis. Reliable results can be attained even when <1-ppm acrylonitrile is present (71). A comprehensive review and a description of the development of environmental test methods for air, water, soil, and sediment samples have been done (72).

Storage and Transport. Acrylonitrile must be stored in tightly closed containers in cool, dry, well-ventilated areas away from heat, sources of ignition, and incompatible chemicals. Storage vessels, such as steel drums, must be protected against physical damage, with outside detached storage preferred. Storage tanks and equipment used for transferring acrylonitrile should be electrically grounded to reduce the possibility of static spark-initiated fire or explosion. Acrylonitrile is regulated in the workplace by OSHA (29 CFR 1910).

Acrylonitrile is transported by rail car, barge, and pipeline. Department of Transportation (DOT) regulations require labeling acrylonitrile as a flammable liquid and poison. Transport is regulated under DOT 49 CFR 172.101. Bill of lading description is Acrylonitrile, Inhibited, 3, 6.1, UN 1093, PGI, RQ.

Health and Safety Factors. Acrylonitrile is absorbed rapidly and distributed widely throughout the body following exposure by inhalation, skin contact, or ingestion. However, there is little potential for significant accumulation in any organ, with most of the compound being excreted primarily as metabolites in urine. Acrylonitrile is metabolized primarily by two pathways: conjugation with glutathione and oxidation. Oxidative metabolism leads to the formation of an epoxide, 2-cyanoethylene oxide, that is either conjugated with glutathione or directly hydrolyzed by epoxide hydrolase.

The acute toxicity of acrylonitrile is relatively high, with 4-h LC₅₀s in laboratory animals ranging from 300 to 900 mg/m³ and LD₅₀s from 25 to 186 mg/kg (73,74). Signs of acute toxicity observed in animals include respiratory tract irritation and two phases of neurotoxicity, the first characterized by signs consistent with cholinergic overstimulation and the second being CNS (central nervous system) dysfunction, resembling cyanide poisoning. In cases of acute human intoxication, effects on the CNS, characteristic of cyanide poisoning, and effects on the liver, manifested as increased enzyme levels in the blood, have been observed.

Acrylonitrile is a severe irritant to the skin, eyes, respiratory tract, and mucous membranes. It is also a skin sensitizer. Acrylonitrile is a potent tumorigen in the rat. Tumors of the CNS, ear canal, and gastrointestinal tract have been observed in several studies following oral or inhalation exposure. The mechanism of acrylonitrile's tumorigenesis in the rat and the relevance of these findings to humans are not clear. Available data are insufficient to support a consensus view

or a plausible mode of action. There is evidence for weak genotoxic potential, but no evidence of DNA-adduct formation in target tissues.

Indications are that oxidative stress and resulting oxidative DNA damage may play a role. There is extensive occupational epidemiology data on acrylonitrile workers. These investigations have not produced consistent, convincing evidence of an increase in cancer risk, although questions remain about the power of the database to detect small excesses of rare tumors. In 1998, The International Agency for Research on Cancer reevaluated the cancer data for acrylonitrile and made a rare decision to downgrade the cancer risk classification (from “probably carcinogenic to humans” to “possibly carcinogenic to humans”) based primarily on the growing epidemiology database (75).

Experimental evaluations of acrylonitrile have not produced any clear evidence of adverse effects on reproductive function or development of offspring at doses below those producing paternal toxicity. The results of genotoxicity evaluations of acrylonitrile have been mixed. Positive findings *in vitro* have occurred mainly at exposures associated with cellular toxicity, and the most reliable *in vitro* tests have been negative.

Acrylonitrile will polymerize violently in the absence of oxygen if initiated by heat, light, pressure, peroxide, or strong acids and bases. It is unstable in the presence of bromine, ammonia, amines, and copper or copper alloys. Neat acrylonitrile is generally stabilized against polymerization with trace levels of hydroquinone monomethyl ether and water.

Acrylonitrile is combustible and ignites readily, producing toxic combustion products such as hydrogen cyanide, nitrogen oxides, and carbon monoxide. It forms explosive mixtures with air and must be handled in well-ventilated areas and kept away from any source of ignition, since the vapor can spread to distant ignition sources and flash back.

Federal regulations, (40 CFR 261) classify acrylonitrile as a hazardous waste and it is listed as Hazardous Waste Number U009. Disposal must be in accordance with federal (40 CFR 262, 263, 264, 268, 270), state, and local regulations, and occur only at properly permitted facilities. Strict guidelines exist for clean-up and notification of leaks and spills. Federal notification regulations require that spills or leaks in excess of 100 lb (45.5 kg) be reported to the National Response Center. Substantial criminal and civil penalties can result from failure to report such discharges into the environment.

Acrylonitrile in Air. As a consequence of the 1977 interim results of both the Dow and DuPont studies, OSHA issued an emergency temporary standard on Jan. 17, 1978, specifying that the 8-h time-weighted average exposure to airborne acrylonitrile should not exceed 2 ppm; prior to 1977, 20 ppm was allowed. This standard covered all workplaces manufacturing or using acrylonitrile as a raw material, as well as fabrication facilities processing acrylonitrile-based polymers.

The permanent OSHA standard was implemented on Nov. 2, 1980, and it establishes a maximum permissible exposure limit for the vapor of acrylonitrile at 2 ppm as an 8-h time-weighted average, a ceiling limit at 10 ppm as a 15-min time-weighted average, and an action level at 1 ppm as an 8-h time-weighted average. Eye and skin contact with liquid acrylonitrile is prohibited. Other provisions include notification of regulated areas, methods of compliance, respiratory protection, emergency situations, protective clothing and equipment,

housekeeping, waste disposal, hygiene facilities and practices, medical surveillance, employee information and training, signs and labels, record keeping, observation of monitoring, etc (76).

Environmental monitoring around 11 U.S. industrial sites which produce acrylonitrile, acrylamide, acrylic and modacrylic fibers, ABS, SAN, and nitrile elastomers was conducted in 1977. Acrylonitrile in the air was very low, ranging from 0.1 to 325 ng/L (4.3 ppm); and in soils or sediments, none (72). Studies of the atmosphere surrounding several types of commercial equipment processing a high acrylonitrile copolymer (Barex 210) indicate no evidence of acrylonitrile under normal operating conditions (1163). Some typical emission sources in the acrylonitrile-polymerization industry have been identified, control techniques suggested, and plan of action discussed (72). Approaches to remedy toxic chemical problems and provide a safe environment have also been suggested (77).

Acrylonitrile in Polymers. The very low amount of residual acrylonitrile in finished resins or products (ca 1 ppm in acrylic and modacrylic fibers, 20–50 ppm in ABS and SAN) does not pose the threat of acrylonitrile migration or release under normal intended use and handling conditions. Materials made from acrylonitrile are exempt from OSHA regulations, provided they are not capable of releasing acrylonitrile in airborne concentrations in excess of 1 ppm as a 9-h time-weighted average, under the expected conditions of processing, use, and handling, and not heated above 77°C. Thus, certain finished polymers and their fabricated products, such as ABS, SAN, nitrile barrier resins, solid nitrile elastomers, and acrylic and modacrylic fibers, are exempt. Polymers and copolymers of acrylonitrile per se are riskless, but there is concern regarding acrylonitrile in food containers (qv) because of the possibility of migration from the finished products to the contained foodstuff. Therefore, the use of the polymers for food-contact applications requires compliance with governmental regulations.

Well-sealed containers of carbon or stainless, tin-coated metals, or brown glass bottles can be used and labeled DANGER, CONTAINS ACRYLONITRILE, CANCER HAZARD. They should be properly grounded and stored in a well-ventilated area free of excessive heat, flames, sparks, or other sources of ignition. Contamination with strong acids or bases, peroxides, or other initiators should be avoided. Acrylonitrile should be handled in a hood or a ventilated area where the concentration will not exceed OSHA-regulated standards. Testing should be done according to OSHA standards to ensure personnel protection and compliance. Protective equipment such as rubber gloves and apron (or liquid-proof uniform), goggles, and face shield should be used. When acrylonitrile is at or above the action level of 1 ppm, respiratory protection should be implemented. A half-face respirator with organic vapor cartridge can provide adequate protection up to 20 ppm; full-face respirator, up to 100 ppm; and supplied air respirator in positive pressure mode with full-face piece, helmet, suit, or hood, up to 4000 ppm.

Uses. Historically, synthetic fibers consume more than half of the acrylonitrile produced throughout the world, and ABS–SAN copolymers are the second largest users (see Table 7). Nitrile elastomers have the longest history of acrylonitrile usage. Worldwide consumption of acrylonitrile increased from 2.5×10^6 in 1976 to 4.6×10^6 t/year in 1998. The trend in consumption over this time period is shown in Table 7 for the principal uses of acrylonitrile: acrylic fiber, ABS

Table 7. Worldwide Acrylonitrile Uses and Consumption, 10³ t

Use	1998 (Estimated)	1997	1995	1990	1986
Acrylic fibers	2615	2628	2313	2242	2350
ABS resins / SAN	1095	1079	996	781	598
Adiponitrile	494	477	446	330	281
NB (AN/BD) Copolymers	144	143	134	143	125
Miscellaneous	269	264	249	243	189
<i>Total consumptions</i>	<i>4617</i>	<i>4591</i>	<i>4138</i>	<i>3739</i>	<i>3543</i>

resins, adiponitrile, nitrile rubbers, elastomers, and SAN resins. Since the 1960s acrylic fibers have remained the major outlet for acrylonitrile production in the United States and especially in Japan and the Far East. Acrylic fibers always contain a comonomer. Fibers containing 85 wt% or more acrylonitrile are usually referred to as *acrylics*, whereas fibers containing 35–85 wt% acrylonitrile are termed modacrylics (see FIBERS, ACRYLIC). Acrylic fibers are used primarily for the manufacture of apparel, including sweaters, fleece wear, and sportswear, as well as for home furnishings, including carpets, upholstery, and draperies. Acrylic fibers consume about 57% of the acrylonitrile produced worldwide. Growth in demand for acrylic fibers in the 1990s was modest, between 2 and 3% per year, primarily from overseas markets. Domestic demand was flat.

ABS resins and adiponitrile are the fastest growing uses for acrylonitrile. ABS resins are second to acrylic fibers as an outlet for acrylonitrile. These resins normally contain about 25% acrylonitrile and are characterized by their chemical resistance, mechanical strength, and ease of manufacture. Consumption of ABS resins increased significantly in the 1980s and 1990s with its growing application as a specialty performance polymer in construction, automotive, machine, and appliance applications. Opportunities still exist for ABS resins to continue to replace more traditional materials for packaging, building, and automotive components. SAN resins typically contain between 25 and 30% acrylonitrile. Because of their high clarity, they are used primarily as a substitute for glass in drinking cups and tumblers, automobile instrument panels, and instrument lenses. The largest increase among the end uses for acrylonitrile has come from adiponitrile, which has grown to become the third largest outlet for acrylonitrile. It is used by Solutia as a precursor for hexamethylenediamine (HMDA, C₆H₁₆N₂) [124-09-4] and is made by a proprietary acrylonitrile electrohydrodimerization process (78). HMDA is used exclusively for the manufacture of nylon-6,6 (see POLYAMIDES). The growth of this acrylonitrile outlet in recent years stems largely from replacement of adipic acid (C₆H₁₀O₄) [124-04-9] with acrylonitrile in HMDA production, rather than from a significant increase in nylon-6,6 demand. The use of acrylonitrile for HMDA production should continue to grow at a faster rate than the other outlets for acrylonitrile, but it will not likely approach the size of the acrylic fiber market for acrylonitrile consumption.

Acrylamide is produced commercially by heterogeneous copper-catalyzed hydration of acrylonitrile (79–82). Acrylamide is used primarily in the form of a polymer, polyacrylamide, in the paper and pulp industry, and in wastewater treatment as a flocculant to separate solid material from wastewater streams

(see ACRYLAMIDE POLYMERS). Other applications include mineral processing, coal processing, and enhanced oil recovery in which polyacrylamide solutions were found effective for displacing oil from rock.

Nitrile rubber finds broad application in industry because of its excellent resistance to oil and chemicals, its good flexibility at low temperatures, high abrasion and heat resistance (up to 120°C), and good mechanical properties. Nitrile rubber consists of butadiene–acrylonitrile copolymers, with an acrylonitrile content ranging from 15 to 45%. In addition to the traditional applications of nitrile rubber for hoses, gaskets, seals, and oil well equipment, new applications have emerged with the development of nitrile rubber blends with PVC. These blends combine the chemical resistance and low temperature flexibility characteristics of nitrile rubber, with the stability and ozone resistance of PVC. This has greatly expanded the use of nitrile rubber in outdoor applications for hoses, belts, and cable jackets, where ozone resistance is necessary.

Other acrylonitrile copolymers have found specialty applications with good gas-barrier and chemical-resistant properties. An example is BP Chemicals' Barex resins which are acrylonitrile–methyl acrylate copolymers grafted on a nitrile rubber. Barex resins are unique barrier resins with the combinations of excellent oxygen barrier, good chemical resistance, and antiscalping properties.

Another application for acrylonitrile is in the manufacture of Carbon fibers. They are produced by pyrolysis of oriented polyacrylonitrile fibers and are used to reinforce composites for high performance applications in the aircraft, defense, and aerospace industries. These applications include rocket engine nozzles, rocket nose cones, and structural components for aircraft and orbital vehicles where light weight and high strength are needed. Other small specialty applications of acrylonitrile are in the production of fatty amines, ion-exchange resins, and fatty amine amides used in cosmetics, adhesives, corrosion inhibitors, and water-treatment resins. Examples of these specialty amines include 2-acrylamido-2-methylpropanesulfonic acid ($C_7H_{13}NSO_4$) [15214-89-8], 3-methoxypropionitrile (C_4H_7NO) [110-67-8], and 3-methoxypropylamine ($C_4H_{11}NO$) [5332-73-0].

Polymerization of Acrylonitrile

Homopolymerization. Pure acrylonitrile does not polymerize readily without initiators or light, but polymerization proceeds rapidly and exothermically in the presence of free radicals or anionic initiators. Oxygen is a very strong inhibitor and forms peroxides. If oxygen is allowed to react to exhaustion, polymerization may then proceed at a very high rate through the thermal decomposition of peroxides, and explosion can occur. Conventional peroxide initiators, such as benzoyl peroxide and hydrogen peroxide, and azo compounds, such as 2,2'-azobis(isobutyronitrile) and 2,2'-azobis(2,4-dimethylvaleronitrile), can be used at moderate temperatures below 100°C. Redox catalysis systems can be used in aqueous media at low temperatures. Initiation can also be induced by light (83) and radiation (84). Polymerization can be carried out in bulk, emulsion, suspension, slurry, or solution.

Continuous Bulk Process. Polyacrylonitrile is not soluble in its monomer and precipitates from the medium. The polymerization exhibits autocatalytic behavior, and as polymerization proceeds, it becomes increasingly difficult to remove the heat of polymerization as viscosity increases. Consequently, in a batch process, the polymerization can run out of control. Therefore, continuous operation is used to overcome the difficulties (85–87). As an example, the following streams are continuously charged into a 2.5-L reactor at 40°C, equipped with an agitator and filled initially with acrylonitrile to one-half of its volume:

- (1) cumene hydroperoxide 10 g/h
- (2) SO₂ (gas) 120 g/h
- (3) dimethylacetamide 3.2 g/h
- (4) 2-mercaptoethanol 8 g/h

After the first 10 min, acrylonitrile is fed into the reactor at 4000 g/h. The effluent from the reactor has 54.6% conversion of acrylonitrile (85). The mechanisms and kinetic models for acrylonitrile bulk polymerization have been described (88–91), as has the study of high pressure polymerization (8).

Continuous Slurry Process. This process is similar to bulk polymerization, but the monomer is isolated into small suspended droplets in an aqueous medium. This provides heat-removal capability and commercial feasibility. In one example (92), a 60-L stainless steel cylindrical reactor is equipped with a turbine agitator and a pump to circulate a portion of the polymerizing medium from the bottom through a heat exchanger, thus removing the heat of polymerization. Three separate streams of a 0.3% H₂SO₄ aqueous solution, a catalyst solution (15% Na₂SO₃ and 4.22% Na₂ClO₃ in water), and a monomer solution (97% acrylonitrile and 3% water) are continuously charged into the reactor at the rates of 22.4, 1.0, and 11.8 kg/h, respectively. At 35°C and 1.69 h of residence time, the conversion is 90% and the polymer has an average molecular weight of ca 75,000.

Emulsion Process. In the following example, redox catalysis is used to achieve rapid polymerization at low temperatures (20–60°C), yielding a polymer with better color than that obtained by the use of other initiator systems where higher temperatures are required.

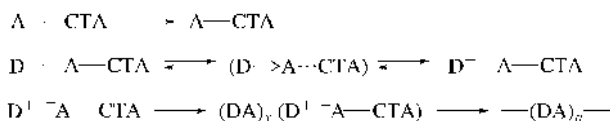
- (1) water 270 parts
- (2) emulsifier (23% sodium salt of sulfonated cumar resin) 26 parts
- (3) ammonium persulfate 0.6 parts
- (4) ammonium bisulfite 0.5 parts
- (5) sodium dihydrogen phosphate 0.8 parts
- (6) dilute H₂SO₄ As required to adjust the solution of pH 4.6

One hundred parts of this solution and 50 parts of acrylonitrile are charged into a reactor. It is then purged with N₂, sealed, and polymerized at 40°C for 2 hs, achieving 85% conversion (93). After polymerization is completed, the polymer is recovered by coagulation with salt (see EMULSION POLYMERIZATION).

Solution Process. The solution process is rather straightforward and is generally used to prepare acrylic polymers suitable for direct wet- or dry-spinning fiber manufacture. Dimethylformamide is one of the best solvents for polyacrylonitrile and is used extensively. In this medium, an overall activation energy for the polymerization has been estimated to be 86.6 kJ/mol (94). Other important solvents are dimethylacetamide, dimethyl sulfoxide, ethylene or propylene carbonate, and concentrated aqueous solutions of NaSCN, HNO₃, H₂SO₄, and ZnCl₂.

Copolymerization. Acrylonitrile copolymerizes readily with electron-donor monomers, and >800 acrylonitrile copolymers have been registered with *Chemical Abstracts*. A comprehensive listing of reactivity ratios for acrylonitrile copolymerizations is available (95). Copolymerization is carried out by bulk emulsion, slurry, or suspension processes. The arrangement of monomer units in acrylonitrile copolymers is most commonly random. Special techniques can be used to achieve specific arrangements.

Alternating Copolymers. Copolymerization of a strong acceptor monomer with a strong donor monomer yields alternating equimolar copolymers; for example, this is the case for maleic anhydride or vinylidene cyanide with styrene. Acrylonitrile, a weak electron acceptor, complexes readily with charge-transfer agents, such as organoaluminum or metallic halides. These complexes are strong electron acceptors, which interact with strong donor monomers to form ground-state comonomer complexes and undergo polymerization to form alternating copolymers. The probable reaction mechanism is as follows:



where A is acrylonitrile, CTA the charge-transfer agent, and D the strong electron-donor monomer.

The polymerization proceeds spontaneously at room temperature or elevated temperatures. The proposed matrix of the comonomer complexes is described in Reference 96. Examples of alternating acrylonitrile copolymerizations involve vinyl cyclohexanes with AlEC₂H₅tCl₂ (97), vinyl acetate with ZnCl₂ (98) or Ziegler-Natta catalyst (99), and styrene.

Block Copolymers. Several methods such as ultrasonics (100), radiation (101), and chemical techniques (102,103), including the use of polymer ions, polymer radicals, and organometallic initiators, are available to prepare Block Copolymers of acrylonitrile. Acrylonitrile can be used as either the first- or the second-phase monomer. Depending on the mechanism of termination, a diblock of the AB type and a triblock of the ABA type can be formed by disproportionation or transfer for the former, and recombination for the latter. Some of the comonomers are styrene, methyl acrylate, vinyl chloride, methyl methacrylate, vinyl acetate, acrylic acid, and *n*-butyl isocyanate. An overview and survey of alternating and block copolymers can be found in Reference 104.

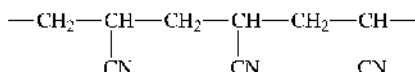
Table 8. Estimate of Phases in Polyacrylonitrile^{a,b}

Sample ^c	Crystalline	Quasi-crystalline	Amorphous
PAN B molded at 200°C	0.47	0.25	0.28
PAN B molded-annealed	0.45	0.34	0.21
PAN B cast	0.42	0.10	0.48
PAN A cast-annealed	0.44	0.23	0.33

^aRef. 109.^bMade by emulsion free-radical polymerization.^cPAN A: 120,000 M_v , cast from DMF, PAN B: 328,000 M_v , cast from DMSO.

Properties of Homopolymer

Polyacrylonitrile adopts the head-to-tail linkage of its monomer units, with nitrile groups on alternate carbon atoms at very close proximity:



By conventional polymerization methods, polyacrylonitrile forms both isotactic and syndiotactic configurations in approximately equal proportion. However, primarily the isotactic polyacrylonitrile is formed in the polymerization.

The compact size and strong polarity of the nitrile groups make them very interactive with their surroundings. The lone pair orbital on nitrogen is suitable for hydrogen bonding, as well as for electron-donor–acceptor complex formation. In addition, the electrons in the π -orbitals of the nitrile triple bond are available for interactions, for example, with transition-metal ions.

The polar nitrile groups exert intramolecular repulsion, compelling the molecules into an irregular helical conformation (105,106), but they ensure intermolecular attraction between polymer molecules. The interactions of polyacrylonitrile molecules and their relationship to macroscopic properties have been reviewed (106).

The prevailing polar nature of polyacrylonitrile provides its unique and well-known characteristics, including hardness and rigidity, resistance to most chemicals and solvents, sunlight, heat, and microorganisms, slow burning and charring, reactivity toward nitrile reagents, compatibility with certain polar substances, ability to orient, and low permeability toward gases. Physical constants and an infrared spectrum of polyacrylonitrile are available (107).

Morphology. The heterogeneous system of polyacrylonitrile contains crystalline, quasicrystalline, and amorphous phases (108,109). The ratio of these three phases has been estimated (Table 8); there is little change in the crystalline phase regardless of specimen preparations. This indicates that the crystals, even though destroyed when dissolved in the solvents, form again to the same extent upon casting from the solvents. However, large differences are shown for the quasicrystalline and amorphous phases, depending on the methods of preparation.

Three regions of transition are defined by dynamic mechanical measurements (109): the main transition for the amorphous phase at 157°C, the dipole–dipole interaction for the quasicrystalline phase at 99°C [generally considered

as the Glass Transition], and the secondary transition for the amorphous phase at 79°C (see DYNAMIC MECHANICAL PROPERTIES). The high temperature transition is usually ascribed to concerted motions of the pendent nitrile groups and is very sensitive to modifications. When the polymer is heat-treated (110) to form a conjugated ring system from the nitrile groups, this high temperature transition disappears as in the case of the dielectric transition (111) (see DIELECTRIC RELAXATION). Furthermore, when a small amount (5–10%) of methyl methacrylate is introduced as a comonomer, the transition behavior changes drastically; the high temperature transition disappears (112). Multiple-transition phenomena have also been shown by birefringence (113), dielectric (114–117), and x-ray diffraction (qv) (118) measurements (see MORPHOLOGY).

Crystallization. Using fractionated polyacrylonitrile, crystallization has been carried out at various temperatures (119), and several morphological growth features have been observed, namely, rectangular single crystals, twinned crystals, ovals, and spherulites. The lamellae are vertically arranged in a manner similar to polyethylene ovals. As in thin-film polystyrene, natural rubber, and gutta-percha, crack-like structure or space between lamellae is found to be associated with fibrils. The growth mechanism for polyacrylonitrile spherulites is similar to that for other polymers (see SEMICRYSTALLINE POLYMERS; CRYSTALLIZATION KINETICS).

Amorphous Polyacrylonitrile. This polymer has been synthesized successfully, using bis(pentamethyleneimino) magnesium as catalyst and *n*-heptane as solvent (120,121). By converting the polymer into poly(acrylic acid) by alkaline hydrolysis, and comparing its infrared spectrum to those of poly(acrylic acid) prepared with azobisisobutyronitrile as initiator, this amorphous polyacrylonitrile has been shown to have the normal head-to-tail structure of the usual, more crystalline polyacrylonitrile described previously. Its density is 1.2% higher, and its configuration is primarily isotactic, like the polymer synthesized through a radiation-induced urea canal complex. Its solubility is remarkably different; it is easily soluble in propylene carbonate at room temperature and in formamide at elevated temperatures. In addition, the viscoelastic properties of the amorphous material show only a single transition at high temperatures of ca 170°C with the absence of the transition at ca 100°C. This fact supports the assignment of the high temperature transition to the molecular motion related to the amorphous region and the low temperature transition to the quasicrystalline region (see AMORPHOUS POLYMERS).

Melting Point. Because polyacrylonitrile decomposes before reaching its melting temperature, the determination of its melting point requires rather unusual approaches. A melting point of 317°C has been obtained by dilatometry (qv) (105). Using a heating rate of 40°C/min, which is sufficiently fast to achieve melting prior to degradation, a value of 326°C has been measured by dta (122). By wide-angle x-ray and stereoscan measurements, at a heating rate of >1000°C/min, a melting point of $320 \pm 5^\circ\text{C}$ has been deduced (123).

Water is known to depress the melting point of acrylonitrile polymer and its vinyl acetate copolymers strongly; degradation during measurement becomes insignificant, and scanning calorimetry has been used effectively to probe the structure of the polymers (124,125). Addition of water continually depresses the polymer melting point until a critical water concentration is reached, whereupon

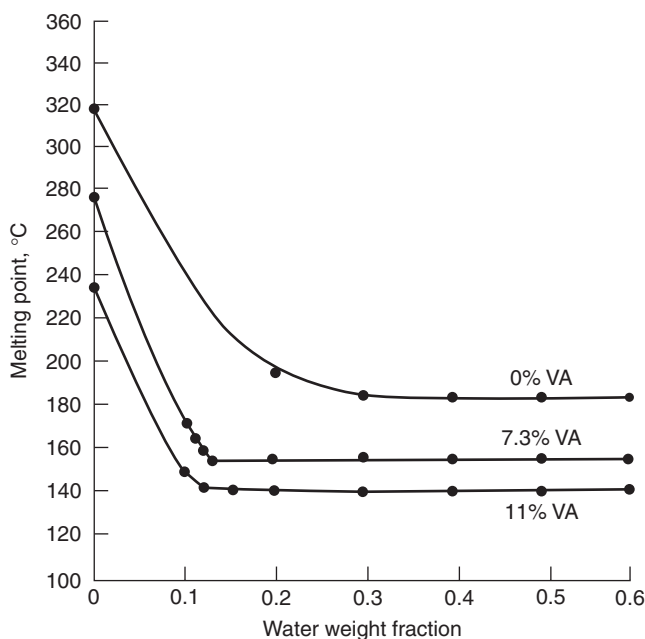


Fig. 2. Dependence of melting point of water content for acrylonitrile–vinyl acetate (VA) copolymer (125).

the molten polymer separates from the water, and no further reduction in melting point is observed (Fig. 2). Both the minimum melting point and the critical water concentration decrease with increasing comonomer content. The melting-point reduction by water is consistent with the Flory theory (126) and can be expected from the nitrile–water interaction, which results in the disruption of the nitrile–nitrile bonding. On the other hand, the depressions of both the melting point and the heat of fusion by the presence of the comonomer (Fig. 3) are attributable to the crystal defect model (127) in which the noncrystallizable comonomer enters the lattice as defects rather than being relegated to an amorphous phase. Thus, the degree of the depressions is interpreted as a measure of the regularity and strength of the intermolecular dipole–dipole bonds that stabilize the lattice.

When the draw ratio of the fiber is extended from 1 to 6 times, the heat of fusion increases from 1.88 to 2.5 kJ/mol, and a secondary endotherm appears at 147°C; the primary endotherm is at 156°C (Fig. 4). These changes are reversible upon relaxation of the fiber. The appearance of the secondary endotherm is interpreted as a disruption in the crystalline phase at high threadline stress, whereas the increase in the heat of fusion reflects the formation of dipole–dipole bonds upon orientation of the polymer chains in the amorphous region of the fiber.

Polarization. Polyacrylonitrile can achieve very high, persistent electrical polarization as inferred from thermally stimulated discharge analysis (128). This can be explained by the strong dipole moment of the nitrile groups and the quasi-crystalline nature of the polymer. Because of the strong dipole moment, an

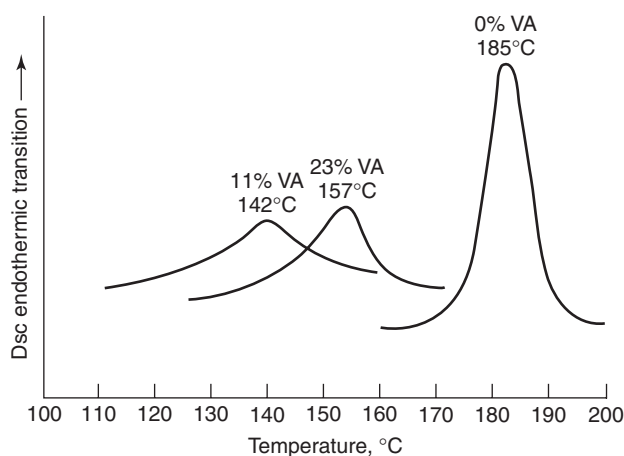


Fig. 3. Melting endotherms of acrylonitrile–vinyl acetate copolymers mixed with two parts of water (125).

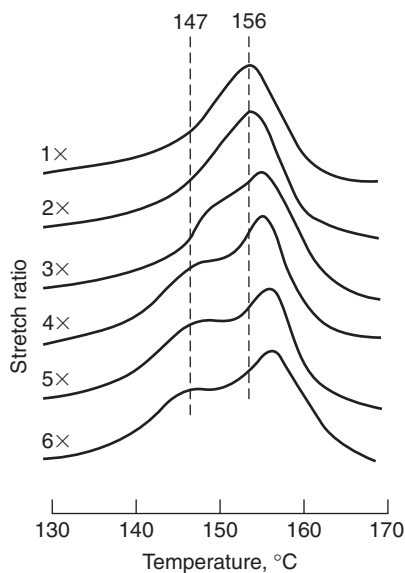


Fig. 4. Melting endotherms of acrylonitrile copolymer fiber (7% vinyl acetate) at different stretch ratios (124).

external electrical field can impose strong torque on the polymer chains and lead to a highly polarized state. Quasicrystallinity permits these chains to be rearranged and packed together, providing a certain degree of molecular reorganization to store the energy. Both x-ray diffraction and high resolution internal-reflection infrared spectroscopy have been used to study the polarization characteristics of polyacrylonitrile films (129).

When the films are exposed to electric fields, x-ray diffraction indicates a densification of laterally ordered regions and an increase in the degree of local order or in the size of the ordered regions. Infrared spectroscopy suggests an intensification of dipolar bonding between adjacent nitriles, and the possibility of vibrational coupling among adjacent groups. It is envisioned that when polyacrylonitrile is subjected to thermoelectric treatment, the structural rearrangement of the polymer chains involves not only a biased orientation of dipoles, but also enhanced dipole-dipole associations forming dipolar clusters.

Solubility. Because of the properties of polyacrylonitrile, an active solvent capable of dissolving this polymer must satisfy some unique and critical chemical property of the polymer chains and, at the same time, separate the polymer molecules with a nonpolar segment. For example, dimethylformamide is an effective solvent, but formamide, methylformamide, and diethylformamide are not; dimethyl sulfone is, but diethyl sulfone is not. The following solvents are effective for polyacrylonitrile at either room temperature or elevated temperatures (107,130): dimethylformamide, dimethylthioformamide, dimethylacetamide, *N*-methyl- β -cyanoethyl formamide, α -cyanoacetamide, tetramethyl oxamide, malononitrile, fumaronitrile, succinonitrile, adiponitrile, α -chloro- β -hydroxypropionitrile, β -hydroxypropionitrile, hydroxyacetonitrile, *N,N*-di(cyanomethyl)-aminoacetonitrile, ϵ -caprolactam, bis(β -cyanoethyl)ether, γ -butyrolactone, propiolactone, 1,3,5-tetracyanopentane, tetramethylene sulfoxide, dimethyl sulfoxide, 2-hydroxyethyl methyl sulfone, methyl ethyl sulfone, sulfolane, *m*-nitrophenol, *p*-nitrophenol, *o*-, *m*-, *p*-phenylene diamine, methylene dithiocyanate, trimethylene dithiocyanate, dimethyl cyanamide, ethylene carbonate, propylene carbonate, succinic anhydride, maleic anhydride, certain *N*-nitro- and nitrosoalkyl amines, some formylated primary and secondary amines, pyrrolidinone derivatives, concentrated sulfuric acid or nitric acid, and concentrated aqueous solutions of LiBr, NaCNS, or ZnCl₂. Copolymers of acrylonitrile are often soluble in dioxane, chlorobenzene, cyclohexanone, methyl ethyl ketone, acetone, dimethylformamide, butyrolactone, and tetrahydrofuran.

Barrier Properties. The remarkable barrier property of polyacrylonitrile to oxygen and carbon dioxide has been demonstrated (131), but high permeability toward helium is noticed. The high polarity of polyacrylonitrile leads to this high permeability and high sorption toward water vapor. This is perhaps the only limitation for the barrier application of the polymer. The activation energies for permeation and their preexponential factors for polyacrylonitrile are available (131). The value of the ratio of the permeabilities to helium and oxygen is exceptionally high; for example, the value for poly(vinylidene chloride), another high barrier polymer, is 58.5, whereas that for polyacrylonitrile is 1770. In addition, the activation energies for permeation are relatively low; for example, the activation energy for poly(vinylidene chloride) is 70.3 kJ/mol for nitrogen, while that for polyacrylonitrile is only 44.4. These two features suggest that the free volume of polyacrylonitrile for gas transport must be very small (see BARRIER POLYMERS; VINYLIDENE CHLORIDE POLYMERS).

The sorption of CO₂ has been studied at high pressures under various temperatures, and the characteristic dual-mode sorption isotherms (superposition of Henry's law and a Langmuir isotherm) of gas-glassy polymer systems have been observed (132). The Langmuir affinity constants and their enthalpy change are

lower than expected. This is interpreted as resulting from the competition for available sites between CO_2 and the immobile residual in the film. The observed behavior suggests unique slow relaxations of polyacrylonitrile during the transient CO_2 permeation process, which are not observed in other glassy polymers. The sorption of water vapor has also been studied (133,134), and like CO_2 , the water-vapor sorption follows the dual-mode model. At high vapor pressures, clustering of the penetrant molecules in nonrandom aggregation is suggested. Again, as in CO_2 sorption, non-Fickian time-lag behavior is observed, indicating relaxations of polyacrylonitrile during the transient sorption transport to accommodate the clustering process of the penetrant.

Chemical Reactions. Polyacrylonitrile is resistant to common solvents, oils, and chemicals, but its nitrile groups and α -hydrogens do react with certain reagents. Hydration with concentrated sulfuric acid forms a solution (135). Hydrogenation results in the formation of polymers with pendent aminonethylene groups (136,137). Hydrolysis with hot aqueous alkali yields a mixture which passes through a thick red stage and eventually becomes the yellow, water-soluble salt of poly(acrylic acid) (138) (see ACRYLIC (AND METHACRYLIC) ACID POLYMERS). Upon reaction with strong alkali in dilute dimethylformamide solution, rapid chain scission ensues (139). Reaction with hydroxylamine produces amidoximes and hydroxamic acids (140,141). Grafting with vinyl acetate proceeds in emulsion, with potassium persulfate as initiator (142). Irradiation induces free-radical sites which initiate grafting or cross-linking (qv), depending upon the presence or the absence of a monomer (143).

Thermal Degradation. Upon heating, discoloration of polyacrylonitrile occurs; it first becomes yellow, then progressively red, and finally black. The mechanism of color formation is thought to be the reaction of the nitrile groups in forming a conjugated system. A comprehensive review of polyacrylonitrile color formation and thermal degradation reaction has been made (144). There are four main categories of Degradation reactions: chain scission, cross-linking, hydrogenation, and cyclization (145). Thermal degradation under reduced pressure, and in air at 200°C , has been studied using Fourier transform infrared spectroscopy (146). A mechanism involving imine-enamine tautomerism explains satisfactorily the observed spectral changes under reduced pressure (146). The reactions in air are more complex, and their interpretation is difficult.

The decomposition products of pure polyacrylonitrile yarn pyrolyzed at 400, 600, and 800°C in either air or nitrogen have been quantitatively analyzed using gas chromatography and gas chromatography-mass spectrometry (147). The main products are HCN, which is the predominant toxic product, and 16 other nitriles. At higher temperatures, the quantities of HCN, acetonitrile, acrylonitrile, and aromatic nitriles increase, whereas those of aliphatic dicyanides decrease. Ammonia is a decomposition product, but its toxicity is insignificant, compared to HCN, and has not been determined. The viscous condensates contain several homologous series of aliphatic nitriles. A similar study of polyacrylonitrile pyrolysis products in oxygen at 400, 700, and 900°C has shown the four chief products to be HCN, acetonitrile, acrylonitrile, and benzonitrile (148). The other 16 products are methane, acetylene, ethylene, ethane, propene, propane, 1,3-butadiene, ethyl nitrile, vinyl acetonitrile, crotonitrile, benzene, pyridine, dicyanobutene,

adiponitrile, dicyanobenzene, and naphthalene. With increased temperature, the relative yields and complexity of products increase to a maximum of ca 700°C. Further increase in temperature produces thermally stable product, including low molecular weight nitriles and aromatic species.

Copolymers

Because of the combination of high melting point, high melt viscosity, and poor thermal stability, acrylonitrile homopolymer has little application. Even in synthetic fibers, small amounts of copolymers are incorporated to improve stability, dye receptivity, and certain other properties. By copolymerizing acrylonitrile with other monomers, the deficiencies of acrylonitrile homopolymer have been tempered and, at the same time, the unusual and desirable properties of acrylonitrile have been incorporated into various melt-processible resins. For general applications, acrylonitrile content ranges up to ca 50%; for barrier applications, to ca 75%. Acrylonitrile copolymer properties, such as rigidity, chemical resistance, melt viscosity, stability, and permeability, generally vary in proportion to the acrylonitrile content. However, the glass-transition temperature (T_g) shows unusual behavior; there is a maximum or a minimum T_g in certain cases, eg, for copolymers of styrene, vinylidene chloride, and methyl methacrylate.

The principal uses of acrylonitrile are in Acrylic fibers, copolymers with styrene (SAN), and in combination with butadiene and styrene (ABS). (see ACRYLONITRILE–BUTADIENE–STYRENE). SAN copolymers are discussed in detail in later sections of this article. Following are a few other copolymers and their properties.

Copolymers of Benzofuran. These alternating copolymers are optically active and are prepared in the presence of optically active aluminum compounds as complexing agents for acrylonitrile. Opposite signs of rotation are obtained using different complexing agents. The highest specific rotation of -8° has been attained with the stoichiometric ratio of menthoxyaluminum dichloride to acrylonitrile. The results indicate that the alternating dyad contributes to the optical activity, and the asymmetric configuration of the carbon atoms of the acrylonitrile unit influences the optical rotation. It is claimed that the optical activity is mainly induced by the copolymers themselves, not by the residual catalysts (149).

Copolymers of Carbon Dioxide. Copolymerization proceeds in the presence of triethylenediamine as initiator at 120–160°C under moderate pressure to yield an ester structure. The yield and molecular weight of the copolymers increase with initiator concentration, but the M_n of the synthesized copolymers is low, ie, 1500–2200. They are transparent viscous liquids or solids, depending on the molecular weight (150).

Copolymers of 2-Dimethylaminoethyl Methacrylate. The cationic nature of this copolymer has been shown to permit heparin attachment and cyclization of the nitrile groups with ethylene oxide gas for controlled structure alterations. The improved blood compatibility suggests Medical applications, including dialysis membranes, ultrafiltration membranes, and adsorbent coatings for hemoperfusion (151).

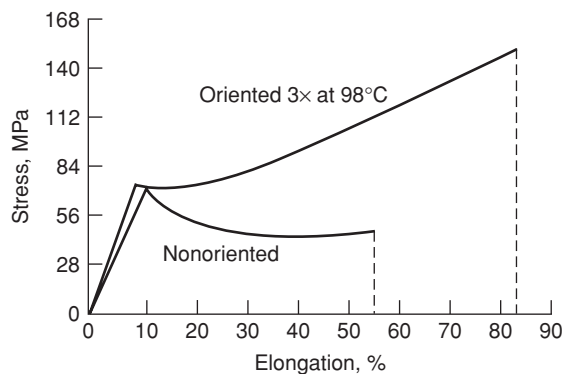


Fig. 5. Stress elongation of Barex 210 sheet (159). To convert MPa to psi, multiply by 145.

Copolymers of Methyl Acrylate. Barex[®] resins, commercial high barrier resins produced by BP Chemicals, are copolymers of acrylonitrile and methyl acrylate [96-33-3]. These resins are excellent examples of the use of acrylonitrile to provide gas and aroma/flavor barrier, chemical resistance, high tensile strength, stiffness, and utilization of a comonomer to provide thermal stability and processability. In addition, modification with an elastomer provides toughness and impact strength. These materials have a unique combination of useful packaging qualities, including transparency, and are excellent barriers to permeation by gases, organic solvents, and most essential oils. Barex resins also prevent the migration and scalping of volatile flavors and odors from packaged foods and fruit juice products (152,153). They also provide protection from atmospheric oxygen. Barex resins meet FDA compliance for direct food contact applications. In April 2000, the FDA approved the use of Barex 210E resin for fruit/vegetable juices, ready-to-use teas, and other specified beverages for fill temperatures less than 150°F (66°C). This new ruling expands the application of Barex resins into the beverage market place.

Barex resin extruded sheet and/or calendered sheet (153) can be easily thermoformed into lightweight, rigid containers (152,154). Packages can be printed, laminated, or metallized. Recent developments in extrusion and injection blow molding (152,155), laminated film structures (152,156), and coextrusion (153,157) have led to packaging uses for a variety of products. Barex resins are especially well-suited for bottle production. These acrylonitrile copolymers also provide a good example of the dependence of properties on the degree and temperature of orientation (158,159). Figure 5 illustrates the improvement in tensile strength, elongation, and the ability to absorb impact energy as a result of orientation (159) by Barex resins (for example, Barex 210). Tensile strength and impact strength increase with the extent of stretching, and decrease with the orientation temperature. Oxygen permeability decreases with orientation. These orientation properties have led to the commercialization of Barex resins to fruit juice containers in France (153). Some typical physical properties of Barex resins are shown in Table 9.

Table 9. Physical/Mechanical Properties of Commercial Barex Resins^a

Property	Barex 210 ^b	Barex 218 ^b	ASTM test method
Specific gravity at 23°C, g/cm ³	1.15	1.11	D792
Tensile strength (yield), MPa ^c	65.5	51.7	D638
Flexural modulus, GPa ^d	3.38	2.69	D790
Melt index (200c, 27.5 lb)	3	3	D1238
Notched Izod impact, J/m ^e	267	481	D790
Heat deflection temperature, °C	77	71	D648
Gas permeability			
Oxygen at 23°C and 100% rh [nmol/(m·s·GPa) ^f]	1.54	3.09	D3985
Carbon dioxide at 23°C and 100% rh [nmol/(m·s·GPa) ^f]	2.32	3.09	D3985
Water vapor at 38°C and 90% rh [nmol/(m·s·MPa) ^g]	12.7	19.1	F1249-90

^aProduct literature from BP Chemicals., m·s·MPa^bExtrusion grade.^cTo convert MPa to psi, multiply by 145.^dTo convert GPa to psi, multiply by 145,000.^eTo convert J/m to ft·lb/in., divide by 53.39.^fTo convert nmol/(m·s·GPa) to (cm³·mm)/(m²·24 h·bar), divide by 5.145.^gTo convert nmol/(m·s·MPa) to (g·mm)/(m²·24h · atm), divide by 6.35.

Copolymers of Methyl Methacrylate. The glass-transition temperatures of these copolymers exhibit a minimum of ca 87°C at ca 40 wt% acrylonitrile; the T_g 's of the homopolymers are ca 105°C. This unusual behavior is explained by the interactions of the dyads and well predicted by the sequence-distribution equation (160).

Copolymers of Styrene. For thermoplastic applications, the largest volume comonomer for acrylonitrile is styrene. Styrene–acrylonitrile copolymers are designated SAN. SAN copolymers are discussed in detail in the later part of this article.

Copolymers of Poly(vinyl alcohol) with Formaldehyde and Hydroquinone. These electron-exchange resins are condensation products of partially cyanoethylated poly(vinyl alcohol) and have a weak acidic nature and lustrous black appearance. The polar groups of acrylonitrile improve the redox capacities over a standard weak-acid electron exchanger, hydroquinone–phenol–formaldehyde (161).

Copolymers of 4-Vinylpyridine. Acrylonitrile improves the tensile strength of these reverse-osmosis membranes. Cross-linking quaternization of the copolymers with diiodobutane improves the performance of the membranes, achieving salt rejection of 95% and hydraulic water permeability of up to 30×10^{-15} cm²/(s·Pa). The quaternized membranes also are anion exchangeable; more than two-thirds of iodide exchanges with chloride (162).

Copolymers of Vinylidene Chloride. The glass-transition temperatures of these copolymers vary nonlinearly with composition, as is the case for copolymers of methyl methacrylate, but these show a maximum. It is a broad

maximum around 105°C at 55–80 wt% acrylonitrile. (The T_g of vinylidene chloride homopolymer is ca –20°C, whereas PAN's is ca 100°C.) Again, sequence distribution explains such behavior (163). These copolymers have good barrier properties and are used for surface Coatings. Acrylonitrile grafting on starch imparts hydrophilic behavior to starch and results in exceptional water absorption capability (164–167). These copolymers can also immobilize enzymes by entrapment or covalent bonding (168).

Grafting on Fibers. By treatment with sodium hydroxide and a low degree of cyanoethylation, the moisture retention of cotton can be improved by as much as 14% (169). X-ray diffraction reveals a decrease in the crystallinity of the cotton, which provides the improved moisture retention (170). Modifications of fibers by grafting with acrylonitrile, followed by hydrolysis, produce water-receptive and soil-repellent fibers (171). Such treatments to nylon result in significant protein-coupling efficiency (172). Grafting onto polypropylene fibers enhances moisture absorption and dye absorption (173).

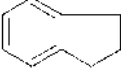
Other Copolymers. Acrylonitrile copolymerizes readily with many electron-donor monomers other than the copolymers mentioned above. More than 800 acrylonitrile copolymers have been registered with *Chemical Abstract* and a comprehensive listing of reactivity ratios for acrylonitrile copolymerizations is readily available (174). Some of the other interesting acrylonitrile copolymers follows: acrylonitrile–methyl acrylate–indene terpolymers, by themselves, or in blends with acrylonitrile–methyl acrylate copolymers, exhibit even lower oxygen and water permeation rates than the indene-free copolymers (175,176). Terpolymers of acrylonitrile with indene and isobutylene also exhibit excellent barrier properties (177), and permeation of gas and water vapor through acrylonitrile–styrene–isobutylene terpolymers is also low (178,179).

Copolymers of acrylonitrile and methyl methacrylate (180) and terpolymers of acrylonitrile, styrene, and methyl methacrylate (181,182) are used as barrier polymers. Acrylonitrile copolymers and multipolymers containing butyl acrylate (183–186), ethyl acrylate (187), 2-ethylhexyl acrylate (183,186,188,189), hydroxyethyl acrylate (185), vinyl acetate (184,190), vinyl ethers (190,191), and vinylidene chloride (186,187,192–194) are also used in barrier films, laminates, and coatings. Environmentally degradable polymers useful in packaging are prepared from polymerization of acrylonitrile with styrene and methyl vinyl ketone (195).

Acrylonitrile multipolymers containing methyl methacrylate, α -methylstyrene, and indene are used as PVC modifiers to melt blend with PVC. These PVC modifiers not only enhance the heat distortion temperature, but also improve the processibility of the PVC compounds (196–200). The acrylonitrile multipolymers grafted on the elastomer phase provide the toughness and impact strength of the PVC compounds with high heat distortion temperature and good processibility (201,202). Table 10 gives the structures, formulas, and CAS registry numbers for several comonomers of acrylonitrile.

Although the arrangement of monomer units in acrylonitrile copolymers is usually random, alternating or block copolymers may be prepared using special techniques. For example, the copolymerization of acrylonitrile, like that of other vinyl monomers containing conjugated carbonyl or cyano groups, is changed in the presence of certain Lewis acids. Effective Lewis acids are metal compounds with nontransition metals as central atoms, including alkylaluminum halides,

Table 10. Monomers Commonly Copolymerized with Acrylonitrile

Monomer	Molecular formula	Structural formula	CAS registry number
Methyl methacrylate	C ₅ H ₈ O ₂	CH ₂ =C(CH ₃)COOCH ₃	[80-62-6]
Methyl acrylate	C ₄ H ₆ O ₂	CH ₂ =CHCOOCH ₃	[96-33-3]
Indene	C ₉ H ₈		[95-13-6]
Isobutylene	C ₄ H ₈	CH ₂ =C(CH ₃) ₂	[115-11-7]
Butyl acrylate	C ₇ H ₁₂ O ₂	CH ₂ =CHCOOC ₄ H ₉	[141-32-2]
Ethyl acrylate	C ₅ H ₈ O ₂	CH ₂ =CHCOOC ₂ H ₅	[140-88-5]
2-Ethylhexyl acrylate	C ₁₁ H ₂₀ O ₂	CH ₂ =CHCOOC ₈ H ₁₇	[103-11-7]
Hydroxyethyl acrylate	C ₅ H ₈ O ₃	CH ₂ =CHCOOC ₂ H ₄ OH	[818-61-1]
Vinyl acetate	C ₄ H ₆ O ₂	CH ₂ =CHOOCC ₃ H ₇	[108-05-4]
Vinylidene chloride	C ₂ H ₂ Cl ₂	CH ₂ =C(Cl) ₂	[75-35-4]
Methyl vinyl ketone	C ₄ H ₆ O	CH ₂ =CHCOCH ₃	[78-94-4]
α -Methylstyrene	C ₉ H ₁₀	CH ₂ =C(CH ₃)C ₆ H ₅	[98-83-9]
Vinyl chloride	C ₂ H ₃ Cl	CH ₂ =CHCl	[75-01-4]
4-Vinylpyridine	C ₇ H ₇ N	CH ₂ =CHC ₅ H ₄ N	[100-43-6]
Acrylic acid	C ₃ H ₄ O ₂	CH ₂ =CHCOOH	[79-10-7]

zinc halides, and triethylaluminum. The presence of the Lewis acid increases the tendency of acrylonitrile to alternate with electron-donor molecules, such as styrene, α -methylstyrene, and olefins (203–207). This alternation is often attributed to a ternary molecular complex or charge-transfer mechanism, where complex formation with the Lewis acid increases the electron-accepting ability of acrylonitrile, which results in the formation of a molecular complex between the acrylonitrile–Lewis acid complex and the donor molecule. This ternary molecular complex polymerizes as a unit to yield an alternating polymer. Cross-propagation and complex radical mechanisms have also been proposed (208).

A number of methods such as ultrasonics (209), radiation (210), and chemical techniques (211–213), including the use of polymer radicals, polymer ions, and organometallic initiators, have been used to prepare acrylonitrile block copolymers. Block comonomers include styrene, methyl acrylate, methyl methacrylate, vinyl chloride, vinyl acetate, 4-vinylpyridine, acrylic acid, and n-butyl isocyanate.

Living radical polymerization (atom transfer radical polymerization) has been developed which allows for the controlled polymerization of acrylonitrile and comonomers to produce well defined linear homopolymer, statistical copolymers, block copolymers, and gradient copolymers (214–217). Well-defined diblock copolymers with a polystyrene and an acrylonitrile–styrene (or isoprene) copolymer sequence have been prepared (218,219). The stereospecific acrylonitrile polymers are made by solid-state urea clathrate polymerization (220) and organometallic compounds of alkali and alkaline-earth metals initiated polymerization (221).

Acrylonitrile has been grafted onto many polymeric systems. In particular, acrylonitrile grafting has been used to impart hydrophilic behavior to starch

(124,222,223) and polymer fibers (224) as discussed above. Exceptional water absorption capability results from the grafting of acrylonitrile to starch, and the use of 2-acrylamido-2-methylpropanesulfonic acid [15214-89-8] along with acrylonitrile for grafting results in copolymers that can absorb over 5000 times their weight of deionized water (225). For example, one commercial product made by General Mills, Inc., Super Slurper, is a modified starch suitable for disposable diapers, surgical pads, and paper towel applications. Acrylonitrile polymers also provide some unique applications. Hollow fibers of acrylonitrile polymers as ultrafiltration membrane materials are used in the pharmaceutical and bioprocessing industries (226). Polyacrylonitrile-based electrolyte with $\text{Li/LiMn}_2\text{O}_4$ salts is used for solid-state batteries (227). Polyacrylonitrile is also used as a binding matrix for composite inorganic ion-exchanger (228).

SAN Copolymers

Because of the difficulty of melt processing the homopolymer, acrylonitrile is usually copolymerized to achieve a desirable thermal stability, melt flow, and physical properties. As a comonomer, acrylonitrile contributes hardness, rigidity, solvent and light resistance, gas impermeability, and the ability to orient. These properties have led to many copolymer application developments since 1950. The utility of acrylonitrile [107-13-1] in thermoplastics was first realized in its copolymer with styrene (C_8H_8) [100-42-5], in the late 1950s. Styrene is the largest volume of comonomer for acrylonitrile in thermoplastic applications. Styrene-acrylonitrile copolymers [9003-54-7] are inherently transparent plastics with high heat resistance and excellent gloss and chemical resistance (229). They are also characterized by good hardness, rigidity, dimensional stability, and load-bearing strength (due to relatively high tensile and flexural strengths). Because of their inherent transparency, SAN copolymers are most frequently used in clear applications. These optically clear materials can be readily processed by extrusion and injection molding, but they lack real impact resistance.

The subsequent development of acrylonitrile-butadiene-styrene resins [9003-56-9], which contain an elastomeric component within a SAN matrix to provide toughness and impact strength, further boosted commercial application of the basic SAN copolymer as a portion of these rubber-toughened thermoplastics (see ACRYLONITRILE-BUTADIENE-STYRENE). When SAN is grafted onto a butadiene-based rubber, and optionally blended with additional SAN, the two-phase thermoplastic ABS is produced. ABS has the useful SAN properties of rigidity and resistance to chemicals and solvents, while the elastomeric component contributes real impact resistance. Because ABS is a two-phase system and each phase has a different refractive index, the final ABS is normally opaque. A clear ABS can be made by adjusting the refractive indexes through the inclusion of another monomer such as methyl methacrylate. ABS is a versatile material and modifications have brought out many specialty grades such as clear ABS and high temperature and flame-retardant grades. Saturated hydrocarbon elastomers or acrylic elastomers (230,231) can be used instead of those based on butadiene (C_4H_6) [106-99-0] as weatherable grade ABS.

Table 11. Physical/Mechanical Properties of Commercial Injection-Molded SAN Resins^a

Property	Lustran 31-2060	Tyrl 100	ASTM test method
Specific gravity at 23°C	1.07	1.07	D792
Vicat softening point, °C	110	108	D1525
Tensile strength, MPa ^b	72.4	71.7	D638
Ultimate elongation @ breakage, %	3.0	2.5	D638
Flexural modulus, GPa ^c	3.45	3.87	D790
Impact strength notched Izod, J/m ^d	21.4 @ 0.125 in.	16.0 @ 0.125 in.	D256
Melt flow rate, g/10 min	8.0	8.0	D1238
Refractive index n_D	1.570	1.570	D542
Mold shrinkage, in./in.	0.003–0.004	0.004–0.005	D955
Transmittance at 0.125-in. thickness, %	89.0	89.0	D1003
Haze at 0.125-in. thickness, %	0.8	0.6	D1003

^aProduct literature from Bayer (Lustran 31-2060) and Dow (Tyrl 100).

^bTo convert MPa to psi, multiply by 145.

^cTo convert GPa to psi, multiply by 145,000.

^dTo convert J/m to ft-lb/in., divide by 53.39.

SAN Physical Properties and Test Methods. SAN resins possess many physical properties desired for thermoplastic applications. They are characteristically hard, rigid, and dimensionally stable with load-bearing capabilities. They are also transparent, have high heat distortion temperatures, possess excellent gloss and chemical resistance, and adapt easily to conventional thermoplastic fabrication techniques (232).

SAN polymers are random linear amorphous copolymers. Physical properties are dependent on molecular weight and the percentage of acrylonitrile. An increase of either generally improves physical properties, but may cause a loss of processibility or an increase in yellowness. Various processing aids and modifiers can be used to achieve a specific set of properties. Modifiers may include mold release agents, uv stabilizers, antistatic aids, elastomers, flow and processing aids, and reinforcing agents such as fillers and fibers (232). Methods for testing and some typical physical properties are listed in Table 11.

The properties of SAN resins depend on their acrylonitrile content. Both melt viscosity and hardness of SAN resins increase with increasing acrylonitrile level. Unnotched impact and flexural strengths depict dramatic maxima at ca 87.5 mol% (78 wt%) acrylonitrile (233). With increasing acrylonitrile content, copolymers show continuous improvements in barrier properties and chemical and uv resistance, but thermal stability deteriorates (234). The glass-transition temperature (T_g) of SAN varies nonlinearly with acrylonitrile content, showing a maximum at 50 mol% acrylonitrile. The alternating SAN copolymer has the highest T_g (235,236). The fatigue resistance of SAN increases with acrylonitrile content to a maximum at 30 wt%, then decreases with higher acrylonitrile levels (237). The effect of acrylonitrile incorporation on SAN resin properties is shown in Table 12.

Table 12. Compositional Effects on SAN Physical Properties^a

Acrylonitrile, wt%	Tensile strength, MPa ^b	Elongation, %	Impact strength, notch ^c , J/m ^c	Heat distortion temp., °C	Solution viscosity, MPa (=cP)
5.5	42.27	1.6	26.6	72	11.1
9.8	54.61	2.1	26.0	82	10.7
14.0	57.37	2.2	27.1	84	13.0
21.0	63.85	2.5	27.1	88	16.5
27.0	72.47	3.2	27.1	88	25.7

^aRef. 238.^bTo convert MPa to psi, multiply by 145.^cTo convert J/m to ft-lb/in., divide by 53.39.

SAN Chemical Properties and Analytical Methods. SAN resins show considerable resistance to solvents and are insoluble in carbon tetrachloride, ethyl alcohol, gasoline, and hydrocarbon solvents. They are swelled by solvents such as benzene, ether, and toluene. Polar solvents such as acetone, chloroform, dioxane, methyl ethyl ketone, and pyridine will dissolve SAN (239). The interactions of various solvents and SAN copolymers containing up to 52% acrylonitrile have been studied, along with their thermodynamic parameters such as the second virial coefficient, free-energy parameter, expansion factor, and intrinsic viscosity (240).

The properties of SAN are significantly altered by water absorption (241). The equilibrium water content increases with temperature while the time required decreases. A large decrease in T_g can result. Strong aqueous bases can degrade SAN by hydrolysis of the nitrile groups (242).

The molecular weight of SAN can be easily determined by either intrinsic viscosity or size-exclusion chromatography (sec). Relationships for both multi-point and single-point viscosity methods are available (243,244). The intrinsic viscosity and molecular weight relationships for azeotropic copolymers have been given (245,246):

$$(1) [\eta] = 3.6 \times 10^{-4} \bar{M}_w^{0.62} \text{ dL/g in MEK at } 30^\circ\text{C}$$

$$(2) [\eta] = 2.15 \times 10^{-4} \bar{M}_w^{0.68} \text{ dL/g in THF at } 25^\circ\text{C}$$

$$(3) [\eta] = \frac{\eta_{sp}/c}{1+k_\eta\eta_{sp}}, \text{ where } k_\eta = 0.21 \text{ for MEK at } 30^\circ\text{C and } 0.25 \text{ for THF at } 25^\circ\text{C}$$

Chromatographic techniques are readily applied to SAN for molecular weight determination. Size-exclusion chromatography or gel permeation chromatography (247) columns and conditions have been described for SAN (248). Chromatographic detector differences have been shown to be of the order of only 2–3% (249). High pressure precipitation chromatography can achieve similar molecular weight separation (250). Liquid chromatography can be used with sec-fractionated samples to determine copolymer composition (251). Thin-layer chromatography will also separate SAN by compositional (monomer) variations (250).

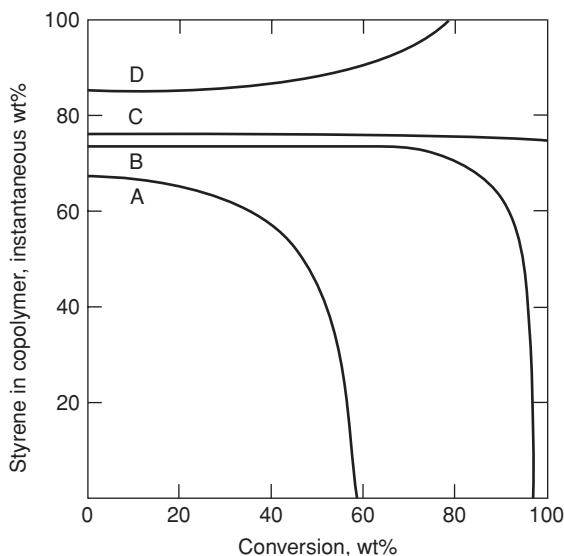


Fig. 6. Approximate compositions of SAN copolymers formed at different conversions starting with various monomer mixtures (256): S/AN = 65/36(A); 70/30(B); 76/24(C); 90/10(D).

Residual monomers in SAN have been a growing environmental concern and can be determined by a variety of methods. Monomer analysis can be achieved by polymer solution or directly from SAN emulsions (252), followed by “head space” gas chromatography (251,252). Liquid chromatography is also effective (253).

SAN Manufacture. The reactivities of acrylonitrile and styrene radicals toward their monomers are quite different, resulting in SAN copolymer compositions that vary from their monomer compositions (254). Further complicating the reaction is the fact that acrylonitrile is soluble in water and slightly different behavior is observed between water-based emulsion and suspension systems, and bulk or mass polymerizations (255). SAN copolymer compositions can be calculated from copolymerization equations (256) and published reactivity ratios (174). The difference in radical reactivity causes the copolymer composition to drift as polymerization proceeds, except at the azeotropic composition where copolymer composition matches monomer composition. Figure 6 shows these compositional variations (257). When SAN copolymer compositions vary significantly, incompatibility results, causing loss of optical clarity, mechanical strength, and moldability, as well as heat, solvent, and chemical resistance (258). The termination step has been found to be controlled by diffusion even at low conversions, and the termination rate constant varies with acrylonitrile content. The average half-life of the radicals increases with styrene concentration from 0.3 s at 20 mol% to 6.31 s with pure styrene (259). Further complicating SAN manufacture is the fact that both the heat (260,261) and rate (262) of copolymerization vary with monomer composition.

The early kinetic models for copolymerization, Mayo's terminal mechanism (263) and Alfrey's penultimate model (264), did not adequately predict the behavior of SAN systems. Copolymerizations in dimethylformamide and toluene indicated that both penultimate and antepenultimate effects had to be considered (265,266). The resulting reactivity model is somewhat complicated, since there are eight reactivity ratios to consider.

The first quantitative model, which appeared in 1971, also accounted for possible charge-transfer complex formation (267). Deviation from the terminal model for bulk polymerization was shown to be due to antepenultimate effects (268). The work with numerical computation and ^{13}C -nmr spectroscopy data on SAN sequence distributions indicates that the penultimate model is the most appropriate for bulk SAN copolymerization (269,270). A kinetic model for azeotropic SAN copolymerization in toluene has been developed that successfully predicts conversion, rate, and average molecular weight for conversions up to 50% (271).

An emulsion model that assumes the locus of reaction to be inside the particles and considers the partition of acrylonitrile between the aqueous and oil phases has been developed (272). The model predicts copolymerization results very well when bulk reactivity ratios of 0.32 and 0.12 for styrene and acrylonitrile, respectively, are used. Commercially, SAN is manufactured by three processes: emulsion, suspension, and continuous mass (or bulk).

Emulsion Process. The emulsion polymerization process utilizes water as a continuous phase, with the reactants suspended as microscopic particles. This low viscosity system allows facile mixing and heat transfer for control purposes. An emulsifier is generally employed to stabilize the water insoluble monomers and other reactants, and to prevent reactor fouling. With SAN, the system is composed of water, monomers, chain-transfer agents for molecular weight control, emulsifiers, and initiators. Both batch and semibatch processes are employed. Copolymerization is normally carried out at 60–100°C to conversions of ~97%. Lower temperature polymerization can be achieved with redox-initiator systems (273).

Figure 7 shows a typical batch or semibatch emulsion process (274). A typical semibatch emulsion recipe is shown in Table 13 (275).

The initial charge is placed in the reactor, purged with an inert gas such as N_2 , and brought to 80°C. The initiator is added, followed by addition of the remaining charge over 100 min. The reaction is completed by maintaining agitation at 80°C for 1 h after monomer addition is complete. The product is a free-flowing white latex with a total solids content of 35.6%. Compositional control for other than azeotropic compositions can be achieved with both batch and semibatch emulsion processes. Continuous addition of the faster reacting monomer, styrene, can be practiced for batch systems, with the feed rate adjusted by computer through gas chromatographic monitoring during the course of the reaction (276). A calorimetric method to control the monomer feed rate has also been described (233). For semibatch processes, adding the monomers at a rate slower than that for copolymerization can achieve equilibrium. It has been found that constant composition in the emulsion can be achieved after ca 20% of the monomers have been charged (277).

Residual monomers in the latex are avoided either by effectively reacting the monomers to polymer or by physical or chemical removal. The use of

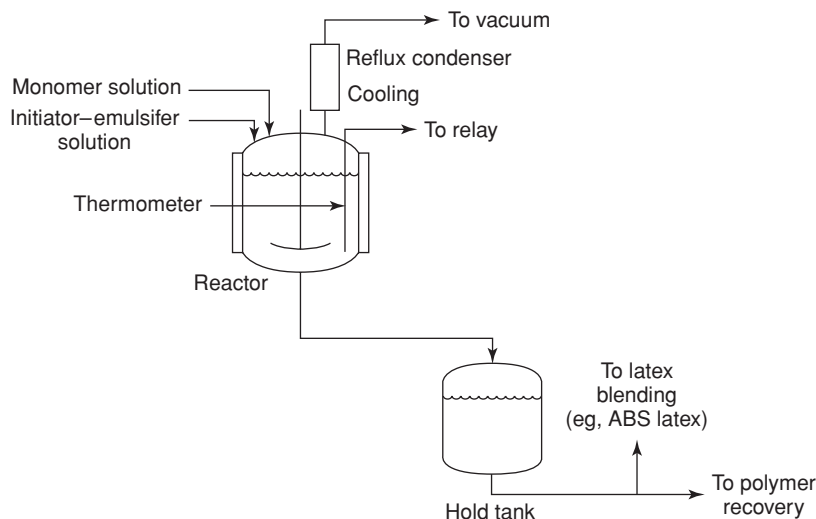


Fig. 7. SAN batch emulsion process (274).

Table 13. Semibatch-Mode Recipe for SAN Copolymers

Ingredient	Parts
<i>Initial reactor charge</i>	
Acrylonitrile	90
Styrene	111
Na alkanesulfonate (emulsifier)	63
K ₂ S ₂ O ₈ (initiator)	0.44
4-(Benzyloxymethylene) cyclohexene (mol wt modifier)	1
Water	1400
<i>Addition charge</i>	
Acrylonitrile	350
Styrene	1000
Na alkanesulfonate (emulsifier)	15
K ₂ S ₂ O ₈ (initiator)	4
4-(Benzyloxymethylene) cyclohexene (mol wt modifier)	10
Water	1600

tert-butyl peroxyvalate as a second initiator toward the end of the polymerization or the use of mixed initiator systems of K₂S₂O₈ and *tert*-butyl peroxybenzoate (278) effectively increases final conversion and decreases residual monomer levels. Spray devolatilization of hot latex under reduced pressure has been claimed to be effective (278). Residual acrylonitrile can also be reduced by postreaction with a number of agents such as monoamines (279) and dialkylamines (280), ammonium-alkali metal sulfites (281), unsaturated fatty acids or their glycerides (282,283) and their aldehydes, esters of olefinic alcohols, cyanuric acid (284), and myrcene (285).

Table 14. Batch-Mode Recipe for SAN Copolymers^a

Ingredient	Parts
Acrylonitrile	30
Styrene	70
Dipentene (4-isopropenyl-1-methylcyclohexene)	1.2
Di- <i>tert</i> -butyl peroxide	0.03
Acrylic acid–2-ethylhexyl acrylate (90:10)	0.03
Copolymer	
Water	100

^aRef. 289.

The copolymer latex can be used “as is” for blending with other latexes, such as in the preparation of ABS, or the copolymer can be recovered by coagulation. The addition of electrolyte or freezing will break the latex and allow the polymer to be recovered, washed, and dried. Process refinements have been made to avoid the difficulties of fine particles during recovery (286,287).

The emulsion process can be modified for the continuous production of latex. One such process (288) uses two stirred-tank reactors in series, followed by insulated hold-tanks. During continuous operation, 60% of the monomers are continuously charged to the first reactor, with the remainder going into the second reactor. Surfactant is added only to the first reactor. The residence time is 2.5 h for the first reactor where the temperature is maintained at 65°C for 92% conversion. The second reactor is held at 68°C for a residence time of 2 h and conversion of 95%.

Suspension Process. Like the emulsion process, water is the continuous phase for suspension polymerization, but the resultant particle size is larger, well above the microscopic range. The suspension medium contains water, monomers, molecular weight control agents, initiators, and suspending aids. Stirred reactors are used in either batch or semibatch mode. Figure 8 illustrates a typical suspension manufacturing process while a typical batch recipe is shown in Table 14 (289). The components are charged into a pressure vessel and purged with N₂. Copolymerization is carried out at 128°C for 3 h and then at 150°C for 2 h. Steam stripping removes residual monomers (290), and the polymer beads are separated by centrifugation for washing and final dewatering.

Compositional control in suspension systems can be achieved with a corrected batch process. A suspension process has been described where styrene monomer is continuously added until 75–85% conversion, and then the excess acrylonitrile monomer is removed by stripping with an inert gas (291,292).

Elimination of unreacted monomers can be accomplished by two approaches: using dual initiators to enhance conversion of monomers to product (293,294) and steam stripping (290,295). Several process improvements have been claimed for dewatering beads (296), to reduce haze (297–300), improve color (301–305), remove monomer (306,307), and maintain homogeneous copolymer compositions (291,292,308).

Continuous Mass Process. The continuous mass process has several advantages, including high space-time yield, and good quality products uncontaminated with residual ingredients such as emulsifiers or suspending agents. SAN

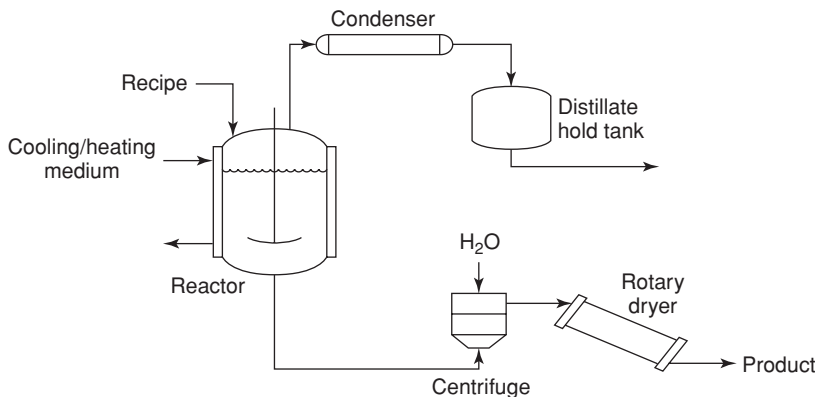


Fig. 8. SAN suspension process (289).

manufactured by this method generally has superior color and transparency, and is preferred for applications requiring good optical properties. It is a self-contained operation without waste treatment or environmental problems since the products are either polymer or recycled back to the process.

In practice, the continuous mass polymerization is rather complicated. Because of the high viscosity of the copolymerizing mixture, complex machinery is required to handle mixing, heat transfer, melt transport, and devolatilization. In addition, considerable time is required to establish steady-state conditions in both a stirred-tank reactor and a linear-flow reactor. Thus, system start-up and product grade changes produce some off-grade or intermediate grade products. Copolymerization is normally carried out between 100 and 200°C. Solvents are used to reduce viscosity or the conversion is kept to 40–70%, followed by devolatilization to remove solvents and monomers. Devolatilization is carried out from 120 to 260°C under vacuum at less than 20 kPa (2.9 psi). The devolatilized melt is then fed through a strand die, cooled, and pelletized.

A schematic of a continuous mass SAN polymerization process is shown in Figure 9 (309). The monomers are continuously fed into a screw reactor where copolymerization is carried out at 150°C to 73% conversion in 55 min. Heat of polymerization is removed through cooling of both the screw and the barrel walls. The polymeric melt is removed and fed to the devolatilizer to remove unreacted monomers under reduced pressure (4 kPa or 30 mm Hg) and high temperature (220°C). The final product is claimed to contain less than 0.7% volatiles. Two devolatilizers in series are found to yield a better quality product as well as better operational control (310,311).

Two basic reactor types are used in the continuous mass process: the stirred-tank reactor (312) and the linear-flow reactor. The stirred-tank reactor consists of a horizontal cylinder chamber equipped with various agitators (313,314) for mixing the viscous melt and an external cooling jacket for heat removal. With adequate mixing, the composition of the melt inside the reactor is homogeneous. Operation at a fixed conversion, with monomer make-up added at an amount and ratio equal to the amount and composition of copolymer withdrawn, produces a

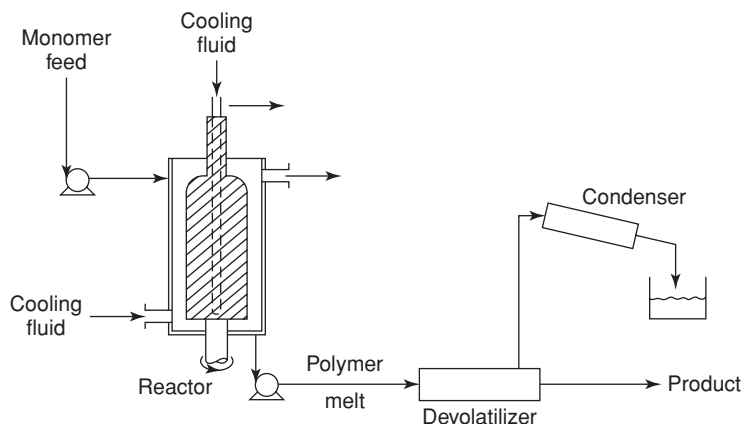


Fig. 9. SAN continuous mass process (309).

fixed composition copolymer. The two types of linear-flow reactors employed are the screw reactor (309) and the tower reactor (315). A screw reactor is composed of two concentric cylinders. The reaction mixture is conveyed toward the outlet by rotating the inner screw, which has helical threads, while heat is removed from both cylinders. A tower reactor with separate heating zones has a scraper agitator in the upper zone, while the lower portion generates plug flow. In the linear-flow reactors the conversion varies along the axial direction, as does the copolymer composition, except where operating at the azeotrope composition. A stream of monomer must be added along the reactor to maintain SAN compositional homogeneity at high conversions. A combined stirred-tank followed by a linear-flow reactor process has been disclosed (315). Through continuous recycle copolymerization, a copolymer of identical composition to monomer feed can be achieved, regardless of the reactivity ratios of the monomers involved (316).

The devolatilization process has been developed in many configurations. Basically, the polymer melt is subjected to high temperatures and low pressures to remove unreacted monomer and solvent. A two-stage process using a tube and shell heat exchanger with enlarged bottom receiver to vaporize monomers has been described (311). A copolymer solution at 40–70% conversion is fed into the first-stage exchanger and heated to 120–190°C at a pressure of 20–133 kPa and then discharged into the enlarged bottom section to remove at least half of the unreacted acrylonitrile. The product from this section is then charged to a second stage and heated to 210–260°C at <20 kPa. The devolatilized product contains ~1% volatiles. Preheating the polymer solution and then flashing it into a multi-passage heating zone at lower pressure than the preheater, produces essentially volatile-free product (310,317). SAN can be steam-stripped to quite low monomer levels in a vented extruder which has water injected at a pressure greater than the vapor pressure of water at that temperature (318).

A twin-screw extruder is used to reduce residual monomers from ca 50 to 0.6%, at 170°C and 3 kPa with a residence time of 2 min (313). In another design,

a heated casing encloses the vented devolatilization chamber, which encloses a rotating shaft with specially designed blades (319,320). These continuously regenerate a large surface area to facilitate the efficient vaporization of monomers. The devolatilization equipment used for the production of polystyrene and ABS is generally suitable for SAN production.

Processing. SAN copolymers may be processed using the conventional fabrication methods of extrusion, blow molding, injection molding, thermoforming, and casting. SAN is hygroscopic and should be dried before use for best results. Small amounts of additives, such as antioxidants, lubricants, and colorants, may also be used. Typical temperature profiles for injection molding and extrusion of predried SAN resins are as follows (321):

- (1) Molding temperatures
 - a. cylinder 193–288°C
 - b. mold 49–88°C
 - c. melt 218–260°C
- (2) Extrusion temperatures
 - a. hopper zone water-cooled
 - b. rear zone 177–204°C
 - c. middle zone 210–232°C
 - d. torpedo zone and die 204–227°C

Health and Toxicology. SAN resins, in general, appear to pose few health problems, in that SAN resins are allowed by the FDA to be used by the food and medical industries for certain applications under prescribed conditions (322). The main concern over SAN resin use is that of toxic residuals, eg, acrylonitrile, styrene, or other polymerization components such as emulsifiers, stabilizers, or solvents. Each component must be treated individually for toxic effects and safe exposure level.

Acrylonitrile is believed to behave as an enzyme inhibitor of cellular metabolism (323) and is classified as a possible human carcinogen of medium carcinogenic hazard (324), and can affect the cardiovascular system and kidney and liver functions (323). Direct potential consumer exposure to acrylonitrile through consumer product usage is low because of little migration of the monomer from such products. The concentrations of acrylonitrile in consumer products are estimated to be less than 15 ppm in SAN resins. OSHA's permissible exposure limit for acrylonitrile is 2 ppm, an 8-h time-weighted average with no eye or skin contact; the acceptable ceiling limit is 10 ppm; and the action level, the concentration level that triggers the standard for monitoring, etc, is 1 ppm. Further information on the toxicology and human exposure to acrylonitrile is available (325–327).

Styrene, a main ingredient of SAN resins, is a possible human carcinogen (IARC Group 2B/EPA-ORD Group C). It is an irritant to the eyes and respiratory tract, and while prolonged exposure to the skin may cause irritation and CNS effects such as headache, weakness, and depression, harmful amounts are not likely to be absorbed through the skin. OSHA has set permissible exposure limits

for styrene in an 8-h time-weighted average at 100 ppm, the acceptable ceiling limit (short-term, 15 min, exposure limit) at 200 ppm (328), and the acceptable maximum peak at 600 ppm (5-min max. peak in any 3 h). For more information on styrene environmental issues, see the CEH Styrene marketing research report (329,330).

In September 1996, the EPA issued a final rule requiring producers of certain thermoplastics to reduce emissions of hazardous air pollutants from their facilities. The final rule seeks to control air toxins released during the manufacture of seven types of polymers and resins, including SAN.

Economic Aspects (Polymers)

The first commercial applications of acrylonitrile polymers were developed by German scientists to provide oil- and gasoline-resistant rubbers during World War II. Although nitrile elastomers (Buna N) no longer account for a main portion of acrylonitrile use, they are still indispensable in many applications. Also, in response to the needs of the war, scientists at U.S. Rubber Company developed the forerunners of modern ABS, ie, tough, shatterproof blends of nitrile rubbers and SAN copolymers. Acrylic fiber manufacture was initiated around 1960, and world production of acrylonitrile has since increased to $>4.0 \times 10^6$ t. Historically, acrylic fibers have consumed $>70\%$ of the acrylonitrile in Europe, the Far East, and Latin America. In the United States, this outlet has been gradually decreasing from 50% to about a 30% share.

SAN Economic Aspects. SAN has shown steady growth since its introduction in the 1950s. The combined properties of SAN copolymers, such as optical clarity, rigidity, chemical and heat resistance, high tensile strength, and flexible molding characteristics, along with reasonable price have secured their market position. Among the plastics with which SAN competes are acrylics, general-purpose polystyrene, and polycarbonate. SAN supply and demand are difficult to track because more than 75% of the resins produced are believed to be used captively for ABS compounding and in the production of acrylonitrile–styrene–acrylate (ASA) and acrylonitrile–EPDM–styrene (AES) weatherable copolymer (331). SAN is considered to be only an intermediate product and not a separate polymer in the production processes for these materials.

There are two major producers of SAN for the merchant market in the United States, Bayer Corp. and the Dow Chemical Co., which market these materials under the names of Lustran and Tyril, respectively. Bayer became a U.S. producer when it purchased Monsanto's styrenics business in December 1995 (332). Some typical physical properties of these SAN resins have been shown in Table 11. These two companies also captively consume the SAN for the production of ABS as well as SAN-containing weatherable polymers. The other two U.S. SAN producers, either mainly consume the resin captively for ABS and ASA polymers (GE Plastics) or toll produce for a single client (Zeon Chemicals). BASF is expected to become a more aggressive SAN supplier in the United States since its Altamira, Mexico, styrenics plant came on-line in early 1999. Overall, U.S. SAN consumption has been relatively stable for the last few years, ranging from 43×10^3 to 44.5×10^3 t (95–98 million pounds) between 1994 and 1996. Most markets

Table 15. U.S. Production/Consumption of SAN, 10³ t (Dry-Weight Basis)

	Production	Consumption ^a
1985	39.5	34.1
1986	41.8	35.9
1987	57.3	38.6 ^b
1988	67.3	41.4
1989	51.4	34.1
1990	61.4	37.3
1991	49.5	37.7
1992	51.4	38.2
1993	47.7	40
1994	62.7	44.5 ^c
1995	59.1	43.6 ^c
1996	55.5	43.6 ^c
1997	43.6	— ^c

^aIncludes captive consumption for uses other than ABS compounding and ASA/AES polymers production.

^bAccording to the SPI, 45 t of SAN resin was consumed domestically in 1987. Industry believes this figure to be incorrect. An estimate of 38.6 t is believed to be more accurate.

^cReported SPI data for 1996–1997 includes both U.S. and Canadian information and, therefore, are not included in this table. The stated CEH statistics represent consumption only.

for SAN are growing at only GDP rates. Consumption growth for SAN in 1996–2001 is expected to continue at an average annual rate approximation of GDP growth at 2%. Use for packaging will be flat and the automotive application may disappear altogether. Other markets, however, are expected to increase at annual rates between 2.3 and 5.9%. Production and consumption figures for SAN resin in recent years are shown in Table 15 (332).

Uses

Acrylonitrile copolymers offer useful properties, such as rigidity, gas barrier, chemical and solvent resistance, and toughness. These properties are dependent upon the acrylonitrile content in the copolymers. SAN copolymers offer low cost, rigidity, processibility, chemical and solvent resistance, transparency, and heat resistance, which provide advantages over other competing transparent/clear resins, such as poly(methyl methacrylate), polystyrene, polycarbonate, and styrene–butadiene copolymers. SAN copolymers are widely used in goods such as housewares, packaging, appliances, interior automotive lenses, industrial battery cases and medical parts. U.S. consumption of SAN/ABS resins in major industrial markets is about 1095 t in 1998.

Acrylonitrile copolymers have been widely used in films and laminates for packaging (333–337) because of their excellent barrier properties. In addition to laminates (338–342), SAN copolymers are used in membranes

Table 16. SAN Copolymer Uses^a

Application	Articles
Appliances	Air conditioner parts, decorated escutcheons, washer and dryer instrument panels, washing machine filter bowls, refrigerator shelves, meat and vegetable drawers and covers, blender bowls, mixers, lenses, knobs, vacuum cleaner parts, humidifiers, and detergent dispensers
Automotive	Batteries, bezels, instrument lenses, signals, glass-filled dashboard components, and interior trim
Construction electronic	Safety glazing, water filter housings, and water faucet knobs battery cases, instrument lenses, cassette parts, computer reels, and phonograph covers
Furniture	Chair backs and furniture shells, drawer pulls, and caster rollers
Housewares	Brush blocks and handles, broom and brush bristles, cocktail glasses, disposable dining utensils, dishwasher-safe tumblers, mugs, salad bowls, carafes, serving trays, and assorted drinkware, hangers, ice buckets, jars, and soap containers
Industrial	Batteries, business machines, transmitter caps, instrument covers, and tape and data reels
Medical	Syringes, blood aspirators, intravenous connectors and valves, petri dishes, and artificial kidney devices
Packaging	Bottles, bottle overcaps, closures, containers, display boxes, films, jars, sprayers, cosmetic packaging, liners, and vials
Custom molding	Aerosol nozzles, camera parts, dentures, disposable lighter housings, fishing lures, pen and pencil barrels, sporting goods, toys, telephone parts, filter bowls, tape dispensers, terminal boxes, toothbrush handles, and typewriter keys

^aRefs. 9 and 145.

(343–346), controlled-release formulations (347,348), polymeric foams (349,350), fire-resistant compositions (351,352), ion-exchange resins (353), reinforced paper (354), concrete and mortar compositions (355,356), safety glasses (357), solid ionic conductors (358), negative resist materials (359), electrophotographic toners (360), and optical recordings (361). SAN copolymers are also used as coatings (362), dispersing agents for colorants (363), carbon-fiber coatings for improved adhesion (364), and synthetic wood pulp (365). SAN copolymers have been blended with aromatic polyesters to improve hydrolytic stability (366), with methyl methacrylate polymers to form highly transparent resins (367), and with polycarbonate to form toughened compositions with good impact strength (368–371). Table 16 lists the most common uses of SAN copolymers in major industrial markets (232,319). Some important modifications of SAN copolymers are listed in Table 17.

Acrylonitrile has contributed the desirable properties of rigidity, high temperature resistance, clarity, solvent resistance, and gas impermeability to many

Table 17. Modified SAN Copolymers

Modifier	Remarks	Reference
Polybutadiene	ABS, impact resistant	^a
EPDM rubber ^b	Impact and weather resistant	371,372
Polyacrylate	Impact and weather resistant	373,374
Poly(ethylene-co-vinyl acetate) (EVA)	Impact and weather resistant	375
EPDM+EVA	Impact and weather resistant	376
Silicones	Impact and weather resistant	377
Chlorinated polyethylene	Impact and weather resistant and flame retardant	378
Polyester, cross-linked	Impact resistant	379
Poly(α -methylstyrene)	Heat resistant	380
Poly(butylene terephthalate)	Wear and abrasion resistant	381
Ethylene oxide-propylene oxide copolymers	Used as lubricants to improve processability	382
Sulfonation	Hydrogels of high water absorption	383
Glass fibers	High tensile strength and hardness	384

^aSee ACRYLONITRILE-BUTADIENE-STYRENE POLYMERS.

^bEthylene-propylene-diene monomer rubber.

polymeric systems. Its availability, reactivity, and low cost ensure a continuing market presence and provide potential for many new applications.

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ACRYLONITRILE–BUTADIENE–STYRENE POLYMERS

Introduction

Acrylonitrile–butadiene–styrene (ABS) polymers [9003-56-9] comprise a versatile family of readily processable resins used for producing products exhibiting excellent toughness, good dimensional stability, and good chemical resistance. Special product features can also be obtained such as transparency, unique coloration effects, higher heat performance, and flame retardancy. ABS is comprised of particulate rubber, usually polybutadiene or a butadiene copolymer, dispersed in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN) [9003-54-7]. The presence of SAN chemically attached or “grafted” to the elastomeric particles compatibilizes the rubber with the SAN component. Altering structural and compositional parameters allows considerable versatility in the tailoring of properties to meet specific product requirements.

Physical Properties

Typical mechanical properties of some commercially available ABS materials are listed in Table 1. It is indicated that a wide range of mechanical and impact properties are achievable for ABS materials.

These property variations are obtained through comonomers, additives, or by making structural changes such as the following: rubber content, extent of rubber cross-linking, rubber particle size and distribution, grafted SAN level and composition, and the composition and molecular weight of the matrix. Depending on the polymerization technique, SAN can be controlled to varying levels as the continuous phase, as grafted polymer attached to the rubber particles, and as occlusions contained within the rubber particles. Thus, both the rubber content and the “rubber phase” (defined as rubber that may contain occluded SAN) volume fraction at a given rubber weight fraction can be independently controlled. Because of the capability to vary such structural and compositional parameters for property enhancements, ABS is a versatile engineering thermoplastic that can be customized to provide a wide range of mechanical and flow properties.

Structural and Compositional Effects. Being a multiphase polymer blend, the effects of the compositional and structural features in ABS are complex and interdependent. However, to a first approximation, the rubber phase contributes toughness, the styrene component contributes rigidity and processability, and the acrylonitrile (AN) phase contributes chemical resistance.

Effect of Dispersed Rubber Phase. The impact toughness of ABS is one of many properties affected by the rubber phase volume fraction, particle size and size distribution, and structure. SAN alone is quite brittle—it is the presence of the uniformly distributed rubber phase (ranging in size from 50 to 2000 nm) that imparts the ductility observed in ABS resins. It is widely reported that rubber particles induce plastic deformation in the SAN phase on a microscopic scale in the form of crazing and shear yielding accompanied (in most cases) by rubber voiding (1–4). A maximum in impact energy seems to occur when the

Table 1. Material Properties of ABS Grades

Properties	ASTM method	Medium impact	High impact	Heat resistant	Flame retardant	High modulus ^a
Notched Izod impact at rt, J/m ^b	D256	160–270	270–530	75–300	140–320	50–150
Tensile yield strength, MPa ^c	D638	35–50	30–45	35–60	35–45	65–95
Elongation at break, %	D638	20–40	25–80	10–60	10–30	2–5
Flexural yield strength, MPa ^c	D790	55–75	50–75	55–90	55–75	95–160
Flexural modulus, GPa ^d	D790	2–3	1.5–2.5	2–3	2–2.5	4–9
Heat deflection ^e , °C at 1825 kPa ^f	D648	75–90	75–85	90–110	70–80	95–105
Vicat softening pt, °C	D1525	100–110	95–105	110–125	85–100	100–110
Rockwell hardness	D785	100–115	80–110	105–115	95–105	110–115

^aFilled with ~10–30% glass.

^bTo convert J/m to ft.lbs/in., divide by 53.4.

^cTo convert MPa to psi, multiply by 145.

^dTo convert GPa to psi, multiply by 145,000.

^eUnannealed at 6.35-mm thickness.

^fTo convert kPa to psi, multiply by 0.145.

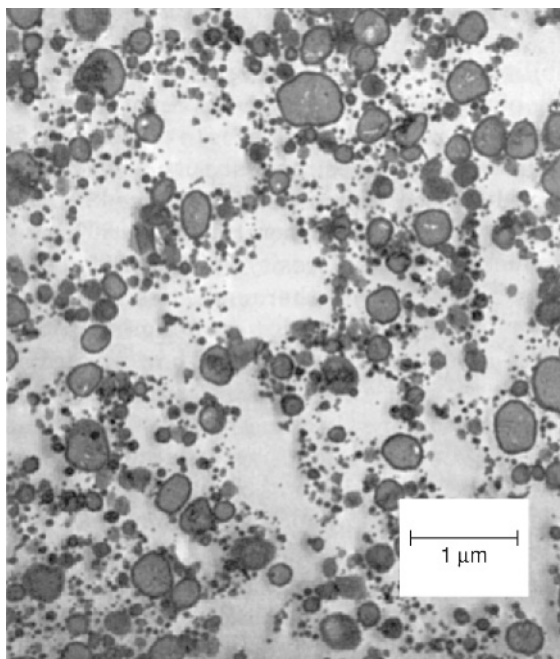


Fig. 1. Transmission electron micrograph of ABS produced by an emulsion process. Staining of the rubber bonds with osmium tetroxide provides contrast with the surrounding SAN matrix phase.

micro deformation process is dominated by shear yielding at the deformation rates involved. The impact strength of ABS increases with rubber phase content usually leveling off at $\sim 30\%$ rubber by weight. Most commercial ABS resins have a rubber content in the range of 10–35 wt%. The volume fraction of the rubber phase at a given rubber level can be much higher for products manufactured by the mass (or sometimes termed a “bulk ABS”) vs emulsion process because of the much higher level of occluded SAN produced in the mass process (see Figs. 1 and 2).

The rubber phase size and size distribution is also affected by the manufacturing process. Typically, the size of the rubber phase averages ~ 200 – 400 nm for resin produced by an emulsion process and ~ 1000 – 2000 nm for resin produced by mass polymerization. The size distribution of the rubber particles can be very broad, narrow monomodal, or bimodal. The dependence of the impact toughness of ABS on rubber phase particle size and size distribution can be of a complex nature because of the interactions with the graft interface. A maximum impact is reported (1) to occur for emulsion ABS at a mean rubber particle size of about 300 nm for a matrix SAN containing 25% AN.

It has been reported (5) that the elastic modulus of ABS resins prepared by either mass or emulsion polymerization can be represented by a single relationship with the dispersed phase volume fraction. This is in agreement with the theory that the modulus of a blend with dispersed spherical particles depends only on the volume fraction and the modulus ratio of particles to matrix phase.

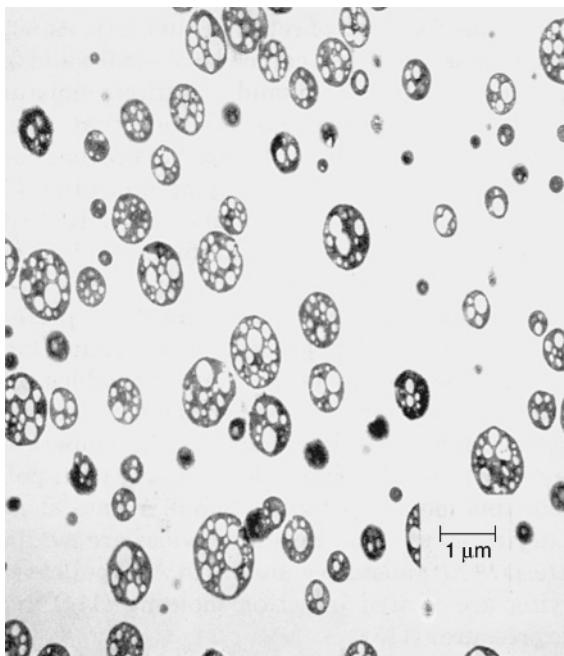


Fig. 2. Transmission electron micrograph of ABS produced by a mass process. The rubber domains are typically larger in size and contain a higher concentration of occluded SAN than those produced by emulsion technology.

Since the modulus of rubber is almost 1000 times smaller than the modulus of the matrix SAN, the rubber particle volume fraction alone is the most important parameter controlling modulus values of ABS resins. Even for rubber particles containing a high occlusion level, as in ABS produced by mass polymerization, the modulus of the composite particle still remains unchanged from pure rubber, suggesting a unique relationship between modulus and dispersed phase volume fraction. Also, the modulus of a material is a small strain elastic property and is independent of particle size in ABS. The effects of rubber content on modulus and on tensile and flexural yield stress are shown in Figures 3 and 4 for an emulsion produced ABS. As illustrated, the tensile and flexural yield stress values are also strongly affected by the rubber volume fraction, although—unlike modulus—the stress values are not independent of rubber particle size. It is known that tensile yield stress decreases at a given rubber volume fraction with an increase in particle diameter; this behavior is explained on the basis of having an increased volume of matrix SAN under higher stress near rubber particles (6).

Effect of Matrix SAN Composition and Molecular Weight. At a given rubber content and grafted rubber particle size and distribution, the mechanical properties of ABS are also strongly affected by the molecular weight and composition of the SAN present as the continuous, matrix phase. Increasing the molecular weight of the matrix SAN increases impact toughness, an effect which tends to level off at molecular weights higher than a number-average molecular weight (M_n) of $\sim 60,000$. If the SAN M_n is less than 25,000, no significant amount of

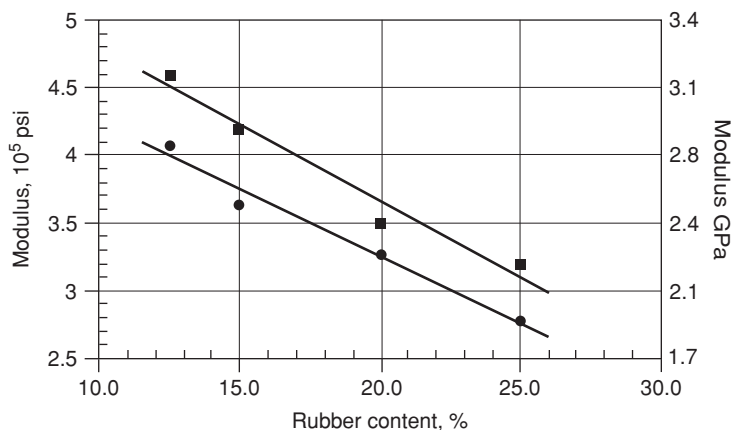


Fig. 3. Effect of rubber content on tensile and flexural modulus of emulsion ABS. The rubber particle volume fraction alone is the most important parameter controlling the modulus values of ABS. ● Tensile mod and ■ flex mod.

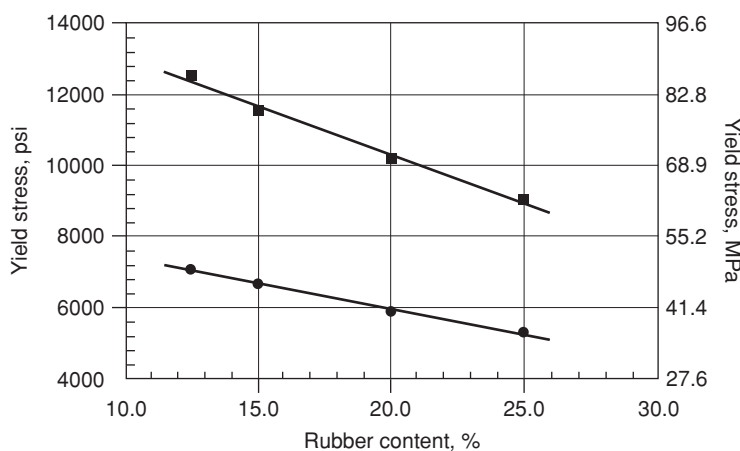


Fig. 4. Effect of rubber content on tensile and flexural yield stress of emulsion ABS at a fixed rubber particle size. ● Tensile stress and ■ flex stress.

crazing deformation is indicated, and therefore, no significant toughening takes place with rubber addition. Yield stress and modulus values of ABS appear to be independent of the molecular weight of the SAN, consistent with the observation that the craze initiation stress value for SAN is independent of molecular weight above an M_n of $\sim 25,000$ (7). A similar relationship between craze initiation stress and molecular weight has been reported for polystyrene (8).

The AN content of SAN has a significant influence on the environmental stress-cracking resistance of ABS, and it is generally observed that increasing AN

content increases the stress-cracking resistance of ABS. Most general-purpose ABS materials contain SAN with AN content of 20–30%, whereas improved chemical resistance ABS grades employ SAN with AN content of about 35%. It is also indicated that AN in SAN improves the crazing resistance of SAN, which can explain the increased ductility of ABS as compared to rubber-modified polystyrene (high impact polystyrene). Creep and fatigue performance also improve as the AN content of the SAN is increased. In addition to the AN content of SAN matrix, the AN content of the grafted SAN plays an important role in ABS materials prepared by the melt blending of grafted rubber with SAN pellets. If the difference between AN levels of matrix SAN and grafted SAN is over 5%, some immiscibility and partial phase separation can take place (9), which can cause rubber aggregation during compounding and processing steps. Surface gloss of final article may be lowered although mechanical properties and impact toughness can be maintained with an AN mismatch of as high as 10% between the grafted SAN and matrix SAN. Surface appearance can also be affected if two different matrix SAN components having a differing AN content are mixed because of the surface of the molded part becoming enriched with the SAN of lower AN content (10).

Effect of Grafted SAN. The extent of grafting is a critical parameter as well. If the level of grafted SAN is lowered, a nonuniform dispersion of rubber may occur, affecting toughness and aesthetic properties (eg, gloss). Furthermore, the rubber aggregates will also have an increased tendency to undergo deformation during processing, resulting in the loss of toughness, mechanical, and aesthetic properties. In commercial ABS materials, SAN molecular weight and composition, graft amount, and rubber particle size and structure are properly balanced to achieve an optimal balance of mechanical properties, toughness, melt viscosity, and aesthetics.

Rheology. The ABS manufacturer controls rheological properties through structure variations which can have a complex effect dependent on shear rate. Effects of structural variations on viscosity functions are more evident at lower shear rates ($<10/s$) vs higher shear rates. At high shear rates, the melt viscosity is controlled primarily by the composition and molecular weight of the ungrafted SAN and by the percentage of the grafted rubber phase. The modulus curves correspond in their shape to that of the ungrafted SAN component, and the rubber particle type and concentration have little effect on the temperature dependence of the viscosity function (11). The extrudate swell, however, becomes smaller with increasing rubber concentration (12).

By contrast, the graft phase structure has a marked effect on viscosity at small deformation rates. The long time relaxation spectra are affected by rubber particle–particle interactions (13,14), which are strongly dependent on particle size, grafting, morphology, and rubber content. Depending on particle surface area, a minimum amount of graft is needed to prevent the formation of three-dimensional networks of associated rubber particles (14). At low shear rates, the associated rubber particles behave similar to a cross-linked rubber; the network structure, however, is dissolved by shearing forces. Extensive studies on the viscoelastic properties of ABS in the molten state have been reported (11–18). Effects of lubricants and other nonpolymeric components have also been described (19). Techniques for characterizing melt-flow differences include melt-flow rate, melt index, spiral flow, and capillary rheometry.

High shear rate viscosity (eg, 1000/s) is considered more relevant to injection-molding applications, and, in general, molding grades have lower melt viscosities than extrusion grades. Designers are striving to further reduce costs through thinwall design. ABS exhibits both low melt viscosity and good impact strength, key characteristics making ABS suitable for thinwall applications (20).

Gloss. Surface gloss values can be achieved ranging from a very low matte finish at <10% (60° Gardner) to high gloss in excess of 95%. Gloss is dependent on the specific grade and the mold or polishing roll surface. Low gloss is achieved either through the use of large rubbery domains, aggregates of smaller rubber particles, or through the addition of dulling agents.

Thermal Properties. Higher heat ABS grades are achieved through copolymerization with monomers (eg, alpha methyl styrene or *N*-phenyl maleimide) in the matrix phase or through the use of ABS as a base polymer in high performance alloys. Most common are ABS–polycarbonate alloys which extend the property balance achievable with ABS to offer even higher impact strength and heat resistance (21).

Color. ABS is sold as an unpigmented powder, unpigmented pellets, pre-colored pellets matched to exacting requirements, and “salt-and-pepper” blends of ABS and color concentrate. Color concentrates can also be used for on-line coloring during molding.

Transparency. Standard ABS grades are opaque because of the refractive index mismatch between the dispersed rubber phase and the continuous SAN matrix. However, ABS-type systems are available as transparent grades for clear applications, with transparency achieved by the matching of the refractive index of the rubber and matrix phases through the incorporation of comonomers. Typically, refractive index of the rubber phase is increased through the use of styrene–butadiene rubber and the matrix phase reduced and matched to the rubber phase through terpolymerization with methylmethacrylate.

Chemical Properties

The behavior of ABS may be inferred from consideration of the functional groups present within the polymer.

Chemical Resistance. The term *chemical resistance* is generally used in an applications context and refers to resistance to the action of solvents in causing swelling or stress cracking as well as to chemical reactivity. Environmental stress cracking can be assessed by applying a chemical to a prestressed sample and determining its stress-crack resistance over a specified period of time. As previously discussed, the presence of AN enhances environmental stress-cracking resistance. In ABS, the polar character of the nitrile group reduces interaction of the polymer with hydrocarbon solvents, mineral and vegetable oils, waxes, and related household and commercial materials. Good chemical resistance provided by the presence of AN as a comonomer combined with relatively low water absorptivity (<1%) results in high resistance to staining agents (eg, coffee, grape juice, beef blood) typically encountered in household applications (22).

Similar to most polymers, ABS undergoes stress cracking when brought into contact with certain chemical agents under stress (22,23). Injection-molding

conditions can significantly affect chemical resistance, and this sensitivity varies with the ABS grade. Certain combinations of melt temperature, fill rate, and packing pressure can significantly reduce stress-cracking resistance, and this effect is interactive in complex ways with the imposed stress level that the part is subjected to in service. Both polymer orientation and stress appear to be considerations; thus, critical strains can be higher in the flow direction (24). Consequently, all media to be in contact with the ABS part during service should be evaluated under anticipated end-use conditions.

Processing Stability. Processing can influence resultant properties by chemical and physical means (25,26). Degradation of the rubber and matrix phases has been reported under very severe conditions (27). Morphological changes may become evident as agglomeration of dispersed rubber particles during injection molding at higher temperatures (26). Physical effects such as orientation and molded-in stress can have marked effects on mechanical properties. Thus, the proper selection and control of process variables are important to maintain optimum performance in molded parts. Antioxidants added at the compounding step have been shown to help retention of physical properties upon processing (25).

Appearance changes evident under certain processing conditions include color development (25), changes in gloss (27), and splaying. Discoloration may be minimized by reducing stock temperatures during molding or extrusion. *Splaying* is the formation of surface imperfections elongated in the direction of flow and is typically caused by moisture, occluded air, or gaseous degradation products; proper drying conditions are essential to prevent moisture-induced splay.

Techniques for evaluating processing stability and mechanochemical effects include using a Brabender torque rheometer (28,29), injection molding (26,28), capillary rheometry (26,28), and measuring melt index as a function of residence time (25).

Thermal Oxidative Stability. ABS undergoes autoxidation and the kinetic features of the oxygen consumption reaction are consistent with an autocatalytic free-radical chain mechanism. Comparisons of the rate of oxidation of ABS with that of polybutadiene and SAN indicate that the polybutadiene component is significantly more sensitive to oxidation than the thermoplastic component (30–32). Oxidation of polybutadiene under these conditions results in embrittlement of the rubber because of cross-linking and the introduction of polar oxidized groups; such embrittlement of the elastomer in ABS results in the loss of impact strength. Studies have also indicated that oxidation causes detachment of the grafted SAN from the elastomer, which contributes to impact deterioration (33).

Examination of oven-aged samples has demonstrated that substantial degradation is limited to the outer surface (33), ie, the oxidation process is diffusion limited. Consistent with this conclusion is the observation that oxidation rates are dependent on sample thickness (31). Impact property measurements by high speed puncture tests have shown that the critical thickness of the degraded layer at which surface fracture changes from ductile to brittle is about 0.2 mm. Removal of the degraded layer restores ductility (33). A demonstration of the effects of an embrittled surface on impact was achieved using ABS coated

with SAN (34). Rates of oxidation can be significantly affected by additives such as colorants (31).

Test methods for assessing thermal oxidative stability include oxygen absorption (30,31,35), thermal analysis (36,37), oven aging (33,38,39), and chemiluminescence (40,41). Such techniques primarily reflect the reactivity of the rubber component in ABS with oxygen.

Antioxidants have been shown to improve oxidative stability substantially (42,43). Hindered phenols, thiodipropionates, and phosphites can be effective in improving processing or end-use stability (44). In multiphase systems like ABS, stabilizers can partition between the component phases. Thus, the additive concentration in each phase can differ significantly from the added or average concentration potentially influencing additive effectiveness. The use of rubber-bound stabilizers to permit concentration of the additive in the rubber phase has been reported (45–47). Scanning electron microscopy (sem) using xeds (energy dispersive x-ray analysis) has been used to determine the partitioning behavior of stabilizers in ABS. The partitioning of various conventional stabilizers between the rubber and thermoplastic phases has been shown to correlate with solubility parameter values (48).

Photo-oxidative Degradation. Unsaturation present as a structural feature in the polybutadiene component of ABS (also in high impact polystyrene, rubber-modified PVC, and ABS–polycarbonate blends) increases lability with regard to photo-oxidative degradation (49–51), which can result in discoloration and loss of impact. Applications involving outdoor exposure require protective measures to maintain an optimum level of performance. Light stabilizers provide some measure of protection (52,53), as illustrated by the very successful use of ABS in interior automotive trim. Colorants have a significant effect on light stability and can either increase or decrease color fastness, depending on colorant type. For extended outdoor exposure, the best protection is provided by a protective coating which can be either paint or a cap layer of a weatherable polymer such as a thermoplastic acrylic, cast acrylic, or ASA (acrylonitrile–styrene–acrylate terpolymer). A cap layer of ASA vs acrylics (PMMA) minimizes brittle surface layer effects. The cap layer is applied by coextrusion over ABS, resulting in a laminate sheet which can be thermoformed into parts providing a favorable balance of cost and part performance that includes excellent weatherability.

The photodegradation of ABS typically occurs in the outermost layer (54,55). Impact loss upon irradiation is due to embrittlement of the rubber and possibly scission of the grafted SAN (49,56). Appearance changes such as yellowing are caused by chromophore formation in both the polybutadiene and SAN components (49,57). Mechanisms describing the photo-oxidative degradation of ABS have been proposed (51,52,58). Oxidation studies with singlet oxygen have shown that initial attack on ABS occurs on the polybutadiene component (59). Weathering studies have been conducted using artificial (60,61) and outdoor exposure (60) conditions. Light wavelength dependence has been studied, and photodegradation of the polybutadiene component has been reported to be primarily initiated by wavelengths below 350 nm (62) but can extend into the visible region (63). For discoloration, photochemical yellowing is caused primarily by wavelengths between 300 and 360 nm, and maximum bleaching of yellow colored species is reported to occur in the 475- to 485-nm region (62). For the above reasons, any spectral difference between accelerated aging and actual exposure could lead to

a lack of correlation, affecting predictive capability by accelerated techniques. Xenon arc is preferred vs other test methods (eg, carbon arc, HPUV) because of the closer simulation of the spectral distribution of sunlight by Xenon arc if the appropriate filter combination is used. Oxidative degradation induced by processing may also affect photosensitivity (49,64). A comparative study on the weathering of ABS and other acrylic-based plastics has shown that elastomer type and SAN phase composition are two key factors affecting both color and impact retention (65).

Test methods that have been used to determine the effects of light aging on embrittlement of ABS include Izod impact, Charpy impact, flexural tests, falling dart, and dynamic mechanical measurements. Because photodegradation occurs only on the outer surface and the interior of the sample remains essentially unaffected, a pendulum type of notched impact will not be sensitive to changes in surface embrittlement. Falling dart types of testing increase sensitivity to surface changes; the use of a high speed puncture test has been described for determining the effect of outdoor exposure on crack-initiation energy values for ABS (65).

Flammability. The general-purpose grades are usually recognized as 94 HB according to the requirements of Underwriters' Laboratories UL94. Flame-retardant (FR) grades (V0, V1, and V2) are also available which meet Underwriters' UL 94/94 5V and Canadian Standards Association (CSA) requirements. Flame retardancy is typically achieved by utilizing halogenated additives in combination with antimony oxide or by alloys with PVC or PC (66–68). A wide variety of brominated flame retardants have been used in ABS with tetrabromobisphenol-A (TBBPA) and brominated epoxy oligomers (BEOs), currently in widespread use. Both are melt-blendable and can be well dispersed on most commercial equipment. TBBPA is very cost effective, providing excellent flame retardancy and good flow properties; however, products formulated with TBBPA generally have poorer light stability and a lower heat-deflection temperature. Although TBBPA exhibits low thermal stability, processing is usually not an issue if recommended guidelines are followed. Flame-retardant ABS grades formulated with BEOs are preferred if reduced color shift upon light exposure is required.

Polymerization

All manufacturing processes for ABS involve the polymerization of styrene and acrylonitrile monomers in the presence of an elastomer (typically polybutadiene or a butadiene copolymer) to produce SAN that has been chemically bonded or “grafted” to the rubber component termed the “substrate.”

Rubber Chemistry. The rubber substrate is typically produced by the free-radical polymerization of butadiene. The radical source can be provided by either thermal decomposition or oxidation–reduction (redox) systems. The primary product is primarily 1,4-polybutadiene with some 1,2-polybutadiene, which contains a pendent vinyl group. Cross-linking of polymer occurs at high conversion through abstraction of reactive allylic sites or by copolymerization through double bonds (especially the double bonds in the more sterically accessibly pendent vinyl groups). Rubber cross-linking is controlled by the use of chain-transfer agents and the concentration and type of the initiator used; the reaction can also

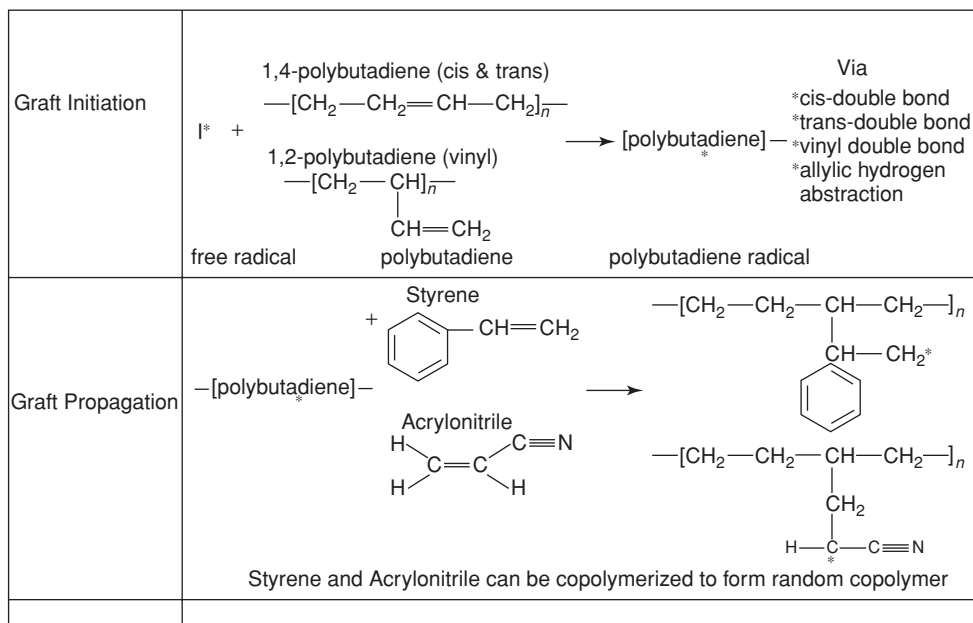


Fig. 5. Mechanisms of graft SAN formation.

be affected by chain transfer to emulsifiers. For emulsion ABS, the rubber is typically both produced and subsequently used for grafting as a latex.

Graft Chemistry. Grafting of styrene and acrylonitrile onto a rubber substrate is the essence of the ABS process. Grafting is a free-radical process initiated by the abstraction of allylic hydrogens on the rubber substrate or by copolymerization through double bonds that are pendent or internal in the rubber substrate, as illustrated in Figure 5 (69). Initiator level and type affects the extent of grafting (69–75) with oxyradicals yielding a higher degree of grafting than carbon radicals because of higher rates of abstraction from the rubber substrate. Chain-transfer agents are also used in controlling overall degree of grafting and graft molecular weight.

Ungrafted SAN is formed concurrently with grafted SAN, with the ratio controlled by factors that include temperature, chain-transfer agent, pendent vinyl content of rubber, initiator level, and initiator type (69–77). As previously described, occlusions of SAN can also form within the rubber particles with the mass process leading to significantly higher occlusion levels than the emulsion process (78,79). In the mass process, block copolymers of styrene and butadiene can be added to obtain unusual particle morphologies (eg, coil, rod, capsule, cellular) (78).

Emulsion Process. The emulsion process for making ABS has been commercially practiced since the early 1950s. Its advantage is the capability of producing ABS with a wide range of compositions, particularly higher rubber contents than are possible with other processes. Mixing and transfer of the heat of reaction in an emulsion polymerization is achieved more easily than in the mass polymerization process because of the low viscosity and good thermal

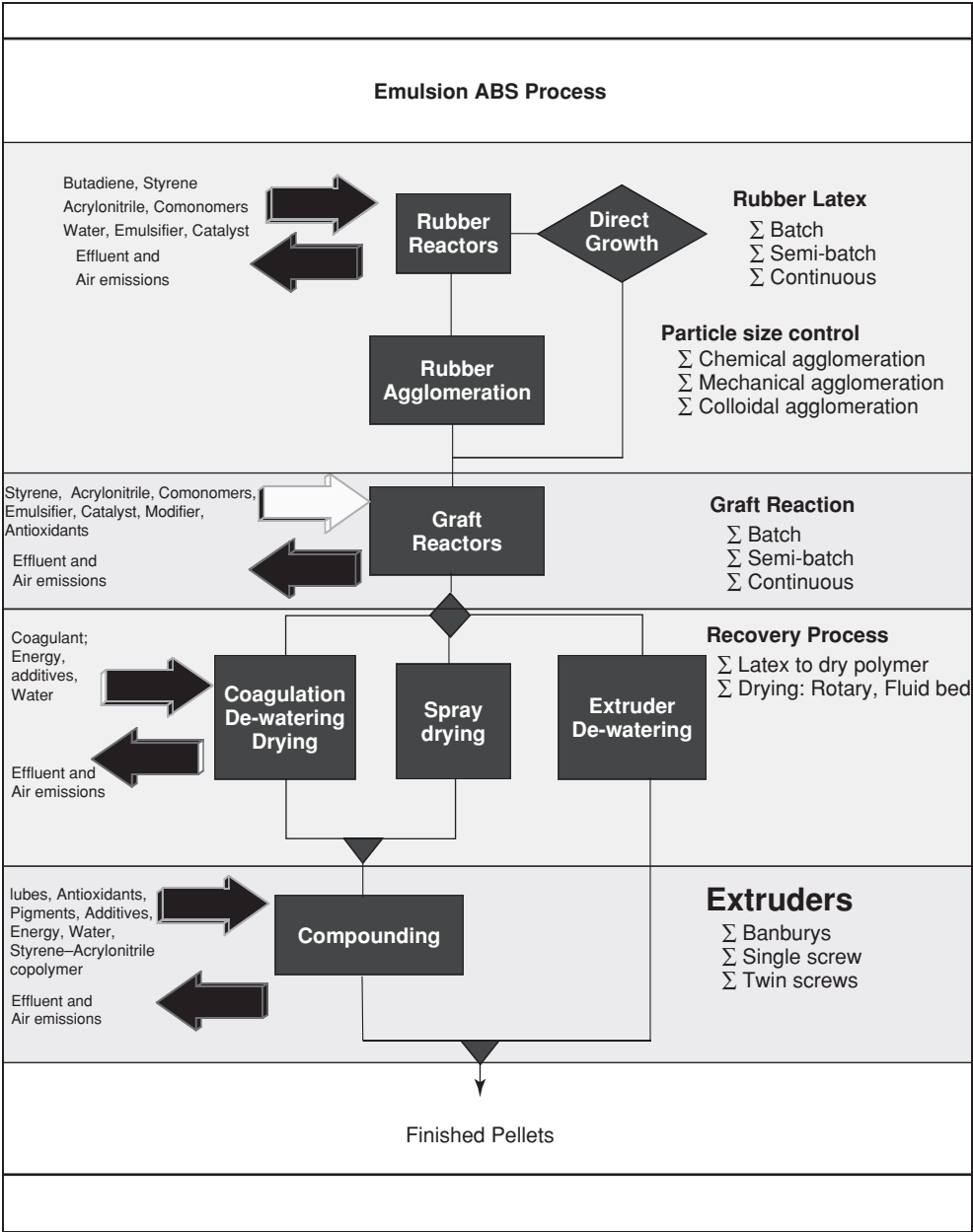


Fig. 6. Emulsion ABS process.

properties of the water phase. The energy requirements for the emulsion process are generally higher because of the energy usage in the polymer recovery area. The emulsion polymerization process is typically a two-stage reaction process (80,81), as illustrated in Figure 6.

In the first stage, a rubber substrate, primarily composed of polybutadiene, is made using an emulsion polymerization process. The desired particle size of the rubber is either obtained by direct growth during polymerization or by an agglomeration process subsequent to polymerization. In a second-stage reaction, styrene and acrylonitrile are grafted onto the rubber substrate by emulsion polymerization. After the graft reaction is complete, the polymer can be recovered from the graft latex and compounded into a final pellet product (81–86).

Rubber Substrate Process. The rubber substrate can be made by a variety of different reaction processes including batch, semi-batch, and continuous (87). Butadiene monomer is primarily used in the substrate reaction, but comonomers such as styrene and acrylonitrile are common (84,85). The amount and type of comonomer employed will affect the glass transition of the rubber substrate and, thereby, influence the impact properties of the ABS polymer. Oxidation–reduction systems (eg, hydrogen peroxide and iron) or thermal initiators (eg, potassium persulfate or azobisisobutyronitrile) are used to initiate polymerization. Cross-link density is controlled by type and level of initiator, type and level of chain-transfer agent, reaction temperature, degree of conversion, or by the addition of comonomers. It is important to note that the graft process also can affect the cross-link density of the rubber. Various surfactant types can be employed to emulsify the monomer and stabilize the latex particles. Standard fatty acid soaps and derivatives are the most common emulsifiers employed; however, detergents such as sodium dobenzyl sulfonate and sodium lauryl sulfate can also be used. The use of nonionic surfactants has been reported (88). The “soap-free” emulsion polymerization of butadiene is possible using reactive surfactants (89), functional monomers such as acrylic acid (90), or high levels of potassium persulfate (91). The incorporation of surfactants into the polymer backbone provides the advantage of minimizing low molecular by-products in the final polymer that could result in mold buildup or juicing.

The incorporation of comonomers into the rubber substrate can be useful in achieving specialized performance of the final ABS polymer, such as adjusting the refractive index of the rubber phase to better match the continuous SAN phase to achieve a clear or more translucent ABS product (92). The incorporation of polymerizable antioxidants or uv stabilizers has also been reported (93). Typically, these modifications increase the cost of ABS and are only employed for specialized applications.

Reactor productivity can be effected by various factors including initiator type, latex particle size, monomer purity, chain-transfer agents, and reaction temperature (87). As previously described, rubber particle size and distribution are important factors controlling the final properties of the ABS polymer. Large particles can be obtained by direct growth in the reactor, but much longer reaction times are needed. Comonomers such as AN can be added to speed the reaction rate and achieve relatively large particles in less time (94,95). Productivity can also be improved by the use of antifouling agents to minimize buildup of polymer on reactor heat-transfer surfaces (96–98). These antifouling agents improve heat transfer and minimize the time the reactor is down for cleaning.

Graft Process. Grafted SAN is critical to achieving effective dispersion of the rubber in the matrix phase, with key factors being SAN composition and

rubber particle surface coverage. The composition of the grafted SAN depends on the monomer-feed composition and the monomer reactivity ratio. The composition of the polymer formed will equal the feed at the azeotropic composition, which occurs at $\sim 3/1$ mass ratio of styrene-to-acrylonitrile (80,88), and compositional drift will occur at monomer feed compositions other than the azeotropic concentration. Note that in aqueous systems, the difference in water phase solubility of acrylonitrile vs styrene can also perturb monomer concentrations at the reaction site and, thus, affect compositional drift. Polymerization techniques such as continuous vs batch processes and controlling pump rates can be used to control compositional drift (99–105). Surface coverage is controlled by rubber particle surface area and is effected by factors including initiator type, monomer feed to rubber level, and chain-transfer agents.

Resin Recovery Process. Typically, the polymer is recovered by the addition of coagulants which destabilize the ABS latex. Different coagulants are used depending on the surfactant. Thus, strong and weak acids work well with fatty acid soaps, and metal salts are used with acid stable soaps (106). The use of nonionic coagulants has also been reported (107,108). Acrylic latices have been used to control the coagulation process and obtain a narrow resin particle-size distribution (109).

Once coagulated, the resulting slurry can then be filtered or centrifuged to recover wet ABS resin, which is then dried to a low moisture content. A variety of dryers can be used for ABS, including tray, fluid bed, and rotary kiln-type dryers. Other methods of recovery have been employed such as spray drying (110) and extruder dewatering (111). Spray drying allows for good control of the final particle size of the resin, but uses a significant amount of energy in the drying process. In extruder dewatering, the latex is either directly fed into the extruder or is first coagulated and then fed into the extruder. Extruder dewatering allows for more efficient stripping and recovery of unreacted monomer than standard drying processes.

Air and Water Treatment. The emulsion process exerts a greater demand on wastewater treatment than other processes (suspension or mass) because of the quantity of water used, and air emissions may be higher because of the types of process equipment employed. Recent federal and state EPA regulations governing air emission from ABS facilities affect the level of styrene, acrylonitrile, butadiene, and other volatile organic compounds that can be emitted into the air or sent to wastewater treatment facilities. In some cases, effluent water can be recycled and reused, but ultimately the water must be discharged, requiring treatment of the water prior to discharge. Air emissions from an emulsion ABS process can be reduced by improving the conversion of the monomers (112), the installation of equipment to strip and recover monomers, or the installation of end-of-pipe controls. End-of-pipe controls such as regenerative catalytic oxidation, regenerative thermal oxidation, fixed and fluid bed carbon absorption, and biofiltration are viable means of addressing air emission issues (113).

Mass Polymerization Process. In the mass (114–122) ABS process, the polymerization is conducted in a monomer medium rather than in water, usually employing a series of two or more continuous reactors. The rubber used in this process is most commonly a solution polymerized linear polybutadiene (or

copolymer containing styrene), although some mass processes utilize emulsion-polymerized ABS with a high rubber content for the rubber component (123). If a linear rubber is used, a solution of the rubber in the monomers is prepared for feeding to the reactor system. If emulsion ABS is used as the source of rubber, a dispersion of the ABS in the monomers is usually prepared after the water has been removed from the ABS latex.

In the mass process (124) using linear rubber, the rubber initially dissolved in the monomer mixture will phase separate, forming discrete rubber particles as SAN polymerization proceeds. This process is referred to as phase inversion since the continuous phase shifts from rubber to SAN during the course of polymerization. Special reactor designs are used to control the phase inversion portion of the reaction (115,117–120). By controlling the shear rate in the reactor, the rubber particle size can be modified to optimize properties. Grafting of some of the SAN onto the rubber particles occurs as in the emulsion process. Typically, the mass-produced rubber particles are larger than those of emulsion-based ABS and contain much larger internal occlusions of SAN. The reaction recipe can include polymerization initiators, chain-transfer agents, and other additives. Diluents are sometimes used to reduce the viscosity of the monomer and polymer mixture to facilitate processing at high conversion. The product from the reactor system is devolatilized to remove the unreacted monomers and is then pelletized. Equipment used for devolatilization includes single- and twin-screw extruders and flash and thin film/strand evaporators. Unreacted monomers are recovered and recycled back to the reactors to improve the process yield.

The mass ABS process was originally adapted from the mass polystyrene process (125). Mass produced ABS typically has very good unpigmented color and is usually somewhat more translucent because of the large rubber phase particle size and low rubber content. Increased translucency can reduce the concentration of colorants required. The extent of rubber incorporation is limited to approximately 20% because of viscosity limitations in the process; however, the mass-produced grafted rubber can be more efficient (on an equal percent rubber basis) at impact modification than emulsion-grafted rubber because of the presence of high occlusion levels in the rubber phase. The surface gloss of the mass-produced ABS is generally lower than that of emulsion ABS because of the presence of the larger rubber particles, but recent advances provide additional flexibility to achieve higher gloss (115–119).

Suspension Process. The suspension process utilizes a mass (126) or emulsion reaction (127,128) to produce a partially converted mixture of polymer and monomer and then employs a batch suspension process (129) to complete the polymerization. When the conversion of the monomers is approximately 15–30% complete, the mixture of polymer and unreacted monomers is suspended in water with the introduction of a suspending agent. The reaction is continued until a high degree of monomer conversion is attained and then unreacted monomers are stripped from the product before the slurry is centrifuged and dried, producing product in the form of small beads. The morphology and properties of the mass suspension product are similar to those of the mass-polymerized product. The suspension process retains some of the process advantages of the water-based emulsion process, such as lower viscosity in the reactor and good heat removal capability.

Compounding. ABS either is sold as an unpigmented product, in which case the customer may add pigments during the forming process, or it is colored by the manufacturer prior to sale. Much of the ABS produced by the mass process is sold unpigmented; however, precolored resins provide advantages in color consistency. If colorants, lubricants, fire retardants, glass fibers, stabilizers, or alloying resins are added to the product, a compounding operation is required. ABS can be compounded on a range of equipment, including batch and continuous melt mixers, and both single- and twin-screw extruders. The device must provide sufficient dispersive and distributive mixing dependent on formulation ingredients for successful compounding, and low work or low shear counterrotating twin-screw extruders as used in PVC are not recommended. In the compounding step, more than one type of ABS may be employed (ie, emulsion and mass-produced) to obtain an optimum balance of properties for a specific application. Products can also be made in the compounding process by combining emulsion ABS having a high rubber content with mass- or suspension-polymerized SAN.

Analysis. Analytical investigations may be undertaken to identify the presence of an ABS polymer, characterize the polymer, or identify nonpolymeric ingredients. Fourier transform infrared (ftir) spectroscopy is the method of choice to identify the presence of an ABS polymer and determine the ABS ratio of the composite polymer (130,131). Confirmation of the presence of rubber domains is achieved by electron microscopy. Comparison with available physical property data serves to increase confidence in the identification or indicate the presence of unexpected structural features. Identification of ABS by pyrolysis gas chromatography (132) and dsc (133) has also been reported. Detailed compositional and molecular weight analyses involve determining the percentage of grafted rubber; determining the molecular weight and distribution of the grafted SAN and the ungrafted SAN; and determining compositional data on the grafted rubber, the grafted SAN, and the ungrafted SAN. This information is provided by a combination of phase-separation and instrumental techniques. Separation of the ungrafted SAN from the graft rubber is accomplished by ultracentrifugation of ABS dispersions (134,135), which causes sedimentation of the grafted rubber. Cleavage of the grafted SAN from the elastomer is achieved using oxidizing agents such as ozone [10028-15-6] (135,136), potassium permanganate [7722-64-7] (137), or osmium tetroxide [20816-12-0] with *tert*-butyl-hydroperoxide [75-91-2] (138). Chromatographic and spectroscopic analyses of the isolated fractions provide structural data on the grafted and ungrafted SAN components (139). Information on the microstructure of the rubber is provided by analysis of the cleavage products derived from the substrate (135,137). The extraction of ungrafted rubber has also been reported (140). Additional information on elastomer and SAN microstructure is provided by ^{13}C nmr analysis (141). Rubber particle composition may be inferred from glass-transition data provided by thermal or mechanochemical analysis. Rubber particle morphology as obtained by transmission or scanning electron microscopy (142) is indicative of the ABS manufacturing process (78) (see Fig. 1).

The isolation and/or identification of nonpolymeric has been described, including analyses for residual monomers (131,143,144) and additives (131,145–147). The determination of localized concentrations of additives within the phases of ABS has been reported; the partitioning of various additives between the

elastomeric and thermoplastic phases of ABS has been shown to correlate with solubility parameter values (48).

Processing

Good thermal stability plus shear thinning allow wide flexibility in viscosity control for a variety of processing methods. ABS exhibits non-Newtonian viscosity behavior. For example, raising the shear rate one decade from 100/s to 1000/s (typical in-mold shear rates) reduces the viscosity by 75% on a general-purpose injection-molding grade. Viscosity can also be reduced by raising melt temperature; typically increasing the melt temperature 20–30°C within the allowable processing range reduces the melt viscosity by about 30%. ABS can be processed by all the techniques used for other thermoplastics: compression and injection molding, extrusion, calendering, and blow molding (see PLASTICS PROCESSING). Clean, undegraded regrind can be reprocessed in most applications (plating excepted), usually at 20% with virgin ABS. Post-processing operations include cold forming; thermoforming; metal plating; painting; hot stamping; ultrasonic, spin, and vibrational welding; and adhesive bonding.

Material Handling and Drying. Although uncompounded powders are available from some suppliers, most ABS is sold in compounded pellet form. The pellets are either precolored or natural to be used for in-house coloring using dry or liquid colorants or color concentrates. These pellets have a variety of shapes including diced cubes, square and cylindrical strands, and spheroids. The shape and size affect several aspects of material handling such as bulk density, feeding of screws, and Injection Molding. Very small particles called fines can be present as a carryover from the pelletizing step or transferring operations; these tend to congregate at points of static charge buildup. Certain additives can be used to control static charges on pellets (148).

ABS is mildly hygroscopic. The moisture diffuses into the pellet and moisture content is a reversible function of relative humidity. At 50% relative humidity, typical equilibrium moisture levels can be between 0.3 and 0.6% depending on the particular grade of ABS. In very humid situations moisture content can be double this value. Although there is no evidence that this moisture causes degradation during processing, drying is required to prevent voids and splay (149) and achieve optimum surface appearance. Drying down to 0.1% is usually sufficient for general-purpose injection molding and 0.05% for critical applications such as plating. For nonvented extrusion and blow-molding operations a maximum of 0.02% is required for optimum surface appearance.

Desiccant hot air hopper dryers are recommended, preferably mounted on the processing equipment. Tray driers are not recommended, but if used the pellet bed should be no more than 5 cm deep. Many variables affect drying rates (150,151); the pellet temperature has a stronger effect than the dew point. Most pellet drying problems can be a result of actual pellet temperatures being too low in the hopper. Large particles dry much more slowly than pellets, thus regrind should be protected from moisture regain. Supplier data sheets should be consulted for specific drying conditions. Several devices are available commercially for analytically determining moisture contents in ABS pellets (152–154).

Alternatives to pellet drying are vented injection molding (155) and cavity-air pressurization (counterpressure) (156).

Injection Molding.

Equipment. Although plunger machines can be used, the better choice is the reciprocating screw injection machine because of better melt homogeneity. Screws with length-to-diameter ratios of 20:1 and a compression ratio of 2–3:1 are recommended. General-purpose screws vary significantly in number and depth of the metering flights; long and shallow metering zones can create melt temperature override which is particularly undesirable with FR grades of ABS. Screws with a generous transition length perform best because of better melting rate control (157). Good results have been realized with a long transition “zero-meter” screw design (158). Some comments on the performance of general-purpose and two-stage vented screws used for coloring with concentrates is given in Reference 159. Guidelines for nozzle and nonreturn valve selection as well as metallurgy are given in References 160 and 161. Gas-nitrided components should be avoided; ion-nitrided parts are acceptable.

A variety of mold types can be used: two-plate, three-plate, stack, or runnerless. Insulated runner molds are not recommended. If heated torpedoes are used with hot manifold molds, they should be made from a good grade of stainless steel and not from beryllium copper. Molds are typically made from P-20, H-13, S-7, or 420 stainless; chrome or electroless plating is recommended for use with FR grades of ABS. Mold cavities should be well vented (0.05 mm deep) to prevent gas burns. Polished, full round, or trapezoidal runners are recommended; half or quarter round runners are not. Most conventional gating techniques are acceptable (160,161). On polished molds a draft angle of 0.5° is suggested to ease part ejection; side wall texturing requires an additional 1° per 0.025 mm of texture depth. Mold shrinkage is typically in the range of 0.5–0.9% (0.005–0.009 cm/cm) depending on grade, and the shrinkage value for a given grade can vary much more widely than this because of the design of parts and molding conditions.

Processing Conditions. Certain variables should be monitored, measured, and recorded to aid in reproducibility of the desired balance of properties and appearance. The individual ABS suppliers provide data sheets and brochures specifying the range of conditions that can be used for each product. Relying on machine settings is not adequate. Identical cylinder heater settings on two machines can result in much different melt temperatures. Therefore, melt temperatures should be measured with a fast response hand pyrometer on an air shot recovered under normal screw rpm and back-pressure. Melt temperatures range from 218 to 268°C depending on the grade. Generally, the allowable melt temperature range within a grade is at least 28°C. Excessive melt temperatures cause color shift, poor gloss control, and loss of properties. Similarly, a fill rate setting of 1 cm/s ram travel will not yield the same mold filling time on two machines of different barrel size. Fill time should be measured and adjusted to meet the requirements of getting a full part, and to take advantage of shear thinning without undue shear heating and gas burns. Injection pressure should be adjusted to get a full part free of sinks and good definition of gloss or texture. Hydraulic pressures of less than 13 MPa (1900 psi) usually suffice for most moldings. Excessive pressure causes flash and can result in loss of some properties. Mold temperatures for ABS range from 27 to 66°C (60–82°C for high heat grades). The final

properties of a molded part can be influenced as much by the molding as by the grade of ABS selected for the application (162). The factors in approximate descending order of importance are polymer orientation, heat history, free volume, and molded-in stress. Izod impact strength can vary severalfold as a function of melt temperature and fill rate because of orientation effects, and the response curve is ABS grade dependent (163). The effect on tensile strength is qualitatively the same, but the magnitude is in the range of 5–10%. Modulus effects are minimal. Orientation distribution in the part is very sensitive to the flow rate in the mold; therefore, fill rate and velocity-to-pressure transfer point are important variables to control (164). Dart impact is also sensitive to molding variables, and orientation and thermal history can also be key factors (165). Heat-deflection temperature can be influenced by packing pressure (166) because of free volume considerations (167). The orientation on the very surface of the part results from an extensionally stretching melt front and can have deleterious effects on electroplate adhesion and paintability. A phenomenon called the mold-surface effect, which involves grooving the nonappearance half of the mold, can be employed to reduce unwanted surface orientation on the noncorresponding part surface (168–170). Other information regarding the influence of processing conditions on part quality are given in References 171–174–175.

Part Design. For optimum economics and production cycle time, wall thicknesses for ABS parts should be the minimum necessary to satisfy service strength requirements. The typical design range is 0.08–0.32 cm, although parts outside this range have been successfully molded. A key principle that guides design is avoiding stress concentrators such as notches and sharp edges. Changes in wall thickness should be gradual, sharp corners should be avoided, and generous radii (25% of the wall thickness) used at wall intersections with ribs and bosses. To avoid sinks, rib thickness should be between 50 and 75% of the nominal wall. Part-strength at weld lines can be diminished; thus, welds should be avoided if possible or at least placed in noncritical areas of the part (176). Because of polymer orientation, properties such as impact strength vary from point to point on the same part and with respect to the flow direction (162). Locations of highest Izod impact strength can be points of lowest dart impact strength because of the degree and direction of orientation. ABS suppliers can provide assistance with design of parts upon inquiry and through design manuals (177). There are a number of special considerations when designing parts for metal plating to optimize the plating process, plate deposition uniformity, and final part quality (178). ABS parts can also be designed for solid–solid or solid–foam co-injection molding (179) and for gas-assisted-injection molding (180).

Extrusion.

Equipment. Since moisture removal is even more critical with extrusion than injection molding, desiccant hot-air hopper drying of the pellets to 0.02% moisture is essential for optimum properties and appearance. The extruder requirements are essentially the same for pipe, profile, or sheet. Two-stage vented extruders are preferred since the improved melting control and volatile removal can provide higher rates and better surface appearance. Barrels are typically 24:1 minimum L/D for single-stage units and 24 or 36:1 for two-stage vented units. The screws are typically 2:1 to 2.5:1 compression ratio and single lead, full flighted with a 17.7° helix angle. Screen packs (20–40 mesh = 840–420 μm) are recommended.

For sheet, streamlined coat-hanger type dies are preferred over the straight manifold type. Typically, three highly polished and temperature controlled rolls are used to provide a smooth sheet surface and control thickness (181). Special embossing rolls can be substituted as the middle roll to impart a pattern to the upper surface of the sheet. ABS and non-ABS films can be fed into the polishing rolls to provide laminates for special applications, eg, for improved weatherability, chemical resistance, or as decoration. Two rubber pull rolls, speed synchronized with the polishing rolls, are located far enough downstream to allow sufficient cooling of the sheet; finally, the sheet goes into a shear for cutting into lengths for shipping.

Pipe can be sized using internal mandrels with air pressure contained by a downstream plug or externally using a vacuum bushing and tank. Cooling can be done by immersion, cascade, or mist. Water temperatures of 41–49°C at the sizing zone reduce stresses. Foamcore pipe has increased in market acceptance significantly over the last few years, and cooling unit lengths must be longer than for solid pipe. Drawdown should not exceed 10–15%.

Profile dies can be flat plates or the streamline type. Flat-plate dies are easy to build and inexpensive but can have dead spots that cause hang-up, polymer degradation, and shutdowns for cleaning. Streamlined, chrome-plated dies are more expensive and complicated to build but provide for higher rates and long runs. The land length choice represents a tradeoff; long lands give better quality profile and shape retention but have high pressure drops that affect throughput. Land length to wall thickness ratios are typically 10:1. Drawdown can be used to compensate for die swell but should not exceed 25% to minimize orientation. Sizing jigs vary in complexity depending on profile design; water mist, fog, or air cooling can be used. The latter gives more precise sizing. Also, water immersion vacuum sizing can be used. Accurate, infinitely adjustable speed control is important to the takeoff end equipment to guarantee dimensional control of the profile.

With sheet or pipe, multilayer coextrusion can be used. Solid outer-solid core coextrusion can place an ABS grade on the outside that has special attributes such as color, dullness, chemical resistance, static dissipation, or fire-retardancy over a core ABS that is less expensive or even regrind. Composites can be created in which the core optimizes desired physical properties such as modulus, whereas the outer layer optimizes surface considerations not inherent in the core material. Solid outer-foam core can provide composites with significant reductions in specific gravity (0.7). Dry blowing agents can be “dusted” onto the pellets or liquid agents injected into the first transition section of the extruder.

Extrusion processing conditions vary depending on the ABS grade and application; vendor bulletins should be consulted for details. Information for assistance in troubleshooting extrusion problems can be found in Reference 182.

Calendering. The rheological characteristics of the sheet extrusion grades of ABS easily adapt them to calendering to produce film from 0.12 to 0.8 mm thick for vacuum forming or as laminates for sheet. The advantages of this process over extrusion are the capability for thinner gauge product and quick turnaround for short runs.

Blow Molding. Although ABS has been blow molded for over 20 years, this processing method has been gaining popularity recently for a variety of applications (183). Better blow-molding grades of ABS are being provided by tailoring the composition and rheological characteristics specifically to the

process. While existing polyolefin equipment can often be easily modified and adjusted to mold ABS, there are some key requirements that require attention.

Pellet predrying is required down to 0.02–0.03% moisture. High shear polyolefin screws must be replaced with low shear 2.0:1 to 2.5:1 screws with L/D ratios of 20:1 to 24:1 to keep the melt temperature in the 193–221°C optimum range. The land length of the tooling can be reduced to 3:1 to 5:1 because ABS shows less die swell; this also helps to reduce the melt pressure resulting from the higher viscosity. The accumulator tooling should be streamlined to reduce hang-up and improve re-knit, and be capable of handling the higher pressures required with large programmed parisons. Mold temperatures of 77–88°C provide good surface finish. It is recommended that the material vendor be consulted to confirm equipment capability and provide safety and processing information (184).

Secondary Operations.

Thermoforming. ABS is a versatile thermoforming material. Forming techniques in use are positive and negative mold vacuum forming, bubble and plug assist, snapback and single- or twin-sheet pressure forming (185). It is easy to thermoform ABS over the wide temperature range of 120–190°C. As-extruded sheet should be wrapped to prevent scuffing and moisture pickup. Predrying sheet that has been exposed to humid air prevents surface defects; usually 1–3 h at 70–80°C suffices. Thick sheet should be heated slowly to prevent surface degradation and provide time for the core temperature to reach the value needed for good formability. Relatively inexpensive tooling can be made from wood, plaster, epoxies, thermoset materials, or metals. Tools should have a draft angle of 2° to 3° on male molds and 0.5° to 1° on female molds. More draft may be needed on textured molds. Vacuum hole diameters should not exceed 50% of the sheet thickness. Mold design should allow for 0.003–0.008 cm/cm mold shrinkage; exact values depend on mold configuration, the material grade, and forming conditions. Maximum depth of draw is usually limited to part width in simple forming, but more sophisticated forming techniques or relaxed wall uniformity requirements can allow greater draw ratios. Some definitions for draw ratios are given in Reference 186. Pressure forming, with well-designed tools, can make parts approaching the appearance and detailing obtained by injection molding. Additional information on pressure forming is given in Reference 187.

Cold Forming. Some ABS grades have ductility and toughness such that sheet can be cold formed from blanks 0.13–6.4 mm thick using standard metalworking techniques. Up to 45% diameter reduction is possible on the first draw; subsequent redraws can yield 35%. Either aqueous or nonaqueous lubrication is required. More details are available in Reference 188.

Other Operations.

Metallizing. ABS can be metallized by electroplating, vacuum deposition, and sputtering. Electroplating (qv) produces the most robust coating; progress is being made on some of the environmental concerns associated with the chemicals involved by the development of a modified chemistry. An advantage to sputtering is that any metal can be used, but wear resistance is not as good as with electroplating. Attention must be paid to the molding and handling of the ABS parts since contamination can affect plate adhesion, and surface defects are magnified after plating. Also, certain aspects of part design become more important with plating; these are covered in References 169 and 178.

Table 2. Markets for ABS Plastics by Region in 1999, 10⁶ lb

Market	United States and Canada	Western Europe	Japan	Total	%
Transportation	374	397	132	903	21
Electrical ^a	501	569	415	1485	34
Miscellaneous ^b	869	457	679	2005	46
Total	1744	1423	1226	4393	100

^aElectrical includes consumer electronics, business equipment, and appliances.

^bMiscellaneous includes construction, pipe, consumer, and others.

Fastening, Bonding, and Joining. Often parts can be molded with various snap-fit designs (189) and bosses to receive rivets or self-tapping screws. Thermal-welding techniques that are easily adaptable to ABS are spin welding (190), hot plate welding, hot gas welding, induction welding, ultrasonic welding, and vibrational welding (191,192). ABS can also be nailed, stapled, and riveted. There are a variety of adhesives and solvent cements for bonding ABS to itself or other materials such as wood, glass, and metals; for more information, contact the material or adhesives suppliers. Joining ABS with materials of different coefficients of thermal expansion requires special considerations when wide temperature extremes are encountered. An excellent review of joining methods for plastics is given in Reference 193.

Applications

Its broad property balance and wide processing window has allowed ABS to become the largest selling engineering thermoplastic. ABS enjoys a unique position as a “bridge” polymer between commodity plastics and other higher performance engineering thermoplastics. Table 2 summarizes estimates for 1999 regional consumption of ABS resins by major use (194). In 1999 the single largest market for ABS resins worldwide was transportation. Uses are numerous and include both interior and exterior applications. Interior injection-molded applications account for the greatest volume. General-purpose and high heat grades have been developed for automotive instrument panels, consoles, door post covers, and other interior trim parts. ABS resins are considered by many the preferred material for components situated above the “waistline” of the car. Exterior applications include radiator grilles, headlight housings, and extruded/thermoformed fascias for large trucks. ABS plating grades also account for significant ABS sales and include applications such as knobs, light bezels, mirror housings, grilles, and decorative trim. Appliances were the second largest market segment for ABS. The majority of this consumption was for major appliances; extruded/thermoformed door and tank liners lead the way. Other applications in the appliance market include injection-molded housings for kitchen appliances, power tools, vacuum sweepers, sewing machines, and hair dryers. Transparent ABS grades are commonly used in refrigerator crisper trays, vacuum sweeper dirt cups, and other applications requiring premium aesthetics.

Table 3. Worldwide Capacity for ABS Plastics 1994–2000 by Region, 10³ t

Region	1994	1995	1996	1997	1998	1999	2000
Western Europe	841	838	865	882	1000	1000	990
Eastern Europe	80	80	81	81	82	82	82
Africa	0	0	0	0	0	0	0
North America	931	894	894	934	1083	1098	1098
Latin America	128	115	127	129	126	230	267
Middle East	0	0	0	0	0	0	0
Asia-Pacific	2130	2535	3158	3292	3712	3857	3977
<i>Total</i>	<i>4110</i>	<i>4462</i>	<i>5125</i>	<i>5318</i>	<i>6003</i>	<i>6267</i>	<i>6414</i>

Table 4. World Capacity of Leading ABS Producers

Producer	2000 Capacity, 10 ³ t	Largest producer in
GE Plastics	855	North America
Bayer	766	Europe
Chi Mei Industrial	1120	Pacific

A large “value-added” market for ABS is business machines and other electrical and electronic equipment. Although general-purpose injection-molding grades meet the needs of applications such as telephones and ink jet printer covers, significant growth exists in more demanding FR applications such as computer housings and displays.

An emerging application base for ABS products has been in consumer applications requiring differentiation through aesthetic appeal vs mechanical performance. A wide range of options featuring inherent aesthetic looks such as metallic, sparkle, metamerism, or even thermochromatic color change can be found in products ranging from computers to telephones.

Pipe and fittings remain a significant market for ABS, particularly in North America. ABS foam core technology allows ABS resin to compete effectively with PVC in the primary drain-waste and vent pipe market.

Other uses of ABS include consumer and industrial applications such as luggage, toys, medical devices, furniture, shower stalls, and bathroom fixtures.

Economic Aspects

Capacity. Estimated ABS capacity worldwide in 2000 is given in Table 3 (195). Accurate ABS capacity figures are difficult to obtain because significant production capability is considered “swing” and can be used to manufacture polystyrene or SAN as well as ABS. From a regional standpoint, Asia-Pacific has the largest ABS nameplate production capability at 3977 t. The United States has approximately 17% of the world’s capacity at 1068 t. Most suppliers have multiple facilities with the largest producers regionally being GE in North America, Bayer in Europe, and Chi Mei in the Pacific. As shown in Table 4, these three producers account for almost 50% of the world’s capacity (195).

Table 5. U.S. Unit Sales Values for ABS Resins

Year	Value, \$/kg	Year	Value, \$/kg
1986	1.56	1993	1.83
1987	1.68	1994	1.87
1988	1.93	1995	2.03
1989	2.03	1996	1.86
1990	1.95	1997	1.67
1991	1.92	1998	1.48
1992	1.86	1999	1.76* est.

Price. The price history of ABS in the United States is presented in Table 5 for the period from 1986 to 1998 (1996). The cyclical nature of prices during this period reflects both the cyclical nature of key feedstocks (197–199) and the increased global capacity available. The change also represents the changing mix of ABS resins and blends toward higher value, higher performance applications. Since late 1999, prices have risen appreciably because of dramatic increases in raw material feedstocks and stronger global demand.

Although ABS resins have a long history by industry standards, the products are anything but mature. ABS resins and blends are, and are expected to remain, the engineering thermoplastics of choice for a wide array of markets.

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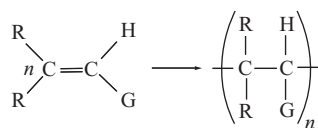
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ADDITION POLYMERIZATION

Addition polymerization is defined succinctly by IUPAC (1) as polymerization by a repeated addition process. That is, monomer units are added so that the resulting chain is a perfect sum of all the atoms in the monomers. This summing distinguishes addition polymerization from condensation polymerization in which small molecules are eliminated as the monomers are assembled into polymers (see CONDENSATION POLYMERIZATION).

A common type of addition polymerization is *olefinic polymerization*, in which alkene molecules, ie, hydrocarbons with carbon–carbon double bonds, are the monomer units. Polymer chains are formed by addition to the double bond of the alkenes. Frequently polymerized olefins are ethylene, propylene, and the butenes; also, the dienes, butadiene and isoprene (see BUTADIENE POLYMERS; BUTENE POLYMERS; ETHYLENE POLYMERS; ISOPRENE POLYMERS; and PROPYLENE POLYMERS).

When the unsaturated monomers are not simply hydrocarbons, their addition polymerization process is termed *vinyl polymerization*. Examples of vinyl polymerization involve such diverse monomers as vinyl halides, acrylates and methacrylates, acrylonitriles and acrylamides, maleic anhydrides, vinyl ethers, vinyl esters, and tetrafluoroethylene. For all examples, the addition polymerization reaction can be represented:



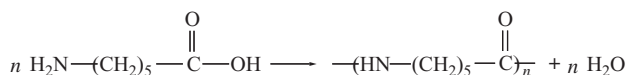
This representation demonstrates the exact summing of monomer units to form the polymer and shows that the formula and mass of the constitutional repeating unit are therefore the same as those of the monomer. The process of addition to the monomers' carbon-carbon double bonds is also shown. Olefinic or vinyl polymerizations invariably lead to addition polymers.

Classification of polymerization reactions as additions or condensations began with Carothers in 1929. Flory (2) and Mark (3) have long since pointed out that mechanistically, it is more useful and less ambiguous to classify reactions in terms of the polymer-growth mechanism, ie, as either chain-growth or step-growth polymerizations (see CHAIN-REACTION POLYMERIZATION; STEP-REACTION POLYMERIZATION). Whereas most addition polymerizations proceed via chain growth and most condensation polymerizations through step growth, the latter mechanistic terms avoid the ambiguities that arise by the formation of "condensation polymers" without the elimination of a small molecule. For example, ring-opening polymerization of lactams would be described as an addition polymerization based on the basic definition, although these reactions lead to the same condensation polymers as may be obtained from appropriate amino acids through condensation polymerization; however, both preparative routes proceed mechanistically via step-growth polymerizations.

Addition



Condensation



In this *Encyclopedia* the expressions "addition" and "condensation" are used only according to their strict stoichiometric meanings, which refer exclusively to the absence or presence of a split-off molecule, and which no necessary relationship to reaction mechanism. The terms chain growth (or chain reaction) versus step growth (or step reaction) are used to distinguish between mechanistic types and also between polymer types based on mode of synthesis (see also CLASSIFICATION OF POLYMERIZATION REACTIONS in addition to the other references made within this article).

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ADDITIVES

Introduction

Additives for plastics are typically organic molecules that are added to polymers in small amounts (typically 0.05 to 5.0 wt.%) during the manufacture, melt processing, or converting operations so as to improve the inherent properties of the polymeric material. Additives can be categorized in three major segments: polymer modifiers, performance enhancers, and processing aids. Pigments and Colorants are not covered in this review. Additives used exclusively in elastomers are also excluded (Antiozonants, curing accelerators, and vulcanizing agents). The global market for plastics additives in 2007–2008 timeframe was estimated in the order of \$ 32 billion in value and over 12 million tons in volume when plasticizers are included (1). When the commodity plasticizers (ca. 50% of additives volume) are omitted, then global consumption was about 4.7–5.5 million tons with value ranging from \$16–19 billion (2). Poly(vinyl chloride) (PVC) by far is the largest consumer of additives (the combined volume of plasticizers and property modifiers account for 74% of global plastic additives). Polyolefins and styrenics together are the second largest volume consuming group. Global additives market growth rates for the time-period 2004–2009 were forecasted to be 4–5% annually, with China growing at 10% per year and the group of North America, Europe, and Asia (ex-China) growing at 3% each annually. The future growth of plastic additives depends on the growth of the various plastics resins and in turn on the market segments consuming plastics (mainly packaging, automotive and construction). (3).

Polymer modifiers are used primarily to alter the physical or mechanical properties of the plastic. These include plasticizers, foaming (blowing) agents, coupling agents, impact modifiers, organic peroxides, and nucleating/clarifying agents. Polymer modifiers continue to account for about 11% of the total volume in 2004 of all additive classes.

Performance enhancers are added to plastics to provide functionality not inherent to the polymer itself. These include Flame Retardants (FRs), Heat Stabilizers for PVC, Antioxidants, Light Stabilizers/light-filters, Biocides, and Antistatic Agents. A newer additive family includes conductive carbon black and carbon nanotubes, graphenes, & organic conducting polymers to impart an antistatic, electromagnetic shielding or a conductive effect to plastics or

paints/coatings. Performance enhancers account for 24% of the total global additives market (3) and are led by FR's with an approximate value of \$827 million in the United States with 3% annual growth rate through 2011 (4).

Processing aids are typically surface-active agents that are added into plastics converter operations to improve throughput and alter the surface properties of the finished article. Additives in this class include lubricants, slip agents, antiblocks, and mold-release agents. In 2005 this class accounted for 7% of global additives volume.

A key driver of change and new product development in the plastics additives markets is a variety of environmental concerns. This has been seen most dramatically in PVC where concerns over the use of heavy-metal heat stabilizers based on lead have motivated a widespread conversion to tin-based materials and even to nonmetallic stabilizers. The widely used phthalate-based Plasticizers for flexible PVC have come under scientific and regulatory scrutiny because of concerns over their potential adverse effects on the human reproductive systems. Concerns over the potential for certain brominated FRs to form dioxins are driving the development of new halogen-free systems.

Furthermore in very recent years there are growing concerns over the environmental sustainability of plastics driven both by high crude oil prices (*affecting raw material costs of monomer feedstreams for plastics manufacture*), high consumer demand for plastics (*e.g. beverage packaging*), and environmental impacts associated with accumulation of plastics in the environment. In response major end-users and brand owner corporations are being challenged, and in turn are challenging the plastics industry value-chain participants to develop strategies and technologies for the enhanced recycling and reuse of plastics. One example is a so-called "Wal-Mart effect" where this major global retailer developed a scorecard for suppliers to document their efforts to satisfy sustainability goals such as energy usage, material efficiency, and natural resources (5,6). For plastics additives producers this has created renewed interest in additives that enable the reuse of post-consumer recycled (PCR) plastics into new or higher-valued applications. Examples include the recycling of used polyester (PET) carpeting into new beverage bottles, or sanitizing and upgrading of post-consumer PET bottles to allow new bottles to be molded using a portion of recycled PET content (7).

Plastics additives are used extensively in food packaging and as such are regulated by the U.S. Food and Drug Administration (FDA) (and related international agencies) as indirect food additives. Regulation by the FDA of a new additive requires submission of toxicity as well as migration data from the polymer in question into a variety of food simulants so as to calculate estimated daily intake. The level of migration and anticipated annual usage determines the extent of toxicity testing that is required. Information on the petition process for obtaining regulations as well as a directory of all indirect food additives can be obtained through the FDA website www.fda.gov.

Additives are incorporated into polymer matrices by a variety of methods and at various points in the manufacturing process. Polymer producers typically incorporate additives as single components or as blends of two or more additives during the polymer pelletization/isolation step. Converters and transformers often introduce additives as a concentrate or master batch or liquid dispersion. A *concentrate* is a mixture of an additive dissolved in a polymer resin carrier at

fairly high (10 – 30%) concentrations. A *master batch* is a blend of additives and often pigments in a resin carrier designed for a specific end-use application. In a *liquid dispersion* additives or colorants are dispersed or suspended in an inert or reactive liquid carrier such as a mineral oil, aliphatic glycols or alkylene esters along with proprietary dispersants. Such liquid systems are directly injected into converting machinery via a peristaltic metering pump.

Modifiers

Plasticizers. Plasticizers, through their use in flexible PVC, are the largest volume polymer additives used in plastics. Flexible PVC accounts for nearly 90% of the volume of plasticizers used in plastics. Plasticizers are added at very high loadings (up to 80%) depending on the degree of flexibility required. Plasticizers are added to inherently hard thermoplastics to increase the flexibility, softness and/or extensibility. In addition, secondary benefits of improved processability, greater impact resistance, and higher ductility can often be achieved.

Plasticizers are often used as carriers for pigments and are the liquid vehicle for PVC plastisols. Plasticizers are predominately esters produced through the reaction of an acid or anhydride with a linear or branched alcohol (8). Typical examples are di- or tri-substituted esters produced by the reaction of phthalic anhydride [88-44-9] with linear or branched alcohols varying in chain length from C₄ to C₁₁ such as with 1-butanol [71-36-3], 2-ethyl-1-hexanol [104-76-7] and 1-octanol [111-87-5]. While somewhat interchangeable, performance properties such as low temperature flexibility, volatility, processability, and extractability are governed by chain length and degree of branching. For example in interior automotive PVC applications, the octyl phthalates have been replaced by isodecyl phthalates because of their lower volatility and thereby enhanced fogging resistance.

The remaining plasticizers are more specialty in nature. Aliphatics are typically 2-ethylhexyl esters of dibasic acids, such as glutarates, adipates, or sebacates. The primary use of aliphatics is when low temperature flexibility and crack resistance are required. When very low volatility and low migration is required, the plasticizers of choice are based on esters of trimellitic anhydride [552-30-7]. A typical application for mellitates is in PVC wire and cable jacketing or automotive interiors which require excellent long-term heat aging properties and extraction resistance. In these applications lower volatility plasticizers such as diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) are replacing dioctyl phthalate (DOP) plasticizers. For particularly demanding performance applications, dibasic acids are polymerized with diols to produce low molecular weight polymeric plasticizers. Esters of phosphorus oxychloride [10026-87-3], the phosphate esters, are typically used as FRs and also impart plasticizing properties. A final class are the epoxies, with epoxidized soybean oil [8013-07-8] (ESBO) being the most common (epoxies based on tall oils and linseed oil are also available). While primarily added as secondary thermal stabilizers in PVC because of their ability to scavenge HCL generated during processing, as plasticizers they exhibit excellent extraction resistance and low migration.

Market drivers for plasticizers today and near future include strong consumptive growth of PVC in the China, continued global consumption of PVC in construction and automotive markets, and ongoing concern in North America and Europe over toxicological implications of DOP plasticizers, the latter driving commercialization of aforementioned non phthalate plasticizers (DIDP, DINP). Polymer processors are switching to DOP alternatives, in the short term are 2-ethylhexyl phthalates and longer term new products such as diisononyl cyclohexane-1,2 dicarboxylate (DINCH) [474919-59-0], (9).

Typically the large producers of plasticizers are backward integrated into either alcohol and phthalate anhydride or both. The key suppliers of the commodity plasticizers in North America are BASF (Palatnol[®], Hexamoll[®]), Eastman (Eastman), and ExxonMobil (Jayflex). Worldwide consumption of plasticizers is about 6 million tons/year. The Chinese market is the highest global volume consumer of plasticizers (34%) followed by Asia (22%), Europe (18%), North America (15%) (10).

Foaming (Blowing) Agents. *Chemical blowing agents* are inorganic or organic additives that produce a foamed structure. They are used extensively in PVC but also in polyethylene (PE), polypropylene (PP), and polystyrene (PS) to improve properties and appearance (insulation against heat and noise, better stiffness, removal of sink marks in injection-molded parts, and improved electrical properties) as well as to reduce parts weight. Chemical-blowing agents can be classified as either physical or chemical. They are typically added via a concentrate or master batch (11). The total market for blowing agents in North America is near 10 kilotons and near 200 kilotons worldwide with China consuming 50% volume. In North America, volume growth is anticipated to move with the construction market segments including foamed plastic-wood composite decking, windows and doors, and composite fence materials (12).

Physical blowing agents are volatile liquids or compressed gasses that are dissolved in the polymer and change state during processing to form a cellular structure. *Chemical blowing agents* (CBAs) decompose thermally during processing to liberate gasses that form a foamed product. Organic CBAs typically are solid hydrazine derivatives that generate nitrogen in an *exothermic* reaction. Most common is azodicarbonamide [123-77-3], which in pure or modified form accounts for up to 80% of all CBAs. It begins to decompose at 390°F. However this product was recently banned in Europe with North America to follow, for use in gaskets that are in contact with food substances, to be replaced by alternative *endothermic* blowing agents (12). Other types are the sulfonyl hydrazides {most common is 4,4'-oxybis(benzenesulfonyl hydrazide) [80-51-3] which is used for low temperature applications} and p-toluene semicarbazides {most common is p-toluenesulfonyl semicarbazide [10396-10-8] which is used in high temperature applications such as acrylonitrile-butadiene-styrene (ABS), poly(phenylene oxide) (PPO), nylon, and high impact polystyrene (HIPS)}. High gas yields and pressures for *exothermic* CBAs make them useful in applications such as cross-linked PE and extruded products. Chemtura and Lanxess are the leading producers of these products in North America. *Endothermic* CBAs are based on blends of inorganic carbonates and polycarbonic acids both emitting carbon dioxide. Proper combination of these materials allows for operating temperature ranges of 150–300°C. A common commercial system is based on citric acid [77-92-9] and sodium

bicarbonate [144-55-8]. Endothermic CBAs generally produce a lower gas yield providing foams with smaller cell structure than do exothermic CBAs.

Coupling Agents. Coupling agents promote adhesion between polymers and inorganic fillers by forming stable chemical bonds between the organic matrix and the surface of the filler. The highest usage of coupling agents is in the treatment of glass fibers for use in thermosets such as epoxies and polyesters. Other fillers include clay, silica, mica, wollastonite, calcium carbonate and aluminum trihydrate (ATH).

The most common type of coupling agent is the organosilanes. Silanes have the general structure RSi(OR')_3 , where R is a functionalized organic group that binds to the polymer matrix (i.e., amino, epoxy, acrylate, or vinyl) and R' is typically methyl or ethyl. The methoxy or ethoxy groups hydrolyze to silanols which react with surface hydroxyl groups on the inorganic fillers to form oxane bonds. The result is improved mechanical or electrical properties. Amino silanes are typically used for epoxy and phenolic resins, epoxy silanes for epoxy resins, and methacrylate silanes with unsaturated polyesters. Fillers are typically pretreated with an aqueous dispersion of silane at levels of 0.2–0.75%. The treated fillers are then reacted with the polymer matrix during compounding. The silane improves wetting during the compounding process thereby reducing the surface tension of the organic-inorganic interface for better dispersion. Evonik and Momentive are major suppliers of silanes in North America.

In addition to silanes, a variety of organometallics (primarily titanates but also zirconates, aluminates, and zircoaluminates) are used as coupling agents, although in significantly lower volumes. While mechanistically similar, titanates are more versatile than silanes because they can react with a broader range of fillers (i.e., calcium carbonate). However they are more susceptible to hydrolysis. Titanates are often used as dispersing agents for fillers in polyolefins by reducing the surface energy of the filler, resulting in better impact strength, lower melt viscosity, and better aged mechanical properties. In North America DuPont and Kenrich are the primary suppliers of organometallics.

A specialty class of coupling agent are the maleated polyolefins (13). The pendant maleic anhydride unit reacts with surface hydroxyl groups (or siloxy group in the case of pretreated fillers) while the polymeric portion cocrystallizes with the polymer matrix. Their main applications are in glass-filled PP composites and in non-halogenated FR wire and cable applications. The addition of 1–2% maleated PP can improve the tensile strength of a 30% glass-filled PP by up to 40%. In FR applications, 4% maleated PE in a PE/EVA (polyethylene/ethylene-co-vinylacetate) blend containing 65% ATH gives up to three times improvement in elongation. The maleic anhydride reacts with the basic inorganic FR, fillers, ATH, and magnesium hydroxide (14). Maleated polyolefins are marketed in North America by Chemtura, DuPont, Eastman and ExxonMobil as major suppliers.

A relatively new class of property modifiers are chain extenders additives. These function to increase polymer molecular weight by reactively combining polymer endgroups. Some chain extenders can be used to produce alloys of two dissimilar polymers through reactive coupling. Renewed interest in these additive technologies has arisen in part to public and industry interest in improving the sustainability of plastics, in particular by improving the quality and

properties of recycled polyesters and polyamides (7). Recycled PET and PA can be reused into higher valued articles such as fiber or incorporating a portion of PET recycle into beverage bottle manufacture (15–17). Suppliers of these chain extenders include BASF (Joncryl®), DSM (ALLINCO).

Organic Peroxides. Organic peroxides are used in the plastics industry to catalyze polymerization reactions or to modify the properties of polymers (18,19). On the polymerization side, peroxides are used as initiators for PVC, low density polyethylene (LDPE), polystyrene (PS), and acrylics. As modifiers for existing polymers, peroxides are used for the curing of unsaturated polyester resins, as cross-linkers of PE silicones, and a variety of ethylene-based elastomers and to break down the molecular weight of polypropylene in a process known as *visbreaking* or *controlled rheology* (20). Peroxides function through the thermal decomposition of the unstable peroxide bond to generate two free radicals. The reactivity of the peroxide is modified by altering the organic substituents attached to the peroxide or through the use of coadditive promoters. The reactivity of the peroxide is defined by the *ten-hour half-life temperature*, or the temperature at which one-half of the peroxide decomposes in a 10-h period. The lower the 10-h half-life temperature, the more reactive is the peroxide. Organic peroxides fall into seven basic groupings depending on the organic substituent. These are dialkyl peroxides, diacyl peroxides, hydroperoxides, ketone peroxides, peroxydicarbonates, peroxyesters, and peroxyketals (21).

The choice of organic peroxide used for initiating polymerizations is dictated by the polymerization temperature used to produce the polymer. The low temperatures used for PVC polymerization, for example, dictate the use of organic peroxides with low 10-h half-life temperatures. For the higher polymerization temperatures used for LDPE, an organic peroxide with a higher 10-h half-life temperature may be used. When used as polymerization catalysts, organic peroxides are typically used in the 0.1–0.5% range. Approximately half of all organic peroxides by volume are used in the various polymerization processes.

Unsaturated polyesters are produced through the cross-linking of low molecular weight polyester resins and comonomers such as styrene present at 1.0–2.5% based on resin weight. Fillers, pigments, and reinforcements such as glass fiber are often added. Depending on the cure temperature, co-catalyst promoters are often used. For room-temperature cures and resin-transfer molding, organic cobalt and copper promoters are added to the ketone peroxides, which are typically used. Unsaturated polyester resin production is the largest single application of organic peroxides, accounting for 30–40% of total consumption.

For the cross-linking of ethylene-based polymers for applications such as wire and cable jacketing and tubings, peroxides are added during compounding/processing at levels of 0.2–0.4%. In the visbreaking of controlled-rheology PP similar levels are used, to reduce the molecular weight and melt viscosity of the polymer. Controlled-rheology PP is particularly common for fiber and extrusion grades. When peroxides are used together with other additives, particularly antioxidants, a careful balance of concentrations must be chosen since the radicals formed during thermal decomposition can react with the other additives, lowering the effective concentrations of each (19).

A new specialty technology for the vis-breaking of PP utilizes a hydroxylamine ester as an alternative to organic peroxides. The additive is incorporated

into the extruder of a meltblown nonwoven fiber line where a controlled vis-breaking occurs to produce PP of high melt flow rate. Reported advantages are the production of non-wovens exhibiting improved air permeability and thermal stability (22,23). Key suppliers of organic peroxides in North America include Akzo Nobel (Trigonox, Perkadox) and Arkema (Luperox). The supplier of hydroxylamine ester is BASF (Irgatec® CR).

Impact Modifiers. Impact modifiers function by absorbing the impact energy and dissipating it in a nondestructive manner. Typically impact modifiers are elastomer materials and are added to a wide range of thermoplastic materials at levels up to 20%. The major types of impact modifiers are acrylics, styrenics including methacrylate-butadiene-styrene (MBS) copolymers and acrylonitrile-butadiene-styrene copolymers, chlorinated polyethylene (CPE), EVA copolymers, and the ethylene-propylene copolymers and terpolymers. The major market for impact modifiers is in PVC, although they are used in a wide range of other polymers such as polyolefins and engineering polymers.

MBS is the highest volume of the styrenic types. These terpolymers consist of an elastomeric core with a hard outer shell, which provide good impact resistance together with excellent processibility. Typically used in transparent PVC packaging because of its good clarity, its market growth has slowed as PET and polyolefins have replaced PVC in packaging applications. Because of poor weatherability owing to the butadiene component, outdoor applications are limited. Kaneka and Rohm and Haas are the major producers.

ABS is used in a variety of resins with PVC again being the major market. Similar to MBS, ABS suffers from poor weatherability and is therefore useful in outdoor applications only when a uv-resistant capstock is applied.

Acrylics are the fastest growing impact modifiers because of their usage in exterior PVC siding and profile. While they function in the same way as MBS and ABS, the graft phase is based on butyl or ethylhexyl acrylates which are far more uv-stable than butadiene. Arkema, Kaneka, and Rohm and Haas are the major producers in North America.

EPDM and EPR are used to modify polyolefins, primarily in the automotive industry. The largest volume is in automotive PP bumpers. This application is being replaced by impact-resistant polymer produced by metallocene technology, providing better performance and economics. Dow, Dupont, and Exxon are leading producers in North America. When used with plastics such as nylon, PET, and PBT, the EPDM and EPR are often modified with a functionalized monomer to allow them to react with these plastics. Additionally, the shell of a core-shell modifier can be modified to include a reactive group.

CPE is most widely used in PVC, although it does find applications in polyolefins. It can only be used in opaque applications but it does have excellent weatherability, making it useful for PVC pipe, siding, and profiles. Dow is the leading producer in North America.

Nucleating/Clarifying Agents. Materials added to semicrystalline plastics prior to processing and fabrication, which affect the rate of crystallization and spherulite size, are referred to as *nucleating agents*. These are typically insoluble or immiscible materials which provide sites for crystal formation. The main benefit for the addition of nucleating agents is improved cycle time during injection molding. When the addition of nucleators decreases the size of the crystallites to

less than the wavelength of visible light, these agents are referred to as *clarifying agents* because they reduce haze and improve transparency (25).

For nucleation of nylon and PP, sodium benzoate [532-32-1] is the traditional material of choice. Use levels are on the order of 0.1% with injection-molded packaging closures being a major application. Sodium benzoate does not impart any improvement in optical properties. Low molecular weight polyolefins, ionomers, as well as plasticizers such as ESBO are used for nucleation of semicrystalline plastics such as PET. Modified benzylidene sorbitols dominate the market for nucleation and clarification of PP. They are used at 0.1–0.3% levels in both homopolymer and copolymers, with injection-molded housewares, medical devices such as syringes, and other packaging being the major applications. Metal salts of organic phosphates have been introduced for nucleation/clarification of PP as well as newer non-sorbitol technology (26,27).

Talc and other minerals are often used as nucleators. In North America, Amfine (AdekaStab North America), BASF (Irgaclear®), and Milliken (Millad) are key suppliers.

Property Extenders

Antimicrobials/Biocides. Biocides are used to provide protection against mold, mildew, fungi, and bacterial growth on the surface of polymers. Left unchecked, these organisms can grow on plastic surfaces resulting in discoloration, odor, and parts failure. Since they function by being toxic to the microorganisms which cause growth, biocides are considered as pesticides under the Federal Insecticide, Fungicide and Rodenticide Act and as such are carefully regulated by the U.S. EPA (and in Europe under the Biocides Product Directive (BPD)). All end-use applications and related performance claims must be registered through the EPA and supported with toxicity, safety, handling, environmental, as well as efficacy data. Since microorganisms grow at the surface of plastics, in order to be effective biocides must migrate. Their rate of migration is closely related to their efficacy (28).

The primary use of biocide additives is for flexible PVC which has dropped from 70 to about 60% of total demand in the past decade as other plastics applications are developing or replacing PVC. While PVC is inherently resistant to microbial attack, the phthalate plasticizers are quite susceptible. Moisture contact and external factors such as uv-exposure can increase susceptibility by providing surface crazing/defects as sites for growth. Typical applications for biocide use in PVC are pool and pond liners, outdoor furniture, marine upholstery, roofing membranes, garden hoses, shower curtains, and wire and cable jacketing. Use of biocides in polyolefins is growing with applications such as children's toys and furniture, kitchen utensils, cutting boards, and trash bins. Biocides are also used in a variety of engineering polymers (PET, PA), and in PUR foams.

A variety of organic and inorganic biocides have been developed for use in plastics, including arsines, isothiazolinones, chlorinated phenols, silver, and zinc compounds. Among the arsines, 10,10'-oxybisphenoxyarsine (OBPA) [58-36-6] is the most common and is used at an active level of 0.02–0.05%. A typical isothiazolone is 2-n-octyl-4-isothiazolin-3-one (OIT) [26530-20-1]. These are used at

levels of 0.1–0.15% and are available as a concentrate in a plasticizer (either dialkylphthalate or ESBO). Zinc-2-pyridinethianol-1-oxide [13463-41-7] (commonly known as omacide or zinc omadine) and trichlorophenoxyphenol [3980-34-5] (Triclosan) are other common biocides. A variety of silver based biocide products have emerged, functioning primarily as bactericides. They have comparatively safe toxicological profiles, and in some cases are approved for food or water-contact applications or for medical applications. Well over 20 producers of biocide additives and formulated products exist. Due to the costs and risks to develop and register formulated biocide products, typically the producers of biocide compounds do not provide formulated products. In North America, some biocide producers & formulators include Akros Chemicals, Arch Chemicals, BASF, Ferro, and Rohm and Haas. The global market for biocides used in plastics is about 15 kilotons.

Antioxidants. Polymers may become oxidized during melt processing and fabrication, and end use resulting in loss of aesthetic and mechanical properties. This thermally induced autooxidation results in the formation of free radicals which will react with oxygen to form hydroperoxides. These hydroperoxides are themselves thermally unstable and their ensuing decomposition results in polymer chain scission, cross-linking, and the formation of color chromophores. The extent of these decomposition processes depend on the particular polymer and the exposure environment. In order to inhibit the initiation of polymer oxidation and to retard the resulting destructive chemical processes, antioxidants are added during the manufacture, processing, and/or during fabrication of plastic articles (29,30). The global market for antioxidants in 2004 was estimated to be 700 million pounds or \$750 million, the largest volume region being Asia-Pacific (excl. China) at 34% with Europe and North America at 25% each (31).

Traditional antioxidants are classified as either primary or secondary types depending on their mode of action. Primary antioxidants act by trapping free radicals, usually hydroperoxy radicals, through donation of a labile hydrogen to the radical species. Secondary antioxidants interfere with the propagation steps of autooxidation by decomposing hydroperoxides to form stable, nonradical species. It is quite common for a combination of primary and secondary antioxidants to be used to provide the maximum stabilization of a plastic. Use of antioxidants in plastics is ubiquitous, since nearly all polymer types require some form of stabilization in order to provide useful and durable materials.

The two most common classes of primary antioxidants are the aromatic amines and hindered phenols. Aromatic amines, such as substituted diphenylamines are extremely effective, acting as both radical chain terminators and peroxide decomposers. A major drawback of aromatic amines is their tendency to form highly discolored oxidation products during use (hence sometimes called staining antioxidants) (32). As a result their use is restricted to applications where discoloration is not an issue, such as carbon black filled or pigmented systems. As such their major usage is in the rubber industry. In plastics a major application is black wire and cable jacketing. Chemtura (Naugard), Eliochem (Wingstay), Lanxess (Vulkanox) are among the leading suppliers of aromatic amines. For stabilizing end-use articles, relatively high levels of amine are used – typically 0.5–1.0 wt%. When used as a storage stabilizer for polyols which in turn are used in polyurethane (PUR) manufacture, lower levels (typically

500–2000 ppm) are used. The standard primary antioxidants used in plastics are based on hindered phenols which in turn are usually based on derivatives of 2,6-di-*t*-butylphenol [128-39-2] (BHT). While highly effective, BHT is volatile and is susceptible to discoloration upon oxidation. In order to improve on the properties of BHT, a host of analogues have been developed. These modifications generally involve either altering the hindering alkyl groups or changing the substituent in the 4-ring position. In order to improve on the volatility of BHT, antioxidants with two, three, and four hindered phenols linked together are available and commonly used. Hindered phenols are effective both during polymer processing and during end use. Typically they are used in combination with a secondary antioxidant to maximize their effectiveness during high temperature processing and to minimize color formation resulting from the over-oxidation of the phenol. Use levels of 0.1–0.5% are common. Hindered phenols are available from a number of producers, with BASF (Irganox®) and Chemtura (Anox, Lowinox) are the two leading volume producers in North America and globally. Non-traditional antioxidant compounds are used in niche applications. Vitamin E (α -tocopherol) [10191-41-0], a high molecular weight but extremely reactive phenol has found use primarily in food-contact packaging applications because of its effectiveness at low levels (100–200 ppm) and its ‘green’ image. Its major limitation is its tendency to form highly discoloring chromophores upon oxidation. Another stabilizer class, the hindered-amine light stabilizers (HALS) can be used as antioxidants when use temperatures are below 135°C, primarily in polyolefins (33). The primary benefit of using a HALS as an antioxidant their oxidation products are colorless unlike aromatic amines or hindered phenols. Since HALS do not provide higher temperature stability they must be used in conjunction with a melt-processing stabilizer such as phosphites.

Secondary antioxidants generally fall into two classes: the organophosphites and thioesters. Organophosphites are typically trivalent arylphosphites which react with hydroperoxides in the polymer to generate a pentavalent phosphate and a nonreactive alcohol. Phosphites are effective at the high temperatures used in polymer processing but do not provide any stabilization during end-use. As such they are nearly always used with hindered phenols in practical applications. Tris-nonylphenylphosphite [26523-78-4] has been commonly used ranging from 500–1500 ppm, but is being replaced in some cases by more complex arylphosphites with improved hydrolytic stability. There is also increasing scrutiny about the health effects of nonylphenol that can be produced via hydrolysis of the phosphite). BASF (Irgafos®), Chemtura (Ultranox) and Clariant (Sandostab) are major suppliers. Thioesters are derivatives of 2,2'-thiobispropionic acid [5811-50-7], the most common being the lauryl esters, dilaurylthiodipropionate [128-28-4], and stearyl esters, distearylthiodipropionate [693-36-7]. In contrast to the arylphosphites, thioesters are active at the lower end-use temperature range 125–150° C and are often used in combination with hindered phenols to stabilize polyolefins for under-the-hood automotive applications. They are not active as melt-processing stabilizers. The primary drawback of thioesters is poor organoleptic properties, which limit their use in food-contact applications. Typical use levels are in the range of 1.0–1.5%. BASF (Irganox), Cytec (Cyanox) and Chemtura (Argus) are major suppliers in North America.

Alternative antioxidant systems (34–36) include higher performing stabilizers which can be used at low levels with enhanced ancillary properties such as low color and odor. Dialkylhydroxylamines used in combination with HALS provide an excellent, low color stabilization system for PP fiber.

Antistats. Due to their low electrical conductivity (surface resistivity in the order of 10^{15} – 10^{17} ohm/sq), plastics are known for their ability to accumulate electrostatic charges. The static charge can be generated during processing, transportation, handling, or final use, and typically occurs because of friction between the plastic and another material. The build up of static charge leads to a number of undesirable properties such as dust/dirt buildup, solids buildup on walls of plastic containers during filling, clinging effects during fabrication or conversion of films, destruction of electronic parts packaged in plastic materials, and ignition of vapors or particulates. A number of approaches have been developed to address these problems including topically applied antistatic additives, carbon black and other conductive fillers, intrinsically conductive polymers, and the classical migratory additives such as ethoxylated amines and glycerol monostearates (37). The total market for antistats in North America is estimated to be \$ 30 million. Polyolefins, styrenics, and PVC consume the majority of antistatic agents.

For nondurable applications, topical, external antistats can be applied to the finished plastic article through dipping or spraying of the part. The most common type is the quaternary ammonium salts or “quats”, which are typically applied as a water or alcohol solution. Since these materials are easily removed during handling or use, they are only effective for relatively short duration (<1 year). For more durable applications, internal antistats added during compounding have been developed. The classical systems have a lipophilic tail which remains in the bulk phase of the polymer while a hydrophobic head migrates to the polymer surface to form a moisture-absorbing layer allowing for static dissipation. These systems rely on migration of the additive and sufficient humidity to form the moisture layer. The most common type of migratory antistat is the nonionics, essentially surfactants. This class is dominated by the ethoxylated alkylamines and alkylamides, and fatty acid esters like glycerol monostearate. In the ionic antistat family examples are metal salts of alkylsulfonates and alkylphosphates. These antistats are effective at lower loadings (<2%), require at least 50% relative humidity, have an induction time before being active, can ultimately be wiped or washed from the surface compromising their permanence, and can have adverse surface effects such as plate-out and poor printability. To achieve the optimum blend of performance characteristics (permanence versus fast induction time) a blend of fast and slow migrators can be used (38). Key suppliers of migratory antistats in North America are Akzo (Armostat), BASF (Laurostat), Croda (Atmer).

In order to improve on the performance of the classical migratory antistats with respect to permanence and humidity sensitivity, newer approaches have been developed. These include inherently conductive polymers (ICP), conductive fillers, and hydrophilic polymers. The most common ICPs are based on polyaniline, a highly conjugated polymer which is converted to a cationic salt with an organic acid. The relatively high cost has relegated these materials to niche, albeit high value applications (39).

Fillers such as carbon black and nickel-coated graphite have good permanence but can affect mechanical properties and are highly colored. The hydrophilic polymers also known as static dissipative additives, have experienced good growth rate over the past decade as permanent antistat technologies. These are based typically on segmented copolymers of polyether and either polyamide or polyester blocks. They develop a conductive network in the host plastic when used at 10–30% loadings. These types of permanent antistats are available in North America from Arkema (Pebax), BASF (Irgastat®), DuPont (Entira). Typical applications are to dissipate static electricity buildup in business machines such as fax and copier parts in typically HIPS and ABS plastics, electronic parts packaging transport trays in HIPS and polyesters.

Starting in the mid 1990's new electrostatic dissipative additives based on conductive carbon nanotubes (CNTs) moved from research to commercial products. Carbon nanotubes have a very high aspect ratio (long length to small diameter particles). What once were research curiosities have become commercial products as the production optimization has improved the yield, quality and purity and prices are now in the range of \$100/pound or lower (40,41). A desirably low surface or volume resistivity can be achieved with low concentrations of CNTs (2–5%) allowing a low percolation threshold where a conductive network is formed. At such low loadings the bulk mechanical properties of the host plastic are not compromised as sometimes occurs with static dissipated polymers discussed earlier. Disadvantages of CNTs are their black color which affects the transparency and coloration when used in plastics. Also their dosage into host polymers must be carefully controlled to achieve sometimes narrow static dissipation target values. Masterbatch forms of CNTs are available from some suppliers to facilitate proper letdown into the host plastic, yet again careful attention to proper extrusion or injection molding parameters is required to ensure adequate dispersion of CNTs occur for optimum static dissipative performance. Major suppliers of CNTs include Arkema (Graphistrength), Bayer (Baytubes), Hyperion Catalysis (FIBRIL), Nanocyl.

Flame Retardants. Worldwide consumption of flame retardants for plastics was nearly 1.7 million tons in volume and \$4.2 billion in 2007 (excluding textiles & rubber applications). North America had the largest volume share of FRs (30%) share followed by Europe and Asia (ex-China) about 25% each and China at 17%. In North America ATH was the single largest FR class in volume due to its comparatively low cost, with brominated products next at 16% volume, followed by phosphate esters (1). These chemical additives in plastics inhibit ignition and retard the spread of flame. Flame retardants (FR) can be categorized as one of the following families by their mechanistic function (42,43):

- (1) **Char Formers:** Typically phosphorus-based organic compounds which when burned provide a physical and insulating barrier between the flame and the fuel or polymer.
- (2) **Heat Absorbers:** Examples include aluminum trihydrate (ATH) or magnesium hydroxide which decompose at high temperatures to generate water and in turn removes heat from the system through evaporation. Additionally they form glassy oxide barrier layers.

- (3) **Radical Sources:** Typical are brominated or chlorinated hydrocarbons. They act by interfering with the radical-chain mechanism occurring in the gas phase. High energy hydroxyl and oxygen radicals formed during the chain-branching phase of combustion are trapped in the gas phase and are replaced by much lower energy halogen radicals. A new niche subset of organic latent radical sources are non-halogenated compounds capable of producing carbon or oxygen free radicals that interfere with the mechanisms of polymer decomposition and fire production. Efficacious in some polyolefin applications as flame retardants are novel chemistry families such as N-alkoxy-substituted piperidines, or bis-alkylidene azo compounds (44–46).
- (4) **Synergists with Antimony Oxides:** Antimony trioxide [1309-64-4] which shows no FR activity on its own, synergizes with halogen-containing compounds through the formation of antimony halides which have lower volatility and longer persistence in the gas phase.

By chemical class, FRs can be categorized as follows:

Brominated Hydrocarbons. Accounting for the highest dollar value, these consist of additives such as decabromodiphenyloxide [1163-19-5] and tetrabromo bisphenol A [79-94-7] and like derivatives. These products are used in engineering resins primarily (HIPS, ABS, PC) for the business machine and television cabinet markets. Typically they are used with antimony oxide [1309-64-4] as a synergist in approximate ratio of 3:1 respectively. Major global suppliers of brominated FRs are Albemarle, Chemtura, and ICL Industrial Products.

Chlorinated Hydrocarbons. The chlorinated paraffins are used as FR's and plasticizers for PVC and in certain elastomeric materials. Dover Chemicals (Chlorez) is the major U.S. supplier. Declorane Plus [13560-89-9] (Occidental) has its main application in nylon and polyolefin wire and cable jacketing. Often the chlorinated FR compounds are used with antimony synergists.

Phosphate Esters. The phosphate esters can be subdivided into halogenated and non-halogenated versions. Halogenated phosphate esters are used almost exclusively in PUR foams. Albemarle (Antiblaze), Chemtura (Firemaster), and Supresta (Fyrol), and are key suppliers. The non-halogenated phosphate esters are primarily aryl esters and are used in engineering plastics (PET, PBT, PC, nylons). They are widely used in lubricants and as plasticizers in PVC. Chemtura, Clariant (Exolit), and Supresta (part of ICL) are the key producers.

Antimony. Antimony trioxide (ATO) is the primary product yet antimony pentoxide is also used to a lesser extent. Antimony compounds are used as synergists with halogenated FRs, with Chemtura (Fireshield) and China Minmetals as major producers/distributors. China produces about 90% of global ATO.

Aluminum Trihydrate. Since aluminum trihydrate (ATH) [21645-51-2] begins to decompose at relatively low temperature, it can only be used in polymers which can be processed at temperatures not exceeding 200° for long periods of time (polyolefins, acrylics, unsaturated phosphate esters, and PVC). When higher temperature processing is required, magnesium hydroxide can be substituted. It is used at very high loading levels (60 wt% or greater). ATH is used in significant quantities in household cabinetry tabletops in polyester or acrylic

resins, as well as an FR in elastomeric latex carpet backings. (42). These high loadings can have a detrimental effect on physical properties. There are numerous global distributors.

Heat Stabilizers. Chlorinated polymers, primarily PVC, decompose during processing to liberate HCl via dehydrochlorination reactions. The liberated HCl catalyzes the dehydrochlorination leading to rapid discoloration, embrittlement, and loss of mechanical properties. Since the decomposition is not free radical chain mechanisms, the traditional antioxidant stabilizers are not effective as heat stabilizers. The Primary Heat Stabilizers act by trapping the liberated HCl and also by reacting with labile chlorines on the polymer chain formed during polymerization (e.g., allylic chlorines) (47). There are three major types of primary heat stabilizers: lead compounds, mixed metal salts, and organotin. Major producers in North America include Arkema (Thermite), Chemtura (Mark), Ferro (Therm-chek), and Rohm and Haas (ADVASTAB). In 2007 the total market in North America was over 79 kilotons and value just below \$400 million. Globally the heat stabilizer market was valued in 2003 at about 1.2 billion pounds (about \$1.8 billion) (48).

Lead Compounds. These may be either organic or inorganic with dibasic lead stearates and phthalates, tribasic lead sulfate, and dibasic lead phosphite and carbonate, as examples. Their primary usage is in wire and cable insulation because of their nonconductive properties due to the water insolubility of the lead chloride which is produced in thermal processing in the case of PVC. Once extensively used in a wide variety of applications, they have largely been replaced by mixed metals and tins because of intense regulatory pressure. Only in wire and cable have lead compounds persisted since no suitable technical replacement is available despite significant R&D activity.

Mixed Metal Salts (or Soaps). These consist of Ba/Cd, Ba/Zn, and Ca/Zn salts. The Ba/Cd salts were very effective but now largely replaced by non-cadmiums in Western countries owing to regulatory pressure). The efficacy of these 'mixed metal salts' as thermal stabilizers follows that order. Mainly used in flexible or semirigid PVC, they are available in solid and liquid versions. Solids are typically salts of fatty acids such as stearates and laurates while liquid versions are octoate, phenolate, and neodecanoate salts. Mixed metal salts are almost always used in the presence of secondary stabilizers such as organophosphites, epoxies (e.g., epoxidized soybean oil), and β -diketones. This is particularly the case for the less active Ba and Ca/Zn. The ratio of metal salt to secondary stabilizer is typically 4:1. Mixed metal salts or soaps are available in North America from Baerlocher, Chemtura, Ferro, and Rohm and Haas.

Organotin. Primarily used in rigid PVC, the most widely used types are the dibutyl and octyltin mercaptides. While excellent stabilizers, they suffer from odor, staining, and poor uv-stability. Sulfur-free organotin which include the dibutyltin maleates are useful in applications requiring good weatherability such as extruded siding and profile. Methyl tins are the most active (particularly at high temperature and shear) and are favored from a toxicity and regulatory perspective. Arkema, Chemtura, and Rohm and Haas are the leading suppliers in North America.

Light Stabilizers. Most polymers degrade as a result of photo-induced oxidation so that for durable applications requiring weatherability it is necessary

to add light stabilizers. Ultraviolet induced degradation results in the loss of both aesthetic (color, gloss, clarity) as well as mechanical properties. The uv-portion of sunlight has sufficient energy to break chemical bonds in polymers resulting in the formation of free radicals. Light stabilizers interfere with these processes, slowing the harmful effects of uv-radiation (49).

Light stabilizers fall into three general categories: ultraviolet absorbers (UVAs), hindered amine light stabilizers (HALS), and nickel quenchers. While the largest consumption of light stabilizers is in polyolefins, there are significant usages in engineering resins, styrenics, PURs, and in coatings. HALS account for approximately half of the sales of light stabilizers and has approximately double the growth rates of UVAs in total. The North American light stabilizer market is valued about \$150 million.

UVAs are organic molecules that preferentially absorb uv-radiation and dissipate it in the form of heat. They are transparent in the visible region so as not to impart color and are highly photostable in order to provide long-term protection. UVAs are added to polymers at levels of 0.2–0.5%, depending on the type of polymer and the weatherability requirements of the end use application. UVAs fall into two major classes: 2-hydroxy-4-alkoxybenzophenones and substituted 2-hydroxy-benzotriazoles. A wide variety of modifications have been made to these basic types to provide for enhanced ancillary properties such as reduced volatility, better polymer compatibility, and enhanced photostability. Benzophenones are widely used in PVC and polyolefins. Because of their superior performance, benzotriazoles are used in high performance resins such as PC, nylon, and acrylics. Other minor types include benzoates, salicylates, and diphenyl acrylates. The most recent class of high performance UVAs are based on 2-(2-hydroxyphenyl)-1,3,5-triazines. These products have superior inherent photostability compared to the standard UVA types making them suitable for applications such as automotive and construction having high weatherability requirements.

The other important class of light stabilizers, the HALS, are based on substituted 2,2,4,4-tetramethylpiperidines. During light exposure, HALS are converted to nitroxyl radicals which are effective scavengers of the free radicals formed as a result of photolysis or photo-oxidation during weathering. A wide range of variations of HALS are available to optimize volatility and migration and to minimize interaction with other additives. For example, high molecular weight HALS have been developed to minimize volatility from high surface area PP fibers or polyolefin thin films. Other developments involve modifying the piperidine nitrogen with alkyl or alkoxy groups to reduce basicity, and hence interaction with other additives such as FRs, thioester antioxidants, and environmental agents such as pesticides and acid rain. The HALS major application is in polyolefins but they are also used extensively in styrenics, acrylics, and PVC. Typical use levels are from 0.15–0.3%. For the combined light stabilizers (UVAs and HALS together), the acquisition of BASF in 2009 by BASF (Tinuvin[®], Uvinul[®]) created the volume leader globally, followed by the cluster of Cytec (Cyasorb), Adeka, Chemtura, and Clariant (Sanduvor). In 2007 the global volume of combined light stabilizers was over 64 kilotons (50).

Because HALS and UVAs function via different stabilization mechanisms, they are often used together for synergistic performance and optimum weatherability.

Nickel quenchers such as nickel dibutyldithiocarbamate [13927-77-0] and 2,2-thiobis-(4-octylphenolato)-*n*-butylamine nickel (II) [14516-71-3] deactivate excited chromophores which act as sensitizers for the photolysis of hydroperoxides (49). Once widely used in PP fibers they have been replaced almost entirely by HALS. Their usage is declining because of concerns over the toxicity of the nickel.

Processing Aids

Lubricants. Lubricants are added to polymers during processing to improve their flow characteristics. While primarily acting as processing aids to reduce energy consumption and enhance the surface properties of extruded articles, they provide additional benefits in terms of mold release, improved anti-static properties, and better pigment dispersion. These additives act either “internally” as friction modifiers between polymer chains to decrease melt viscosity or “externally” by coating or treating the metal surfaces of the processing equipment, thereby reducing the friction at the polymer-metal interface. A wide variety of chemical classes of lubricants are available, including metal stearates, fatty amides, fatty acid and glycerol esters, waxes of various types, and fluoropolymers. Depending on the application, many of these exhibit both external and internal lubricating properties (51).

Metal stearates including predominantly calcium stearate as well as zinc stearate, are the most widely used lubricants. In PVC calendaring and extrusion, the stearates provide heat stabilizing effects as well as act as an internal lubricant. In polyolefins stearates act as external lubricants as well as deactivators of catalyst residues. Baerlocher, Chemtura, and Ferro are the major producers of metal stearates in North America.

Fatty amides provide multifunctionality, acting both as external lubricants and as slip agents and antiblocks. Primary amides such as oleamide [301-0202], erucamide [112-84-5], and stearamide [1309-64-4] are primarily used as slip and mold-release agents for polyolefins. The higher molecular weight ethylene bis-stearamide is used as a lubricant in both rigid and flexible PVC and in engineering polymers such as polyacetal, nylon, and ABS. Croda, Lonza and PMC Group are major suppliers of amides in North America.

Fatty alcohols are used primarily in rigid PVC where their excellent compatibility makes them useful where clarity is important. Fatty acids, represented by stearic acid, find some use in calendered and blow-molded PVC. Fatty esters, such as glycerolmonostearate [31566-31-1] function as either internal or external lubricants depending on molecular weight (compatibility). Again, PVC is the primary substrate but PC, PS, and PUR can be processed with these materials.

Polyethylene and paraffin waxes are used widely as external lubricants for PVC because of their high level of incompatibility. They are often used in combination with calcium stearate in unplasticized PVC pipe formulations. BASF, Clariant, and Ferro are leading North American suppliers of waxes.

Table 1. Cross-reference of Chemical Producers and Tradenames Cited herein:

Akzo Nobel	Armoslip [®] , Armostat [®] , Trigonox [®] , Perkadox [®]
Amfine	AdekaStab
Arkema	Kynar [®] , Luperox [®] , Pebax [®] , Graphistrength [®] , Thermolite [®]
Baerlocher	Baerostab [®]
BASF	Hexamoll, Irgatec CR, Irgaclear, Irgastat, Irganox, Irgafos, Joncryn, Laurostat, Palatnol, Tinuvin, and Uvinul are registered trademarks of BASF SE
Bayer	Baytubes [®]
Chemtura	Anox [®] , Fireshield [®] , Lowinox [®] , Mark [®] , Naugard [®] , Ultrinox [®]
Clariant	Sanduvor [®] , Sandostab [®]
Croda	Atmer ^(TM) , Crodamide ^(TM)
Cytec	Cyanox [®] , Cyasorb [®]
Dover	Chlorez [®]
DSM	ALLINCO [®]
DuPont	Entira ^(TM)
DuPont Dow	Viton [®]
Eliochem	Wingstay [®]
ExxonMobil	Jayflex ^(TM)
Ferro	Therm-chek [®]
Hyperion Catalysis	FIBRIL ^(TM)
Lanxess	Vulkanox [®]
Milliken	Millad [®]
Occidental	Declorane Plus [®]
Rohm & Haas	ADVASTAB ^(TM)
3M/Dyneon	Dynamar ^(TM)

Fluoropolymers, a small but high value (about \$30/kilogram) type of external lubricant/processing aid, are based on tetrafluoroethylene (52–55). These fall in two classes, those that are used in spray-on mold release agent formulations, and in-polymer incorporated products act as lubricants or processing aids. These materials form monomolecular layers on metal surfaces and are primarily used in PE-blown film applications to reduce “shark-skin” and gels. These materials are particularly suitable in metallocene PE which is more difficult to process than conventional resins. DuPont Dow (Viton), 3M/Dyneon (Dynamar), and Arkema (Kynar) supply these types of lubricants.

Slip/Antiblock Agents. Slips and antiblocks are used primarily in PE films to modify the inherent self-adhesion which causes the film layers to stick together. In the case of antiblocks, inorganic particles such as silk, talc, and diatomite (processed diatomaceous earth) are added at the compounding step to form a roughness at the surface which prevents the films from sticking (56). Slip agents, primarily migratory fatty acid amides, are added to provide a lubricity or reduced coefficient of friction at the surface, allowing a plastic film to slide over itself or another plastic (57). Erucamide [112-84-5], a C-22 fatty amide, is the most widely used slip agent because of its slower migration rate and better

thermal stability than the stearamides and oleamides, accounting for over half of the total consumption. In North America, the major suppliers of slip agents are Akzo Nobel (Armoslip), Croda (Crodamide), and PMC Group. In polyolefin films a combination of slip and antiblock agents are used to impart desirable surface properties in such consumer applications as packaging and garbage and other bags.

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ADHESION

Definition of Adhesion and Adhesive Joint

Adhesion is the attraction between two different condensed phases when they are in contact. Attractive forces range in magnitude from strong chemical bonds (≈ 25 – 100 kcal/mol) to much weaker physical forces, known as van der Waals interactions. An adhesive joint is a structure usually consisting of two bodies (adherends, substrates), which are held together by adhesion. The bodies may be directly bonded to each other, or coupled by an adhesive layer. The science of adhesion is multidisciplinary and can be divided into two parts: one dealing with surfaces and interfaces and the other with the fracture of adhesive joints. The former is largely concerned with bond formation and predicting attractive forces and energies, whereas the latter deals with test methods to measure joint strength.

One of the most important findings in adhesion science is that the *mechanical* energy required to fracture an adhesive joint (so-called *work of detachment* or *interfacial fracture energy*) is larger than the *intrinsic* interaction energy holding the joint together. The latter is a reversible quantity—equal to the *minimum* energy needed to disrupt an interface or the energy gained upon forming it. However, in general, the fracture of an adhesive joint is not a reversible process. When a joint is loaded, only some of the input mechanical energy is available (stored) to disrupt the interface and the rest is converted (dissipated) into increased molecular motion (heat). Additional input energy is required to attain sufficient elastic energy at the interface to disrupt it. Thus, bulk energy dissipation augments joint strength and causes the mechanical work of detachment to be larger than the interfacial interaction energy.

To judge the intrinsic adhesion at an interface by the measured fracture energy may be misleading. For example, if an adhesive is modified by adding fillers or tackifiers, and the modified adhesive gives a higher fracture energy than the unmodified one, it is tempting to conclude that intrinsic adhesion has been enhanced. But, by adding filler, the bulk properties of the adhesive are also modified and the improved performance may reflect merely a higher dissipation of mechanical energy within the adhesive layer.

Adhesion is important in many technologies (eg, adhesives, coatings, composites) and usually involves bringing solid and liquid surfaces, or two liquid surfaces, into contact. This article begins by considering characteristics of solid and liquid surfaces and then proceeds to discuss their contact to form interfaces and interphases. Next, the various types of adhesive bonds are discussed as well as the thermodynamics of adhesion. This is followed by a section on surface treatments to enhance the bondability of plastics and metals, and one dealing with the special case of elastomer tack. Two final parts deal with test methods to measure joint strengths and a discussion of the relationship between joint fracture energy and intrinsic adhesion.

Surfaces

Solids. Nearly all solid surfaces are rough at dimensions of a few nanometers. They may contain asperities, pores, projections, depressions, etc. In addition, surface regions of solids generally have different compositions than their bulk. All metals that have been exposed to the atmosphere have an oxide layer on them (1). The thickness of the oxide depends on the nature of the metal and the environment. Some metals, eg, aluminum and titanium, form thin, tough, tenaciously adhering oxides, which passivate the surface and prevent continued oxidation. Others, like iron, have oxides which continue to grow, especially in a humid environment.

In practice, metal oxides are covered with organic molecules and water adsorbed from the atmosphere (2). Other common sources of surface contamination are residual processing oils and lubricants. Another source of surface species is from the bulk. For example, iron containing only 10 ppm of carbon has been shown to form a carbon-rich structure on its surface upon heating or straining. In addition to carbon, other species, including sulfur, nitrogen, boron, and oxygen, have been shown to diffuse from the interior of metals to their surfaces (1).

It is also common for polymeric compounds to form surface regions with compositions different from the bulk material, by selective diffusion of components. This process is termed *blooming* when the surface component is solid, and *bleeding* if it is liquid. Sulfur and fatty acid blooms can inhibit adhesion in rubber laminates (3). Laser desorption mass spectroscopy has been employed to identify surface species on vulcanized rubber (4). X-ray scattering methods for the study of polymer surfaces and interfaces have been reviewed (5). Other surface analysis techniques commonly used with polymers include attenuated total reflectance (6–8), electron microprobe (9), Auger electron spectroscopy (10), x-ray photoelectron spectroscopy (11), and scanning probe microscopic methods (12). Overviews on polymer surface analysis have been published (13,14).

Liquids. Consider a pool of a simple, pure, low molecular weight liquid. Its molecules are mobile and diffusing about. Molecules in the bulk of the liquid interact with other molecules in all directions, while those at the surface experience a net attraction tending to pull them toward the interior. This causes surface molecules, on average, to be at greater spacing than bulk molecules and possess greater free energy. This gives rise to a surface tension, as the liquid behaves as if it has an elastic skin. Moreover, since nature seeks to minimize free energy, a

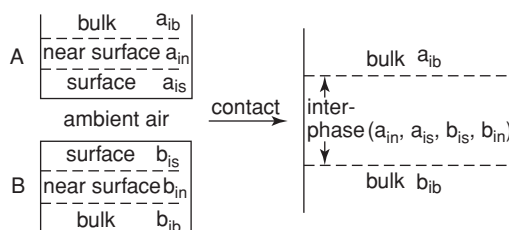


Fig. 1. Two hypothetical “real” materials A and B: (a) prior to contact and (b) after contact. Surface and near surface components form the interphase, which contains the interface(s) as well as (gradient) compositions and structures different from the bulk materials. In general, the interphase is quite complex. See text for further description.

volume of liquid in the absence of other forces takes a spherical shape to minimize the number of surface molecules. At constant temperature and pressure, the increase in Gibbs free energy accompanying a unit area increase in surface area of a liquid is, by definition, its surface tension γ . Alternatively, γ may be viewed as the force per unit length, tending to contract the surface and cause a liquid to resist spreading.

Real adhesive liquids are often complex mixtures, and, like solids, may have surface compositions different from their bulk. In addition, practical adhesive liquids are often reactive and/or polymeric.

Interfaces, Interphases, and Weak Boundary Layers

Schematically, Figure 1 shows two “real” materials, say A and B, that are composed of molecular components a_i and b_i , respectively. These are located in the bulk (a_{ib} , b_{ib}), at the surface (a_{is} , b_{is}), and/or within the near surface region (a_{in} , b_{in}). Upon contacting A and B under ambient conditions, the *interface*, defined as the locus of interactions between the two materials, initially involves the surface species on each and any entrapped air. In general, the interface will not be continuous at first. Entrapped air and surface rugosity prevent immediate, full molecular contact, although applied pressure can speed interface formation. With time, depending on the particular system, the region between the two bulk materials, the so-called *interphase*, changes. Along with increased molecular contact, diffusion of surface and near-surface species can change the composition and structure of the interface and interphase. For example, the interface may thicken by interdiffusion and chemical reactions may occur. (Specific examples are considered later.) If the interphase contains a mechanically weak layer (weak boundary layer), it may be the site of fracture when the adhesive joint is loaded. Weak boundary layers (WBLs) may originate on or near the surface of materials before they are contacted, or they may develop *in situ* during the dynamic conditions of contact. To provide a strong joint, the *structural* components, ie, those responsible for the cohesive strengths of A and B, must interact well at the final interface, and a WBL must not be present. WBLs may be removed prior to bonding or be disrupted by diffusion during bonding.

After an adhesive contacts a solid substrate, it is normally necessary to convert it to a hardened state (setting) so that the joint will be capable of supporting stress. However, since setting severely reduces the molecular mobility required to achieve true contact and good bond formation, it should not take place too quickly. Many weak adhesive joints can be traced to rapid setting before sufficient interface formation. Setting of adhesives can occur by physical or chemical means. In order to minimize internal stresses in a joint, there should not be a large change in volume of the adhesive during solidification, and the thermal expansion coefficients of the adhesive and adherends should be similar. This is especially important when the solid adhesive has a high modulus. Furthermore, joints with plane interfaces have been suggested (15) to be more sensitive to adhesive shrinkage than are joints made with complex, high surface area adherends. Solvent-based adhesives experience the most shrinkage during setting compared to those which harden by cooling (hot melt) or by chemical reaction (usually thermosets). The fact that epoxy resins shrink only about 3% upon setting is one reason for their good performance. Another advantage of epoxy solidification reactions compared to many other condensation polymerizations is that no small molecules, eg, water, which can interfere with bonding, are created during setting. Polyurethane reactions are also favorable in this regard.

Some inorganic substances adhere exceptionally well because they expand upon freezing. For example, ice will adhere to almost any surface, even those not wetted well by water (16). When water freezes in a depression in a solid surface, expansion causes it to lock against the sides of the depression and form a strong joint. Attempts (17,18) have been made to develop organic adhesives, based on ring opening polymerizations, that expand upon setting.

Bond Classification

When two different materials are contacted, a complete description of the interaction between them requires understanding the number, type, and distribution of bonds formed. This depends on surface topography and the extent of molecular mixing between the materials. In the following subsections, we classify various types of adhesive bonds. It is beyond the intent of this article to consider all the detailed possibilities, which become apparent from the previous discussion of interface and interphase complexity. Rather, we primarily discuss relatively simple systems, from which general principles may be gleaned.

Adsorption on Planar Substrates. The simplest type of adhesive bond occurs when a liquid is contacted with a planar solid with which it is totally immiscible and into which it cannot diffuse. Bonding is limited to physical and/or chemical adsorption at specific sites on the substrate surface. A sharp and planar interface is formed. This is the usual situation when an organic adhesive adheres to a very smooth inorganic substrate. The time-dependent process during which interfacial bonds form is called *wetting*. In general, it involves an increase in the number of interactions (more actual contact area) and/or a change in the type of interactions.

Surface species can be a hindrance to wetting. Many polar substrates such as glasses or metals, which have been exposed to ambient air, have several

molecular layers of adsorbed moisture on them. Wetting is expected to be speeded if the liquid readily solubilizes surface moisture. Perhaps this is one role of polar groups in a typical adhesive. Certainly an adhesive that is completely incapable of displacing or solubilizing surface moisture (or other surface contaminants) would find it difficult, if not impossible, to attain molecular contact with the actual substrate. Furthermore, air entrapped during contact may slow wetting.

Adsorption on Substrates with Complex Surface Topography. As in the previous case, the substrate is completely immiscible with the liquid adhesive, so that adhesive–substrate interactions are limited to adsorption at surface sites. However, the substrate surface topography is now rough and complex. The interface is still two-dimensional and sharp, but now has the complex shape of the substrate surface. Because of pores, depressions, and/or asperities, there are many more surface sites available to interact with an adhesive as compared to a planar substrate. Thus, if the adhesive has sufficient mobility and the wetting forces are high enough, the extent of adhesion may be increased by surface roughening. On the other hand, very viscous adhesives may form relatively few interactions with roughened substrates, especially if the (wetting) time from adhesive application to solidification (setting) is short.

Another consequence of a complex topography is mechanical interlocking between the adhesive and substrate. This is analogous to fastening with a “hook” and “eye” or with Velcro[®], where a resistance to separation is present without intrinsic adhesion. Of course, joint strength is improved if both mechanical interlocking and intrinsic adhesion are operative. Mechanical interlocking plays an important role in bonding wood, textiles, and paper because of their finely divided and porous nature. In addition, many metals and plastics are etched before bonding so that the adhesive can penetrate and lock into them. When mechanical interlocking is substantial, the region around the interface forms a composite interlayer within the interphase.

Interdiffusion. When two polymers are contacted, the interface will not be two-dimensional, but rather will become a region (volume) consisting of interdiffused molecules from each material (19,20). The thickness of this interlayer depends on the thermodynamic compatibility of the materials, the contact time, and molecular diffusion rates. Molecular interdiffusion is quite different from mechanical interlocking. The former is analogous to a homogeneous solution and involves interpenetration at the molecular level, whereas in the latter case, analogous to a heterogeneous mixture, the bulk adhesive flows into and around surface features of the substrate that are much larger than molecules. Interdiffusion increases the number of interactions among dissimilar chains, and, if the interdiffused distance is sufficient, interchain entanglements develop. Reviews on polymer interdiffusion have been written (21,22).

When two incompatible polymeric melts A and B are contacted, the equilibrium interface width a_1 is dependent on the Flory–Huggins interaction parameter χ and the molecular weights of each polymer. A mean field approach has been used (23,24) to predict that a_1 is given by

$$a_1 = \frac{2b}{\sqrt{\chi \cdot c}} \frac{1}{\sqrt{1 - 2\ln 2 \left(\frac{1}{\chi N_A} + \frac{1}{\chi N_B} \right)}} \quad (1)$$

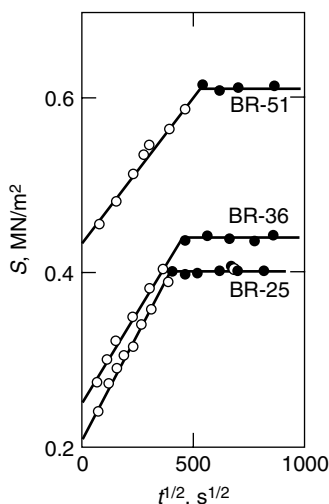


Fig. 2. Development of tensile strength S of autohesion with time of contact for different types of polybutadiene (35) ($\text{MN/m}^2 = \text{MPa}$). To convert MN/m^2 to psi, multiply by 145.

where b is the statistical segment chain length, and N_A and N_B are the degrees of polymerization of A and B, respectively. The parameter $c = 6$, when a_I is small compared to the chain radius of gyration, R_g , while $c = 9$ in the limit $a_I \gg R_g$ (25). Neutron reflectivity experiments (26,27) have established the validity of Helfand's mean field approach.

When two pieces of the same material are contacted, their bonding is termed *autohesion* (or *self-bonding*) (19). This has also been called *healing* (28). Using reptation theory (29), chain interdiffusion across the original contact junction has been analyzed. The crossing density, which is the number of times the interdiffusing molecules intersect the contact plane per unit area after a time t , has been calculated (30,31) as has the average interpenetration distance (28,32–34). Both measures of healing are predicted to be proportional to $t^{1/2}$. Furthermore, for polybutadienes with different vinyl contents it has been shown that the tensile strengths of autohesion increase linearly with $t^{1/2}$ (see Fig. 2) before reaching plateau values (35). Further discussion of autohesion is delayed until a later section, in which pressure-sensitive tack and time/temperature effects are also considered.

Effect of Interdiffusion on Joint Strength. The joint strength of a thermodynamically compatible adherend pair [poly(methyl methacrylate) and poly(vinyl chloride)] has been found to be quite high, while that for an incompatible pair [poly(butyl methacrylate) and poly(vinyl chloride)] was low (36). Furthermore, using electron microscopy, it was shown that the interfacial thickness for the compatible pair was about $0.1 \mu\text{m}$, whereas the incompatible pair formed a much sharper interface, too narrow to be determined experimentally. In principle, compatible polymer pairs will form an interface thickness that will continue to increase as long as the adherend molecules remain mobile. On the other hand, the

equilibrium width of the interface between incompatible polymers is typically in the range of 2–50 nm (37).

The effect of interdiffusion on the autohesion of rubbery adherends has been studied using a peeling geometry (38). Two layers, each composed of a butyl rubber network and miscible, unattached (non-network) polyisobutylene (PIB) chains, were contacted for 14 h at 60°C. The PIB chains were free to diffuse through the butyl network and across the contact junction. Joints were peeled apart over a wide range of rates and temperatures, and peel energies G were superposed to form a mastercurve covering eight decades of reduced rate. At intermediate peel rates, G was about 10 times the value obtained for a butyl network control containing no PIB. However, at both sufficiently low and high reduced rates, autohesion was little affected by PIB. The behavior at low rates was attributed to ready disentanglement of interdiffused PIB molecules from the network, while, at high rates, it was proposed that interdiffused molecules had little influence on joint strength, because they broke during separation rather than disentangling. The authors hypothesized that disentanglement of interdiffused PIB chains takes place at intermediate rates, with substantial viscous energy expended in the process.

Ellipsometry (39) has been used to determine the interface thickness between layers of poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN) contacted at 130°C. PMMA and SAN are miscible when the SAN contains 9.5–33 wt% acrylonitrile, but they are immiscible outside this composition range. Figure 3 shows interfacial thicknesses for both miscible and immiscible cases. The interface thickness for the miscible pair grows linearly with $t^{1/2}$. On the other hand, the interfacial thickness for the immiscible pair quickly reaches a value of about 20 nm and remains constant even after contacting for 12 h above T_g . Figure 4 shows tensile strengths of adhesion (normalized with respect to the tensile strength of the weaker SAN) for the compatible adherends plotted against the square root of the interface thickness. The data are linear and a surprisingly high interface width of about 200 nm is necessary for the joint strength to reach the tensile strength of the SAN.

Autohesion between two uncross-linked layers of polybutadiene has been studied (40). The self-diffusion coefficient was measured using small-angle neutron scattering, and T-peel specimens were used to determine joint strengths. The contact time required to reach the cohesive strength was 3 orders of magnitude greater than the time required for a diffusion distance equal to the chain radius of gyration. The authors speculated that low autohesion, even with significant interdiffusion, was due to different diffusion rates of branched and linear chains within the polybutadiene. Branched chains were proposed to impart increased bond strength, but have suppressed interdiffusion. Therefore, during the early stages of contact, the interdiffusion layer is rich in linear chains, resulting in lower strength. A much longer time is required for branched chains to interdiffuse and for the joint to obtain the full cohesive strength. There appears to be a difference in structure between bulk chains and the interdiffused layer during the initial stage of healing.

Forward recoil spectroscopy has been employed to determine interdiffusion widths for the autohesion of a polyimide film (41). In addition, fracture energies G were measured by T-peel testing. When a_I was less than 20 nm, G was so low

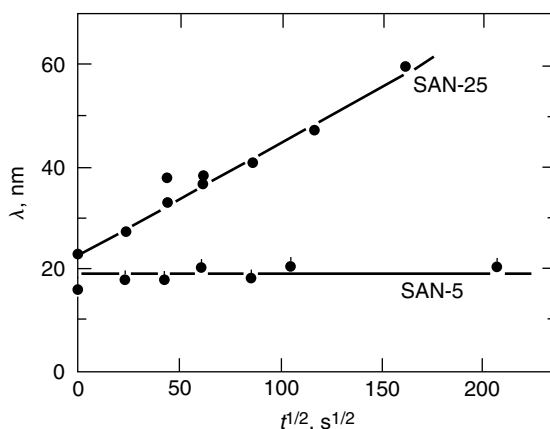


Fig. 3. Interface thickness after various contact times for miscible (PMMA/SAN-25) and immiscible (PMMA/SAN-5) pairs (39).

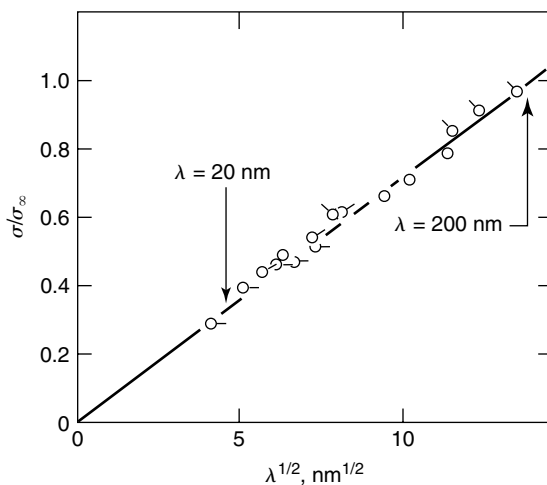


Fig. 4. Normalized strength of PMMA/SAN joints as a function of interface thickness (39).

(<10 J/m²) that it was difficult to measure. At larger extents of interdiffusion, G increased linearly with a_I . Again, an unexpectedly large interdiffusion distance of at least 200 nm was required before complete healing was attained.

Adhesion between the nearly compatible pair, polystyrene and poly(*p*-methyl styrene), has been investigated (42). Variations in annealing temperature and molecular weight were used to change interface widths, which were measured by neutron reflectivity. Fracture energies, determined using double cantilever beam test-pieces, increased linearly from about 100 to 450 J/m² as a_I increased from 9 to 11 nm. The large, fourfold increase in G over this rather narrow range of a_I was attributed to increased energy dissipation with the onset of sufficient interchain entanglements to induce crazing.

Bonding Involving Diffusion and Chemical Reaction. A number of technologically important adhesive bonds are formed by contacting materials which have components that diffuse to the interfacial region and chemically react. The strength of the reaction product and its interaction with each material controls joint strength. The generality and success of the approach will be demonstrated by discussing industrially important examples involving polymer/polymer, polymer/inorganic glass, and polymer/metal bonding.

Nitrile Rubber/Polypropylene. Nitrile rubber (NBR), a copolymer of butadiene and acrylonitrile, is quite incompatible with polypropylene (PP) and forms a very weak bond when contacted with it. As a result, a blend of these two polymers, prepared by melt mixing, produces a heterogeneous material that processes poorly and has very low strength and extensibility. Adhesion between the phases can be increased by adding to the blend a small amount of two reactive components: a telechelic, amine-functionalized NBR oligomer and an anhydride-terminated PP (43). These materials react *in situ* to form an NBR/PP block copolymer, which is thought to locate at the interface and increase bonding between the NBR and PP phases. The modified blend processes easily and has excellent strength. A similar methodology has been used to promote bonding between nitrile rubber and butyl rubber (44). An analogue of this approach is interfacial polymerization (45), in which immiscible phases (aqueous and organic) containing reactive components (diamine and diacid chloride) are contacted and polymer forms at the interface (so-called nylon-rope trick). Similarly, immiscible polymers may contain certain reactive components which can diffuse to the interface and form a product that increases adhesion between phases.

Adhesion between immiscible polymers has also been increased by using already prepared block or graft copolymers composed of segments of each polymer. In one approach (46), the copolymer is added to one or both of the adherends before contacting them. However, here, the copolymer may itself phase separate *away* from the interface. In another approach (47), the copolymer is spun-coated sparingly on one of the adherends to assure its presence at the interface.

In general, a third component, "technological compatibilizer," may couple phases in different ways. The compatibilizer may

- (1) phase separate, at least in part, as a distinct layer *between* the two phases. In this case, the cohesive strength of the layer and its interaction with each phase are important;
- (2) locate at the interface and form a "monolayer" or less coverage. In this case, the degree to which the compatibilizer alters the bonding between phases will depend on its concentration at the interface and the extent to which it is entangled and/or linked to each phase;
- (3) dissolve in each phase and increase the thermodynamic compatibility between the phases, thereby causing the interface to thicken.

The compatibilizer may not be *directly* involved in improving interphase bonding, but rather cause the molecules of each phase to interdiffuse more extensively. (Analogous behavior is known with small molecules. For example, an immiscible mixture of water and benzene forms one phase upon the addition of

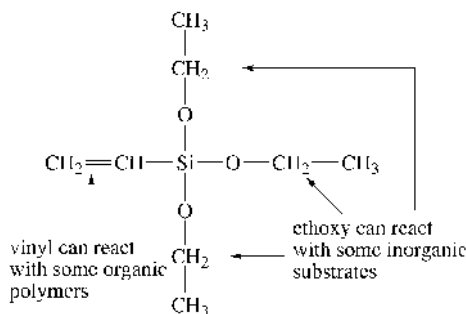


Fig. 5. Vinyltriethoxysilane coupling agent.

Table 1. Silane Coupling Agents

Type	Formula	Used With
Vinyl triethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_3)_3$	Cross-linked polyethylene, thermosetting polyester, diene elastomers
γ -Glycidoxypentyl trimethoxy silane	$\text{CH}_2\text{OCHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Epoxy, urethane, poly(vinyl chloride), phenolic
γ -Aminopentyl triethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$	Epoxy, melamine, nylon, polycarbonate, polyimide
γ -Mercaptopentyl trimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Epichlorohydrin, urethane, polyvinylchloride

methanol.) This mechanism may explain the increased adhesive tack and cured adhesion of dissimilar elastomers containing certain tackifier resins and so-called bonding agents.

Silane Coupling Agents. Silane coupling agents are very effective in promoting the adhesion of various polymers to inorganic glasses and are widely used in composites as well as joined structures (48–50). Silanes may be directly applied to substrates or may be added to a polymer prior to bonding. In the latter case, the silane diffuses to the glass–polymer interface and reacts as discussed next.

Silane coupling agents have four functional groups as shown in Figure 5. The three alkyloxy groups undergo hydrolysis to become silanols, which are capable of reacting with glass or self-condensing to form a polysiloxane. The fourth functional group reacts with the polymer. Thus, an *in situ* polysiloxane layer forms between the glass and polymer and couples them together. Table 1 gives several types of silane coupling agents and some polymers commonly used with them.

Brass/Rubber. When rubber containing sulfur curatives is pressed into contact with brass (typical alloy ~65% copper, 35% zinc) and then vulcanized,

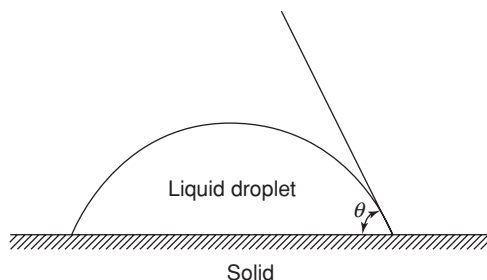


Fig. 6. Contact angle of a liquid droplet on a planar solid surface.

copper diffuses to the brass surface and reacts with sulfur to form cuprous sulfide (51). This interlayer grows outward from the brass surface, strongly interlocking into the rubber phase (52,53). Again, diffusion to an interface and *in situ* reaction to form a “coupling” interlayer is employed to provide bonding. Joint strength can be very high, and, because of this, steel cords used to reinforce tires are brass-plated.

Thermodynamics of Adhesion

Contact Angle. The degree to which a liquid wets a solid is measured by the contact angle θ (Fig. 6). When $\theta = 0$, the liquid spreads freely over the surface and is said to completely wet it. This occurs when the molecular attraction between the liquid and solid molecules is greater than that between similar liquid molecules (54). Surface tensions are related to the contact angle by an expression from equilibrium considerations (55):

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2)$$

where γ_{sv} is the solid–vapor surface tension, γ_{sl} is the solid–liquid interfacial tension, and γ_{lv} is the liquid–vapor surface tension.

The surface tension γ_{sv} of a solid that has adsorbed a layer of vapor is generally less than that of the solid in vacuo γ_s and this reduction is termed the spreading pressure π_s :

$$\pi_s = \gamma_s - \gamma_{sv} \quad (3)$$

However, liquid surface tension is little affected by the vapor phase so that $\gamma_{lv} \approx \gamma_l$.

Whether or not a given liquid will wet a solid surface depends on the surface tension of both substances. The ability of a liquid to wet a solid is often described by the spreading coefficient S_{sl} :

$$S_{sl} = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \quad (4)$$

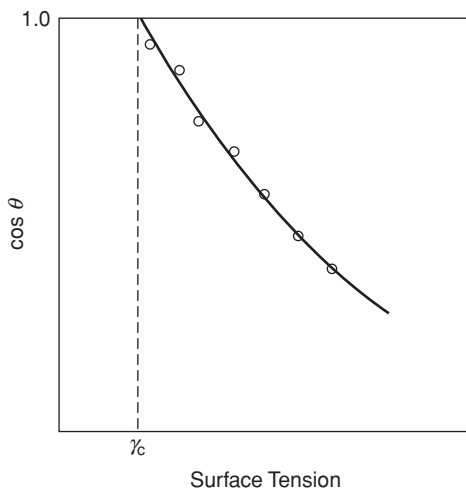


Fig. 7. Zisman plot for a particular solid surface and a homologous series of liquids.

A large positive S_{sl} implies that a liquid will spontaneously wet the solid. A negative S_{sl} indicates incomplete wetting and $\theta > 0$.

A widely used method for determining γ_s was developed using contact angle measurements (56). A plot of $\cos \theta$ against surface tensions for a homologous series of liquids can be extrapolated to give a critical surface tension γ_c at which $\cos \theta = 1$; such a plot is shown in Figure 7. Any liquid with a surface tension less than γ_c completely wets the solid surface. γ_c has been taken as an approximate measure of γ_s . It should be noted, however, that the value of γ_c is generally dependent on the particular series of liquids used to determine it. A series of polar liquids, such as alcohols, will give a higher γ_c than a series, such as simple hydrocarbons, which interacts less strongly with the same surface (57).

Thermodynamic Work of Adhesion. If a liquid is placed on a solid surface with which it has no interaction, then the interfacial tension between them is simply the sum of the surface tensions of the liquid and the solid. However, in all real systems, there are at least van der Waals attractions between the molecules of the liquid and those of the solid. This interaction decreases the interfacial tension so that $\gamma_{sl} < \gamma_l + \gamma_s$. The extent of the decrease is a direct measure of the interfacial attraction, and is termed the thermodynamic work of adhesion W_a :

$$W_a = \gamma_l + \gamma_s - \gamma_{sl} \quad (5)$$

This expression, first given by Dupré (58), states that the reversible work W_a of separating a liquid and a solid in vacuo must be equal to the free energy change of the system. (In wetting phenomena, the surface free energies are given directly by the surface tensions.)

Another expression relates γ_{sl} to the individual surface tensions of the liquid and solid (59):

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\phi(\gamma_s\gamma_l)^{1/2} \quad (6)$$

The last term represents the reduction in interfacial tension owing to molecular attraction between the liquid and solid. The term ϕ is defined by

$$\phi = \frac{W_a}{(W_{cl} W_{cs})^{1/2}} \quad (7)$$

where W_{cl} and W_{cs} are the work of cohesion of the liquid and solid, respectively, ie, the thermodynamically reversible work required to create a unit area of new surface in each material. For simple interfaces, ϕ is approximately unity, but for systems in which there are different types of intermolecular force in the two substances, ϕ may be appreciably less than unity.

By combining equations (2),(3), and (6), an expression for γ_s is obtained:

$$\gamma_s = \frac{[\gamma_{lv}(1 + \cos\theta) + \pi_s]^2}{4\phi^2\gamma_{lv}} \quad (8)$$

If $\pi_s \approx 0$, as has been suggested for high energy liquids on low energy surfaces (60,61) then equation (8) reduces to

$$\gamma_s = \frac{\gamma_{lv}(1 + \cos\theta)^2}{4\phi^2} \quad (9)$$

From the preceding discussion, as $\theta \rightarrow 0$, then $\gamma_{lv} \rightarrow \gamma_c$ (Zisman plot). Substituting this condition into equation (9), it is found that

$$\gamma_c = \phi^2 \gamma_s \quad (10)$$

Thus, γ_c is predicted to be approximately equal to γ_s only when $\phi \approx 1$, ie, for simple interfaces for which

$$\gamma_s = \frac{\gamma_{lv}(1 + \cos\theta)^2}{4\phi^2}$$

When γ_s and γ_l have values appropriate to simple nonpolar substances, about 25 mJ/m², W_a is only about 50 mJ/m², or less. The work for detaching one adhering substance from another has been found to be much larger than this, in the range 1 J/m² to 10 kJ/m². Thus, other contributions to the mechanical strength, from dissipative processes within the joint, greatly outweigh the intrinsic adhesion. Nevertheless, dissipative contributions depend upon the intrinsic adhesion, and in some instances, they are directly proportional to its magnitude (62,63). If there is no affinity between the adherends, there is certainly no mechanical strength of an adhesive bond.

Surface Treatment

In order to obtain a strong and durable adhesive joint, the surfaces of adherends are often treated before bonding. In general, these treatments alter the surface

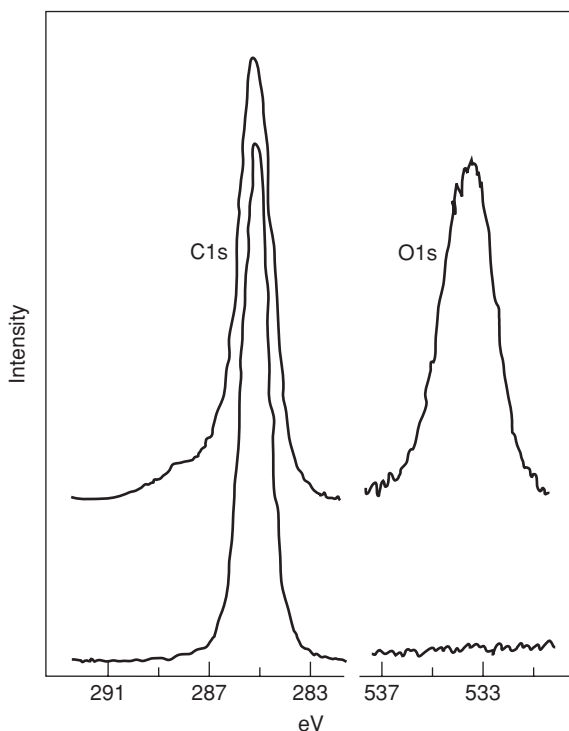


Fig. 8. ESCA spectra of low density polyethylene before (lower curve) and after (upper curve) treatment with a corona discharge (64).

region in one or more of the following ways: removal of a weak boundary layer, change in surface topography, change in chemical nature of the surface, or modification of the physical structure of the surface.

Polyolefins, Polyester.

Corona Discharge. The material is exposed to a corona discharge, usually in air and at atmospheric pressure. Polyethylene treated in this way experiences surface oxidation (64). Figure 8 gives xps spectra for a treated surface of low density polyethylene. The appearance of the O 1s peak indicates the formation of surface oxidation products. These are capable of dipolar or even perhaps acid-base interactions with polar adhesives. In addition, there is fine-scale roughening of the surface (65). This indicates that the corona has degraded and removed portions of the surface in a nonuniform way. Since polyethylene has both crystalline and amorphous regions, it is likely that the corona selectively attacks the more vulnerable amorphous regions. The enhanced bonding of polar adhesives to corona-treated polyethylene is attributed both to the increase in surface roughness and to an increase in surface energy. Only a small degree of oxidation is needed to markedly increase the adhesion of polyethylene to an epoxy adhesive. Oxidation not only increases the *specific energy* of interaction with the epoxy, but also increases the *number* of interactions because of more interdiffusion. Thus, bonding is enhanced autocatalytically by surface oxidation.

The wettability, and hence ability to bond, of oxidized polyethylene decreases quickly upon heating it to 85°C (66). Apparently, oxygen-containing groups in the surface spontaneously turn inward toward the bulk of the sample, so that the surface energy of the material is reduced and the hydrocarbon character of the surface is increased. At room temperature, the loss of bondability is slower since the chains have less mobility for this redistribution.

Acid Etching. Chromic acid is used to treat polyolefins before bonding. This causes selective removal of portions of the surface region and hence surface roughening (67). In addition, hydroxyl, carbonyl, carboxylic acid, and sulfonic acid groups are introduced (68). Bond strengths of epoxy adhesives are dramatically improved after short exposure to a chromic acid etch solution, and quickly become comparable to the cohesive strength of the polyolefin substrate. As with corona discharge treatment, the increase in joint strength after acid etching is attributed both to the introduction of polar groups and to the increased surface roughness. Extended treatment times are detrimental to joint strength because extensively etched polymer becomes a weak boundary layer.

Flame treatment. Polyester and polyethylene films are commonly exposed to flame treatment to increase bondability. Here, an oxidizing flame briefly (~ 0.01 – 0.1 s) impinges on the surface (69,70). XPS analysis (71) has shown that amide surface groups are generated, as well as typical oxidation functionality. Flame-treated films maintain bondability better than those that have been given corona treatment. Moreover, for all types of treatment, it is best to bond surfaces as soon as possible after treatment.

Surface Grafting. Rather than allowing the active species formed at a surface to simply combine with ambient oxygen, it is possible to have a reactive monomer present and form grafts to a surface. In one study (72), radicals and ions were created in a polyethylene surface by irradiation with γ rays in the presence of vinyl acetate monomer. The resulting polyethylene–vinyl acetate graft showed excellent bonding with an epoxy adhesive. Other researchers (73) have grafted acrylic acid onto polyethylene using electron beam irradiation. Adhesion to aluminum was increased about 10-fold.

Fluorocarbon Polymers. Fluorocarbon polymers require treatment with powerful etchants before they can be strongly bonded. Metallic sodium dissolved in either a mixture of naphthalene and tetrahydrofuran, or in liquid ammonia, is effective (74,75). These reagents reduce the polymer surface by defluorination (76). Initially, the surface is discolored, and it will form a carbonaceous black residue if treatment is continued too long. XPS analyses have shown the presence of unsaturation, and carbonyl and carboxyl functionality after treatment (76). Wettability and joint strengths are dramatically improved. Care must be taken not to treat the polymer too long, since substantial degradation of the surface region would generate a weak boundary layer and lower joint strength.

An interesting technique to improve the bonding of an epoxy adhesive to polytetrafluoroethylene (PTFE) has been demonstrated (77,78). Two adherends are abraded in the presence of liquid adhesive. These are then brought into contact and the adhesive allowed to set. The shear strength of the joint is about seven times that obtained if the adherends are abraded in air before applying the adhesive. Presumably, when abrasion is carried out in the presence of the adhesive, active species are created in the PTFE surface as a result of chain rupture

and they react directly with the adhesive. When abrasion takes place in air, these species may decay away before the adhesive is applied.

Metals. A metal that has been exposed to air invariably forms an oxide layer on its surface. This oxide layer may be intrinsically weak or it may adhere poorly to the underlying metal, leading to weak adhesive joints in either case. Furthermore, usually there are organic contaminants present on the surface, ie, residual lubricants from the manufacturing process or substances adsorbed from the atmosphere. In order to prepare a metal surface for bonding, etching techniques have been developed that remove both the surface contaminant and the existing oxide layer. Under controlled conditions, a new oxide layer is then formed, which is strong and adheres firmly to the underlying metal.

Chemical etching removes some of the underlying metal as well. The metal near the surface may have quite a different physical structure from the bulk as a result of the particular process used in forming. For example, if the surface was created by a cutting action, then the metal near the cutting blade, now the surface region, is subjected to high stresses that can cause local yielding and plastic deformation. Because the state of deformation of the surface material influences its reactivity with oxygen, the oxide formed is different from that which would have formed on a strain-free surface. Also, the structure of the deformed surface varies because of the inevitable nonuniformity in local deformations during cutting. After removing the irregular oxide layer by etching, a new oxide with improved uniformity and strength can be formed in a controlled way.

Aluminum. The treatment of aluminum to enhance bonding has received considerable attention because of the widespread use of aluminum/epoxy bonds in aircraft. It is a relatively simple matter to prepare an aluminum substrate so that it will initially bond tenaciously to epoxy adhesives. An aluminum/epoxy lap-shear joint in which the aluminum has been degreased and grit-blasted before bonding is so strong that it fails within the epoxy layer when stressed (79). However, upon modest exposure to a moist environment, bond strength falls and the locus of failure changes to the interfacial region. The decrease in strength is more rapid if the adhesive joint is also stressed while exposed to moisture (80). (The accelerated action of an environmental degradant caused by stress is an important general phenomenon in materials science and has been called mechanochemical degradation.) The oxide (Al_2O_3) on aluminum may change into the hydroxide (AlOOH), boehmite, on exposure to a humid atmosphere (81). Boehmite is weaker than the original oxide and adheres less strongly to the aluminum beneath it. This leads to the decrease in joint strength upon exposure to moisture (82–84). Auger electron spectroscopic analysis of joints broken after exposure to high humidity has shown that fracture occurs at or near the boehmite–metal interface (84).

Both the physical structure of the oxide and its resistance to moisture can be changed by special surface treatments. One treatment is the Forest Products Laboratory (FPL) process (85). This consists of degreasing, alkaline cleaning, and etching in a solution containing $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, H_2SO_4 , and H_2O in a 1:10:30 ratio by weight. Specimens are then thoroughly rinsed and air-dried. Joints made from FPL-etched aluminum bonded with epoxy adhesives are much more resistant to degradation by moisture compared to joints made with unmodified aluminum. Part of the increase in durability is attributed to the physical structure

of the oxide layer, which consists of a uniform layer about 5 nm thick with long oxide spikes (ca 40 nm) protruding outward (86). It is proposed that the adhesive can flow around the protrusions, thereby increasing the area of interaction between the oxide and the adhesive, and also providing mechanical interlocking.

A further enhancement in aluminum/epoxy joint durability in a moist environment is obtained by anodizing the aluminum after FPL treatment (80). Typically, samples are anodized for several minutes in an aqueous solution of phosphoric acid (phosphoric acid anodization or PAA) before rinsing and drying in warm air. The process produces a thin, uniform oxide layer near the bulk metal and a much thicker (400 nm) porous layer on top of it (86). This upper layer is much thicker than that formed using the FPL process alone, and, in addition, after PAA a monolayer of AlPO_4 is present on top of the Al_2O_3 (87). The high durability of joints containing PAA-treated aluminum is again attributed, at least in part, to the microporosity of the oxide layer into which the adhesive may flow and solidify. Water molecules that diffuse to the interfacial region and therefore swell the adhesive within the pores may actually cause it to press more firmly against the cell wall and tend to enhance joint strength. An additional mechanism that may confer high durability on joints containing PAA-treated aluminum is the resistance to moisture provided by the AlPO_4 top layer. This will protect the oxide and delay the formation of the undesirable hydration product, boehmite (87).

Copper. The bonding of polyethylene to copper provides another example of the importance of oxide topography on joint strength (88,89). If copper is first cathodically cleaned or chemically polished, then polyethylene adheres rather poorly. However, if copper is given a wet oxidation treatment with sodium chloride, sodium hydroxide, and sodium phosphate solution before bonding, then polyethylene adheres tenaciously. In the former cases, the oxide layer is rather smooth and uniform, whereas the latter treatment produces a thick, black dendritic oxide that adheres strongly to polyethylene by mechanical interlocking. The bond strength is enhanced by plastic deformation of the composite interlayer, consisting of the fibrous oxide embedded in polyethylene, which interlinks the bulk copper and polyethylene (90).

Steel. Not all metal adherends require chemical surface treatments in order to optimize joint durability. With mild steel, removal of soluble contaminants by vapor degreasing followed by grinding or grit blasting is sufficient (91). However, the freshly created surface of steel is very reactive and reoxidizes almost instantly. It will continue to oxidize, especially in the presence of moisture, eventually forming a visible rust. The treated surface must be coated with a primer or adhesive before the oxide layer becomes too thick, otherwise joint strength and durability will be poor (92).

Tack

Some rubbery materials adhere firmly to themselves (autohesive tack or autohesion) or to a different surface (adhesive tack) after brief contact under light pressure. They have a liquid character which results in rapid bond formation, yet, without setting, they resist detachment like a solid, ie, they are *strong* and *soft*. (Tacky substances are “stroft,” like toilet paper.) Typically, adhesive tack

involves bonding to a hard substrate and interdiffusion is absent or minimal. Adsorption is the principal mechanism of adhesion. On the other hand, autohesion involves both molecular contact and interdiffusion. Autohesion is important in the manufacture of articles, such as tires, which are built by laminating rubbery components.

Adhesive Tack. Adhesives that exhibit adhesive tack are often called *pressure-sensitive adhesives* (PSAs), since joint strengths depend on the pressure applied during bonding. In practice, PSAs are usually carried on a backing; tapes and labels are examples. In order to secure rapid wetting on common surfaces, a PSA must have a creep compliance after 1 s greater than about $10^{-6} \text{ m}^2/\text{N}$ (93). When the compliance is greater than this value, the forces of attraction between molecules of the adhesive and substrate are sufficient to pull the adhesive into intimate contact with the substrate surface, even when that surface is irregular on a microscopic scale. Furthermore, in order to provide a strong joint, a PSA should have a long yield plateau followed by hardening at large strains. Yielding blunts the separation front, reduces stresses, and therefore inhibits detachment. Strain-hardening prevents continued flow and easy rupture of the adhesive. This distinguishes a good PSA from a simple liquid. Both may readily attain molecular contact, but although liquids easily flow apart at low stresses, suitable elastomeric formulations will resist relatively large tensile stresses before rupturing. Some elastomers are self-strengthening upon deforming, by virtue of the steric regularity of their molecules, which allows them to rapidly crystallize on stretching. Since this mechanism is inactive at low strains, it imparts strength without hindering wetting. Natural rubber strain-crystallizes and is widely used in pressure-sensitive adhesive formulations.

Thus, in brief, a successful pressure-sensitive adhesive not only has low resistance to small strain deformation in order to facilitate wetting, but also it can resist large strains without flowing apart easily. Certain neat elastomers such as acrylate-based PSAs possess these features and are intrinsically tacky without additives. Other PSAs are formulated by diluting high molecular weight rubbers with special resins called tackifiers.

Tackifiers. *Tackifiers* are solid resins added to elastomers to improve pressure-sensitive adhesion. They generally have molecular weights in the 500–2000 range, with broad molecular weight distributions. Tackifiers are glassy, with softening points varying from 50 to 150°C, and they often have limited compatibility with the elastomer to which they are added (94,95). Common tackifiers include rosin derivatives, coumarone-indene resins, terpene oligomers, aliphatic petroleum resins, and alkyl-modified phenolics (96). In order to impart tack to an elastomer, a substantial portion of the tackifier must dissolve in the elastomer, thereby reducing entanglements and softening it, without excessive weakening. This requires control of the molecular weight of the tackifier. If it is too high, the tackifier becomes an incompatible filler—stiffening and strengthening, but preventing rapid wetting. On the other hand, if molecular weight is too low, the tackifier becomes a low T_g liquid and acts as a plasticizing solvent. In addition, tackifiers in PSAs have been reported to have marginal compatibility with the elastomer, often resulting in migration of some tackifier to the surface (97).

The effect of adding tackifiers on the rheological properties of elastomers has been investigated (98–100), and the results are instructive in understanding

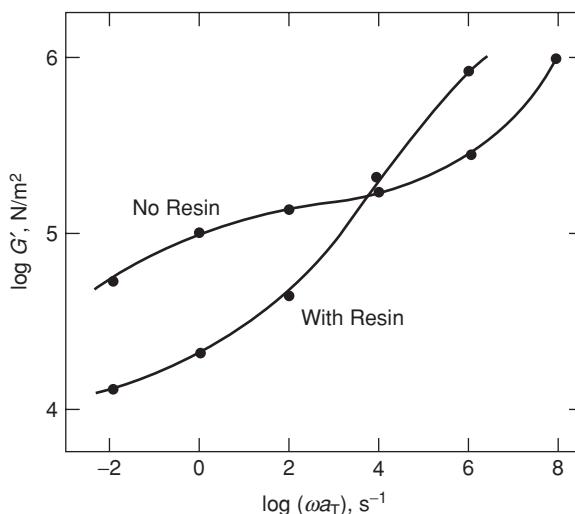


Fig. 9. Effect of a tackifier on the dynamic modulus G' of natural rubber as a function of reduced deformation frequency ωa_T (98). To convert N/m^2 to psi, multiply by 1.45×10^{-4} .

how a tackifier functions. Figure 9 shows a plot of the shear storage modulus G' of natural rubber with and without a tackifying resin (98). When the resin is present, the resistance to deformation is reduced at low rates, ie, lower G' . This results from a reduction in the rubber entanglement density and facilitates wetting on contact. At the same time, when measuring the strength of the bond at higher rates of deformation, the modulus G' is high, reflective of the tackifier's high T_g , and the material is stronger. This behavior can be contrasted with the effects of adding a filler or a simple plasticizer. A filler would increase G' over the entire range of rates of deformation, leading to difficulties in bond formation. A simple plasticizer unduly lowers the cohesive strength of an adhesive, so that, at high dilution, a plasticized rubber is very weak. In contrast, a highly tackified rubber, though soft, nonetheless resists easy fracture (97).

Rate and Temperature Effects. Pressure-sensitive adhesives are soft elastomeric semisolids. Their peel strength depends strongly upon the rate of peel and the test temperature, as shown for a simple model system in Figure 10 (101). At low rates, the peel force increases with rate, and failure takes place entirely within the adhesive layer, which fails by flowing apart. The peel strength is primarily a measure of the work of extending a viscoelastic liquid to the point of rupture. Although the local stress required to disentangle the molecules at low rates is relatively small, the work expended in ductile flow is large and the peel force, which measures the work of separation, is correspondingly high. At a critical rate of peel, which increases as test temperature increases, an abrupt transition takes place to interfacial fracture between the adhesive and substrate. This transition occurs when the rate of deformation of the adhesive layer at the peeling front becomes so high that the adhesive molecules do not disentangle and flow apart like a liquid. Instead, the molecules remain intertwined and respond like

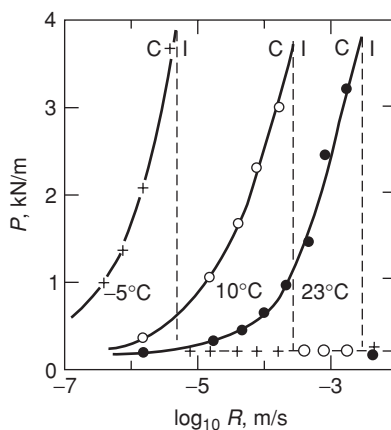


Fig. 10. Peel-force vs. rate of peeling for an elastomeric layer adhering to a polyester film. *C* and *I* denote cohesive and interfacial failure modes, respectively (101). To convert kN/m to ppi, divide by 0.175.

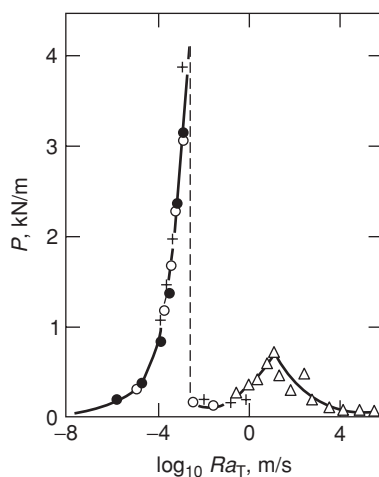


Fig. 11. Results from Figure 10 replotted against the reduced rate of peeling at 23°C, obtained by WLF time-temperature superposition (101). To convert kN/m to ppi, divide by 0.175.

an elastic solid. In the elastic state, the work of separation is expended nearer to the interface, and is relatively small.

The rate of peel and test temperature at which the abrupt transition occurs are directly dependent upon the rate of Brownian motion of molecular segments. Simple viscoelastic adhesives therefore obey the WLF rate-temperature equivalence (102). Applying this principle to the data in Figure 10 results in the mastercurve shown in Figure 11. Thus, it is possible to predict the rate dependence of the peel strength over a wide range of peel rates, using only limited data obtained over a narrow range of rates at various temperatures.

Autohesive Tack (Autohesion). For two layers of the same elastomer to resist separation after being brought into brief contact, the basic criteria already outlined for adhesive tack must be satisfied. The two surfaces must come into intimate molecular contact and the materials themselves must resist high stresses without flowing apart. However, there is an important difference between the two types of tack. Pressure-sensitive adhesives based on hydrocarbon rubbers *always* contain substantial amounts ($\sim 50\%$ or more) of tackifier to allow them to readily achieve wetting. As discussed earlier, this is attributed to the need for the adhesive to be sufficiently compliant so that it will be quickly “pulled” by adsorption forces into intimate molecular contact with common hard substrates. Neat hydrocarbon rubbers exhibit very little adhesive tack, but they can exhibit very strong autohesion. For example, unmodified natural rubber is a poor pressure-sensitive adhesive, but its autohesion is high. When interdiffusion is active, a high resistance to separation develops quickly in spite of relatively low compliance. Although interdiffusion cannot occur until molecular contact has been established, it appears that interdiffusion somehow speeds molecular contact. This apparent paradox is addressed next.

When two layers of the same elastomer are pressed together, molecular contact is not generally complete, but develops in a progressive manner. Thus, after a brief contact time t , some microscopic areas may not have achieved molecular contact and other areas will have achieved intimate contact at times varying from 0 to t . The overall bond strength, then, is the sum of many interactions of varying magnitude at the contact sites, together with interfacial defects (noncontacted regions). As t increases, the defects “close-up.” Perhaps, interdiffusion at contact sites can speed the closing-up of interfacial defects around them.

Finally, it should be noted that the barriers to molecular contact may be different for adhesive tack and autohesion. Surface impurities, eg, from bloom, may readily redissolve into the bulk elastomer during autohesive bonding. On the other hand, impurities on common substrates, such as surface moisture, may not be readily displaced by an adhesive that is too stiff. Molecular mobility and microscopic flow are expected to aid displacement of impurities.

Molecular Weight. The effect of molecular weight on the autohesion and cohesive strength of natural rubber (NR) is shown in Figure 12 (103). As the molecular weight is increased, the cohesive strength rises because of a greater number of molecular entanglements per chain. On the other hand, the autohesion after a given contact time passes through a broad maximum with increasing molecular weight. At the lowest molecular weights, contact and interdiffusion are rapid. (*Relative autohesion*, defined as autohesion divided by cohesive strength, is unity.) Still, the autohesion is low because of the poor cohesive strength. At the highest molecular weights, both contact and diffusion are slow owing to restricted molecular mobility. Thus, the autohesion again is low. Qualitatively, similar results are found for other elastomers.

Dried NR latex has very high molecular weight and low autohesion. However, NR undergoes molecular scission upon mastication and moderate amounts of milling improve autohesion as the molecular weight is reduced (Fig. 12). However, the cohesive strength, and hence, maximum achievable autohesion, becomes low after prolonged milling. Other elastomers, eg, styrene-butadiene

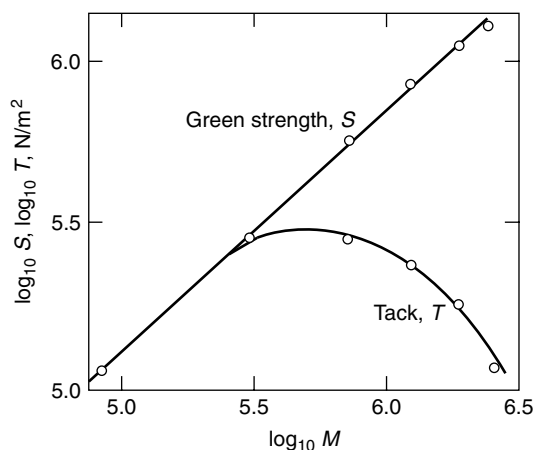


Fig. 12. Tensile strengths of autohesion (tack T) and cohesion (green strength S) of natural rubber as a function of molecular weight M (103).

rubber (SBR), are less susceptible to shear degradation, and autohesion is less altered by mastication. Nonetheless, shearing conditions used to prepare specimens for testing of autohesion should be well controlled.

Rate and Temperature Effects. Like adhesive tack, autohesion of elastomers is strongly dependent on test rate and temperature. Furthermore, as shown in Figure 13 for the T-peel autohesion of a cold emulsion SBR, relative autohesion P_r (for a given time and pressure of contact) is not unique, but it too depends markedly on test conditions (104).

Figure 13 is a mastercurve of relative autohesion after various contact times versus reduced test rate Ra_T at 23°C. The dotted line, $\log P_r = 0$, ie, $P_r = 1$, is the maximum value that relative autohesion can attain. When data lie on this line, tack is equal to the cohesive strength, ie, the joint is as strong as the fully healed one. Of course, if healing were complete, data for all Ra_T would fall on the dotted line. Remarkably, as seen in Figure 13 and discussed below a tack joint may behave as if it was fully healed at certain Ra_T ($P_r = 1$), even though healing is actually quite incomplete ($P_r \ll 1$ at other Ra_T).

After 1 min of contact, $P_r \ll 1$ at the lowest test rates. Clearly, healing is incomplete. However, P_r increases with rate and reaches a value of one at a reduced test rate of about 1.6 m/min [$\log Ra_T$ (mm/min) ≈ 3.2]. At higher rates, P_r decreases to a minimum and the peel response becomes stick-slip. (Ends of the vertical lines in Fig. 13 are extremes of P_r when the peel force oscillates in a regular stick-slip manner.) Thereafter, P_r increases again at the highest peel rates. As contact time is increased, the range of reduced rates where $P_r = 1$ broadens, but even after 100 h of contact, the junction is not fully healed, since, at the lowest test rate, P_r is still less than one. This is probably indicative of a very high molecular weight fraction in this cold-emulsion SBR, with an extremely slow interdiffusion rate. Nonetheless, after just 1 min of contact, the junction behaves as though it were fully healed under certain test conditions. At slow test speeds, substantial interdiffusion is required to attain a high value of P_r , whereas it appears

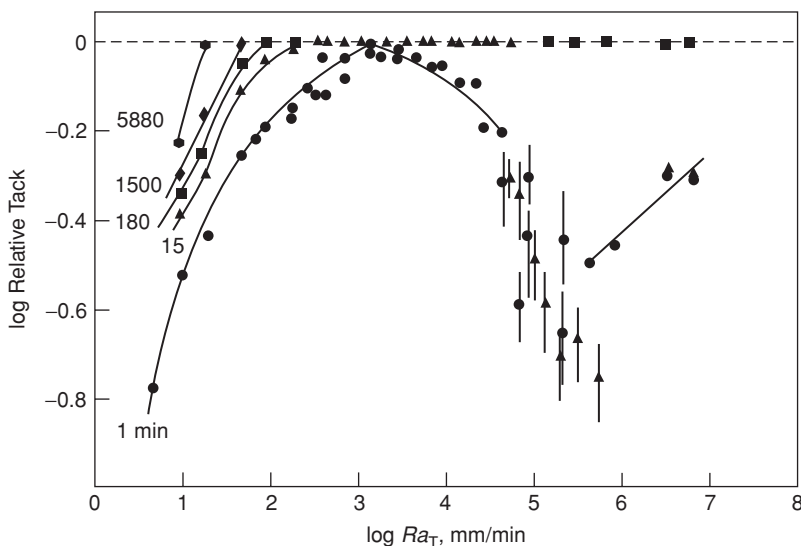


Fig. 13. Mastercurves of relative tack of an SBR versus reduced test rate at 23°C for various contact times, given in minutes for each curve. Ends of vertical lines are extreme values when failure was stick-slip (104).

that only limited interdiffusion is sufficient to give $P_r = 1$ at somewhat higher rates.

For contact times of 1 or 15 min, P_r increases with rate to a value of one, then decreases markedly and the failure becomes stick-slip. It has been hypothesized that this decrease is associated with the presence of small, non-contacted regions or interfacial flaws, which act as stress-raisers, when the elastomer is deformed at sufficiently high rate. If this is correct, then the abrupt decrease in P_r at high rates should be eliminated when the contact time and pressure are sufficient to cause the disappearance of these “defects.” Indeed, after 180 min of contact, the decrease in P_r at high rates no longer occurs. After P_r becomes unity at some critical rate, it retains this value at all higher rates. Furthermore, if, after 180 min of contact, the contact pressure is removed while further healing proceeds, then the autohesion increases as if the pressure had been maintained for the entire contact period. However, for contact times less than 15 min, if pressure is removed for an interval during the contact period then autohesion is reduced. It appears that full molecular contact of surface elastomeric chains takes place between 15 and 180 min of contact. Then, autohesion becomes independent of pressure, since interdiffusion rates are insensitive to light pressures. With full contact, P_r remains equal to one at high rates and there is no stick-slip region where P_r falls off.

There has been disagreement in the literature whether molecular contact is sufficient to give high autohesion or whether substantial chain interpenetration is required (105). The previous results indicate that the answer may depend on the test rate and temperature. At high rates, complete, intimate molecular

content may be sufficient, whereas molecular interdiffusion becomes relatively more important when the debonding rate is low.

Relating Joint Fracture Energy to Intrinsic Adhesion

In an earlier section, it was noted that the mechanical fracture energy G per unit of bonded area is greater, sometimes by several orders of magnitude, than the interfacial interaction energy holding the joint together. This section discusses this important feature in more detail.

Many basic studies attempting to relate fracture energy and intrinsic adhesion have involved the detachment of lightly cross-linked elastomers, usually over a broad range of test rates and temperatures. Work expended irreversibly in stressing these joints up to the point of failure is included in the total work of detachment. To focus attention on interfacial bonding it is therefore necessary to minimize any dissipative processes in the adherends. A simple cross-linked elastomer can no longer flow like a liquid, but it is still not perfectly elastic because of internal friction between moving molecular segments. However, internal losses can be minimized by raising test temperature, so that molecular Brownian motion is more rapid, and by detaching the adhering layer at very low speeds. Under these “threshold” conditions the adhering layer is almost perfectly elastic, and the minimum fracture energy G_0 is determined.

In some simple cases of an amorphous elastomeric network adhered to a hard substrate, it has been found (62,106,107) that the fracture energy obeys the following equation:

$$G = G_0[1 + \phi(Ra_T)] \quad (11)$$

where ϕ is a quantity reflective of bulk energy losses, and dependent on test rate R and temperature T through the WLF factor a_T . ϕ has been related to an elastomer's loss modulus (108). For cross-linked rubbery materials, if the locus of failure stays the same, ϕ generally increases as the test rate is increased and tends to zero as Ra_T becomes sufficiently low. The (total) detachment fracture energy must also be equal to the sum of the ways in which energy is expended during fracture (109):

$$G = G_0 + H \quad (12)$$

where H is the hysteretic energy loss per unit area as a result of irreversible deformation in the *bulk* of the bonded components. Combining these two equations it is seen that

$$H = G_0\phi(Ra_T) \quad (13)$$

so that it is implicit in equation 11 that bulk energy losses depend directly on G_0 .

Gent and Schulz (62) demonstrated that detachment energy was the product of an intrinsic strength and a loss function dependent on molecular mobility.

Peeling of a cross-linked SBR from a polyester substrate was carried out at various rates both in air and in several wetting liquids. Values of G were equal to W_a (which had been determined from wetting experiments) times a much larger dissipative factor. Using a similar, lightly cross-linked SBR, the tensile fracture energy to separate the elastomer from various plastic substrates that had different surface energies was measured (106,107). In accord with equation 11, double-log plots of fracture energy versus reduced rate were parallel.

Although equation 11 is obeyed for certain cases of simple rubbers bonded to hard substrates, deviations from this relationship have been reported (110–112). One reason is that G_0 itself may sometimes be rate dependent (38,112,113). Furthermore, bulk dissipative losses may not be proportional to intrinsic adhesion, especially for joints containing components which can yield during fracture (112).

Next, we consider the relationship between G_0 , the minimum mechanical energy required to disrupt an interface, and W_a , the equilibrium, thermodynamic work of adhesion. Firstly, however, we discuss the corresponding quantities for the *cohesive* fracture of a lightly cross-linked rubber. These are G_{0c} , the threshold tearing energy (114), and W_c , the reversible fracture energy of the bonds acting across the cohesive fracture plane. Values of G_{0c} are of the order of 50 J/m^2 ($0.024 \text{ ft}\cdot\text{lb}/\text{in.}^2$) (115,116). This value is much greater than W_c , which is calculated to be only about 2 J/m^2 ($0.001 \text{ ft}\cdot\text{lb}/\text{in.}^2$). Thus, the minimum mechanical energy to fracture an elastomeric network is about 25 times that needed to (chemically) dissociate the carbon–carbon bonds crossing the fracture plane. The reason for this is that even under threshold conditions, in order to break just one backbone bond in a network chain, it is necessary to stretch all of the bonds in the chain essentially to their breaking point. Energy is not only expended in breaking bonds, but it is also lost within the broken, recoiling network strands. This idea was first proposed by Lake and Thomas (117). In mechanical rupture of a (strong) covalent network, the minimum dimension in which energy is expended away from the fracture plane is equal to the distance between cross-link points. On the other hand, cleaving bonds chemically does not require deformation and hence involves the minimum amount of energy to create new surface.

Although the Lake and Thomas analysis was carried out for cohesive fracture, the principles have been found to apply to the peeling detachment of a cross-linked polybutadiene layer bonded to glass (110). The amount of interfacial bonding was varied in a systematic way by changing the proportions of vinyltriethoxysilane and ethyltriethoxysilane used to treat a glass surface. Vinyltriethoxysilane is capable of forming covalent bonds with polybutadiene during free-radical cross-linking (118), whereas ethyltriethoxysilane is unreactive and interacts with the elastomer only by relatively weak van der Waals forces. The amount of interfacial covalent bonding between the elastomer and the glass surface was thus varied from only van der Waals forces, when ethyltriethoxysilane was used alone, to increasing amounts of interfacial chemical bonding, as increasing proportions of vinyltriethoxysilane were used. The detachment work was found to increase steadily with the amount of interfacial chemical bonding. Furthermore, values of G_0 were about 20–30 times higher than the calculated W_a . For instance, when the glass was treated with ethyltriethoxysilane, G_0 was 1.5 J/m^2 , whereas the thermodynamic work of adhesion calculated from the surface energies of the treated glass and the elastomer was only about 0.05 J/m^2 . Similarly, for glass

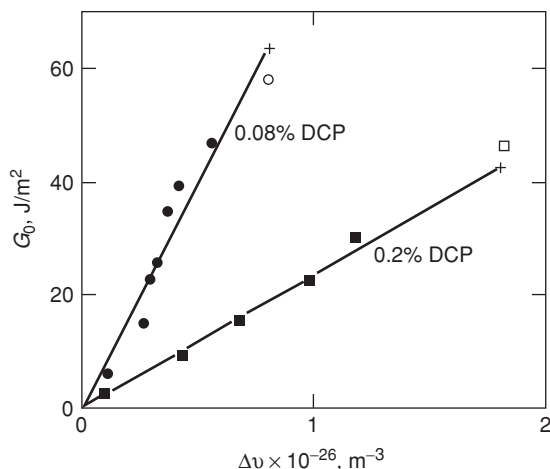


Fig. 14. Threshold work of detachment as a function of interfacial cross-link density for an elastomer (DCP = dicumyl peroxide) (124). To convert J/m^2 to lbf/in. , divide by 175.

treated with vinyltriethoxysilane, G_0 approached the threshold cohesive fracture energy of the elastomer, about 50 J/m^2 , about 25 times greater than the calculated value for rupture of a plane of C—C bonds.

Andrews and Kinloch (106,107) also determined fracture energies for a lightly cross-linked elastomer bonded to various substrates. However, unlike Ahagon and Gent (110), they found approximate agreement between G_0 and W_a . The discrepancy in the two cases may be related to differences in test geometry. Andrews and Kinloch employed a cleavage mode, whereas peeling, which requires more severe bending, was used by Ahagon and Gent.

An easier way to measure G_0 for weakly adhering soft elastomers is the JKR (Johnson, Kendall, Roberts) technique (119,120), which usually involves contacting a hemispherical cap of elastomer with a planar substrate. Contact mechanics are employed to relate contact area to intrinsic adhesion. Using the JKR technique, a value of G_0 has been obtained of 0.12 J/m^2 , about a factor of 2 higher than the expected work of adhesion (121). In other works (122,123) JKR experiments have been employed to determine threshold adhesion energies as low as 0.05 J/m^2 .

In other experiments (124) the density Δv of chemical bonds between two layers of the same elastomer was varied by partially cross-linking the layers before contacting them and completing the cure. In Figure 14, G_0 is plotted against the increase Δv in cross-linking while the two sheets were in contact. Δv is a measure of the amount of interfacial bonding. As can be seen, the threshold work of detachment increased in direct proportion to Δv , up to the measured tear energy of the elastomer, denoted by crosses. Thus, there appears to be a direct relation between the mechanical strength, ie, work of detachment, obtained under threshold conditions and the density of chemical bonds at the interface.

However, it is noteworthy that the bond strengths for sheets prepared with more cross-linking agent were lower than those prepared with a smaller amount. The joints were weaker in adhesion (o and □) and weaker in tearing in the fully

bonded state (+). This again points to the importance of the length of the molecular strands between cross-links. When the strands are long, they contain a large number of bonds that must be highly stressed in order to break or detach one of them. Thus, when the material is highly cross-linked and the molecular strands are short, then it is also less extensible and weaker.

The theoretical relation for the threshold bond strength (117,125), supported by the experimental results, is

$$G_0 = 1.0(C_\infty U/a^{1/2})L^{3/2}\Delta\nu \quad (14)$$

where C_∞ is the characteristic ratio of the molecule, generally lying between 2 and 10, a is the length of a C—C bond, U is its dissociation energy, and L is the contour length of the molecular strand between interlinks. Note that the strand length L is as important as the number $\Delta\nu$ of connecting strands in determining the strength of interlinked layers.

Strength of Adhesives and Joints

Fracture Mechanics of Simple Joints. In general, the strength of an adhesive joint is a function of the mode of loading and the dimensions and elastic properties of the bonded components, as well as the intrinsic strength of the interface. Fracture mechanics is used to relate the breaking load to these factors. One criterion for fracture assumes that a characteristic amount of energy is required to break apart the interface. Originally proposed for the brittle fracture of elastic solids (126), an energy criterion for fracture has been successfully applied to highly elastic materials (127), to materials that become locally dissipative (128,129), and to the separation of two adhering solids (130–142). An alternative criterion for fracture assumes that a critical *stress* is set up at the site of fracture (143). The two criteria are fundamentally equivalent, but energy calculations are often easier to perform.

In applying either criterion to predict the fracture of an adhesive bond, it is, in most cases, necessary to identify an initial failure site, usually a flaw at the interface. Failure is then assumed to take place by growth of this initial debond until the joint is completely broken. When an energy criterion is adopted for fracture, an energy balance is formulated in which changes in the strain energy of the joint and in the potential energy of the loading device when the debond grows by a small amount are equated to the work required for detachment. Strain energy is supplied by a loading device and stored in the deformable material. It is expended at failure in two ways: in supplying the work of fracture or detachment, and in deforming material that was previously undeformed or deformed less. By equating the energy made available to that required, the magnitude of the stored strain energy at the moment of fracture is deduced, and hence the breaking stress σ_b .

Modes of Failure.

Peeling. The peel test is particularly simple to analyze because the elastic energy of the deformed adherends does not change much as peeling proceeds. Most adhering layers do not stretch significantly under peel forces, and

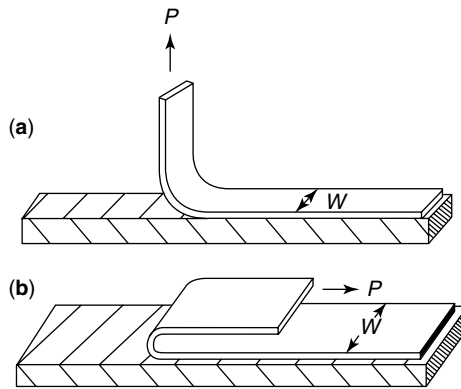


Fig. 15. Peel tests: (a) 90°; (b) 180°.

the amount of material subjected to bending does not alter. Thus, for flexible and inextensible adherends, the work of detachment is provided directly by the loading device. For peeling at 90° (Figure 15a), the peel force P per unit width is given by

$$P = G_a \quad (15)$$

where G_a denotes the work of detachment per unit area of interface. For peeling at 180° (Figure 15b),

$$P = G_a/2 \quad (16)$$

(The factor of 2 arises in this case because the point of loading moves through twice the distance of the detachment front.)

The contribution of plastic yielding to the measured peel force has been analyzed for an elastic-plastic adherend (144,145). If the adherend has a thickness greater than about $6EG_a/\sigma_y^2$, where σ_y is the yield stress, then no plastic deformation occurs and the peel force is unaffected. But if the adherend is thinner than this, it undergoes plastic deformation during peeling. The dissipated energy is provided directly by the peel force, which increases by a factor of up to about 3. However, for much thinner adherends the peel force falls again because now there is less material undergoing plastic deformation and less energy dissipated. Thus, the peel force is higher for adhesives that are capable of dissipating large amounts of energy during detachment, and for thicker adhesive layers, since this provides a greater volume of material in which dissipation occurs.

Lap Shear. Two simple examples of failure in lap shear are considered here. In the first, the adhering layer itself is elastic and stretchable (Fig. 16). The detachment force, applied parallel to the bond plane, stretches the detached layer and uses energy in doing so. For a linearly elastic layer, the relationship between the detachment force P per unit width and the work G_a of detachment per unit of

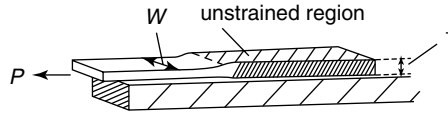


Fig. 16. Detachment of an adhering layer by a force parallel to the interface.

bonded area is

$$P^2 = 2tEG_a \quad (17)$$

where E is Young's modulus of elasticity in tension for the detaching layer and t is its thickness (137). The corresponding tensile stress σ_b in the detaching layer is

$$\sigma_b^2 = 2EG_a/t \quad (18)$$

We note that equation 18 does not contain the size of the debonded zone. Shearing detachment is therefore predicted to take place at a constant force that depends on the elastic modulus and thickness of the adhering layer but not on the length of the bonded region or on the extent of debonding. These features have been verified experimentally for adhering elastomeric layers (137), and the theory has been extended to deal with short overlaps, when bending deformations become important (137), with adherends of unequal thickness (137), and with prestressed layers (146). The success of a simple energy criterion for detachment confirms its general validity.

Pullout of Inextensible Fibers. By applying the same principle of energy conservation during detachment, it can be shown (141) that the pullout force P for an inextensible fiber of radius r embedded in a cylindrical elastic block of radius R (Fig. 17a) is given by

$$P^2 = 4\pi^2 R^2 r EG_a \quad (19)$$

When a bonded elastic cylinder of radius r is pulled out from a cylindrical cavity (Fig. 17b), then the pullout force is also given by equation 19 in the special form (142)

$$P^2 = 4\pi^2 r^3 EG_a \quad (20)$$

Experimental results with rubber cylinders have confirmed the general validity of equations 19 and 20. Measurements of failure loads in compression and torsion and in the presence of friction at the interface have been successfully analyzed in the same way (142). Moreover, a transition from pullout to fracture is expected when the strength of adhesion G_a is relatively large compared to G_c . The transition takes place at a critical ratio of the diameter of the embedded fiber to the diameter of the elastic cylinder in which it is embedded (147). An analysis along these lines also accounts for the brittleness of well-bonded laminar

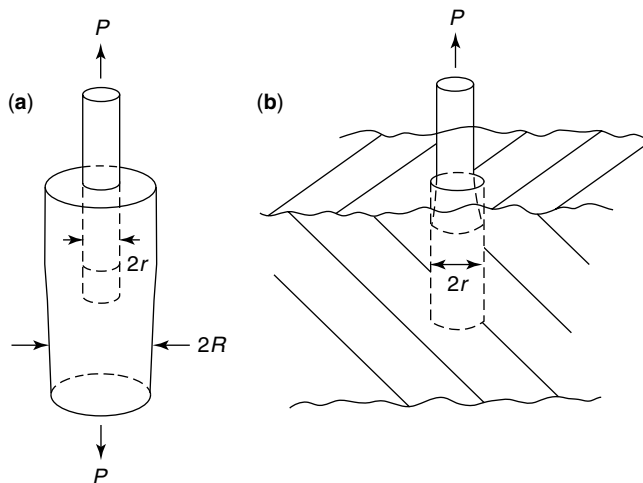


Fig. 17. Pullout of (a), an inextensible rod from an elastic cylinder and (b) an elastic rod from an inextensible block.

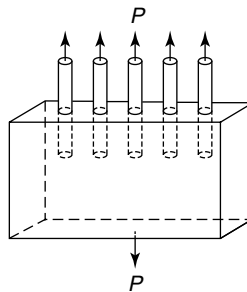


Fig. 18. Pullout of n fibers simultaneously from an elastic block.

composites compared to weakly bonded ones (138). Thus, again, energy considerations account for the principal features of the strength of adhesive joints.

When a number n of fibers are embedded in a single block of elastomer and they are all pulled together (Fig. 18), then the work required for detachment is obviously larger than for a single fiber by a factor of n . The strain energy stored within the block must therefore be larger than before, by a factor of n , and the total force applied for pullout must be increased by a factor of $n^{1/2}$. Thus, energy considerations immediately lead to the surprising conclusion that the total force required to pull out n fibers simultaneously from a single elastic block will increase in proportion to $n^{1/2}$. This prediction has been verified experimentally for 1–10 cords embedded in a rubber block (141). This is a striking example of the success of simple energy calculations in accounting for important features of the strength of joints and structures.

Shear Failure of an Adhesive Layer. Another type of shear failure occurs in a thin adhesive layer that is bonded and sheared between two rigid adherends (Fig. 19). Assuming that the adhesive is an elastic solid, the condition for growth

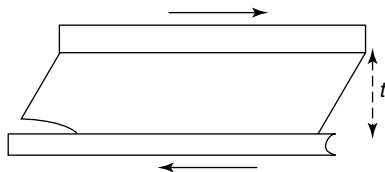


Fig. 19. Debonding in simple shear.

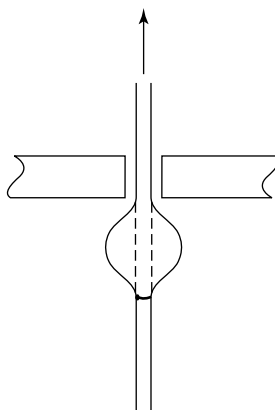


Fig. 20. Shearing a resin droplet from a fiber.

of a debond that is long compared to the adhesive thickness t is (148)

$$G_a = tW \quad (21)$$

where W is the strain energy stored by the shear deformation, per unit volume. Thus, a thinner adhesive layer with higher elastic modulus will be more resistant to growth of a debond. However, the relation for short debonds is more complex. Initially, the value of G_a falls as the debond grows and the rate of debonding therefore slows, but when the debond length approaches t , G_a rises again to reach the value given by equation 21.

Other Shear Tests. A common test method for examining the strength of bonds between a resin and a fiber is the microdroplet test (149), shown in Figure 20. A droplet of resin about $20 \mu\text{m}$ in diameter is applied to a single fiber and then stripped away by pulling the fiber through a narrow aperture. Originally, the stripping force divided by the total bond area was regarded as the failure stress in shear. Later, the microdroplet test was reevaluated using the concepts of fracture mechanics and the stripping force was reinterpreted in terms of the fracture energy required for growth of an initial debond (150–152). It has recently been found necessary to take into account the effects of friction between the fiber and the resin droplet after debonding (153).

Another test method for resin–fiber bond strength employs a single fiber embedded within a long resin bar (154). As the bar is stretched, the less-extensible fiber breaks into smaller and smaller fragments with a final mean length of l_c .

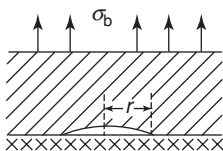


Fig. 21. Penny-shaped debond in a butt tensile test geometry.

Originally, l_c was interpreted in terms of a characteristic failure stress σ_s of the resin–fiber bond in shear (155):

$$\sigma_s = \sigma_f(r/2l_c) \quad (22)$$

where r is the fiber radius and σ_f is its breaking stress in tension. Attempts have been made to reinterpret the repeated fractures of the fiber in terms of the energy required for both debonding and frictional sliding (156,157).

Tensile Detachment from a Rigid Plane. For a circular debonded patch at the interface between a half-space of an elastic material and a rigid substrate (Fig. 21), the applied stress σ_b sufficient to cause growth of the debond is (158)

$$\sigma_b^2 = 2\pi E G_a / 3r \quad (23)$$

The same result is obtained for a pressurized debond, ie, a blister, of radius r at the interface between an elastic half-space and a rigid plane (159) because a tensile stress σ_b applied at infinity is equivalent to a pressure σ_b applied to the inner surface of the debonded region if the material is incompressible in bulk, as is assumed here.

Detachment from a Spherical Inclusion. A relation analogous to equation 23 has been deduced for the applied stress required to detach an elastic matrix from a rigid spherical inclusion (Fig. 22). The relation obtained is (140)

$$\sigma_b^2 = 4\pi E G_a / 3r \sin 2\theta \quad (24)$$

where r now denotes the radius of the inclusion and 2θ denotes the angle subtended by an initially debonded patch located in the most favorable position for growth, ie, in the direction of the applied tensile stress (Fig. 22).

It is clear that σ_b will be extremely large for inclusions of small radius r , even if the level of adhesion, represented by G_a , is relatively small, only of the order of magnitude of van der Waals attractions. For example, when E is assumed to be 2 MPa, representative of soft elastomers, and G_a is given the relatively low value of 10 J/m², then the critical applied stress for detachment is predicted to reach a magnitude similar to E when the radius of the inclusion is reduced to about 20 μ m, even if the initially debonded zone is as large as feasible, $\theta = 45^\circ$. These considerations appear to account for some features of reinforcement of elastomers by particulate fillers (140).

It is noteworthy that equation 24 predicts a decrease in detachment stress as the radius of the spherical inclusion is increased. This trend is in striking contrast to the result for a single fiber (eq. 19), where the pullout force is predicted

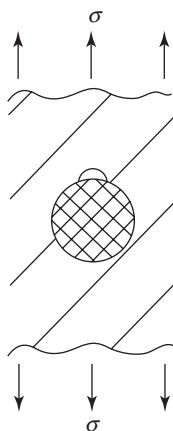


Fig. 22. Detachment from a rigid spherical inclusion.

to increase as the radius of the inclusion is increased. Both trends are predicted by the theoretical analysis, and both are confirmed by experiment (141,160). The surface area to be debonded and the energy required to debond are both greater for fibers of larger diameter and, as a result, the pullout force is increased. For spherical inclusions, on the other hand, the amount of highly stressed material in the vicinity of the debond, which provides the energy needed for propagating the debond in this case, also increases with the size of the inclusion. The highly stressed volume grows in proportion to r^3 , whereas the area to be debonded only grows in proportion to r^2 . In consequence, it is easier to propagate a debond on a larger inclusion than on a smaller one.

Fracture Mechanics for Bonds between Relatively Stiff, Elastic Adherends. Two test methods are now discussed that are particularly convenient for use with relatively stiff adherends. They are denoted cleavage failure and torsional failure. At first sight, a cleavage experiment, shown in Figure 23, resembles simple peeling but the mechanics of separation are quite different. In peeling, the peeled strip is long and flexible, and bends around into alignment with the peel force, as sketched in Figure 15. In a cleavage experiment, on the other hand, the bonded plates are relatively stiff so that they do not deform greatly under the cleavage force (Fig. 23). They bend only slightly so that the cleavage force continues to act effectively at right angles to the plane of the plates, even when the separation distance c is fairly long.

In peeling, the strain energy due to bending the peeled strips does not change as peeling proceeds, because the degree of bending remains constant. Therefore, elastic strain energy does not feature in the relation between work of peeling and work of detachment, equations 15 and 16. On the other hand, in cleavage the bending energy stored in the separated portions of the plates is a function not only of the applied force P but also of the debonded length c . Thus, as debonding proceeds and the debonded length increases, the plates, regarded as long elastic cantilevers, become more compliant. When the corresponding change in strain energy is taken into account, the following relation is obtained between

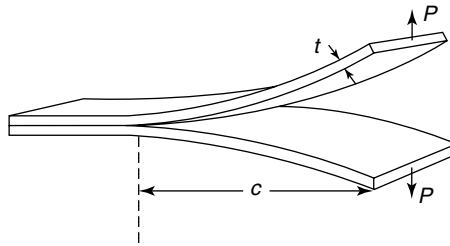


Fig. 23. Cleavage separation of two adhering plates.

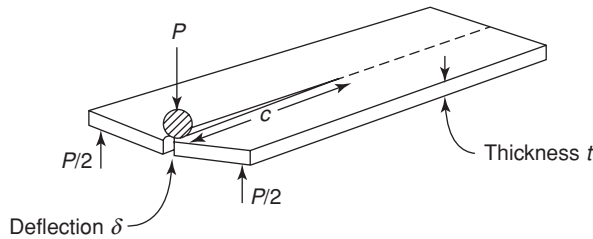


Fig. 24. Propagating a debond between two adhering plates by torsional loading (161, 162).

peel force P per unit width and work G_a of detachment:

$$P^2 = Et^3 G_a / 12c^2 \quad (25)$$

Note that the cleavage force P required to propagate the debond decreases continuously as the debond propagates. If, on the other hand, a constant deflection δ is imposed, then the energy available for debonding is given by

$$G = 3Et^3 \delta^2 / c^4 \quad (26)$$

which decreases strongly as the debond length c increases. Thus, the initial debond will grow until there is no longer a sufficient amount of stored elastic energy to propagate it. This is an attractive feature of cleavage experiments: they can be employed to study the minimum (threshold) strength of the joint.

However, it is experimentally inconvenient to measure the debond length continuously as the debond grows, in order to calculate the energy available for debonding from equation 25 or 26. Another experimental arrangement has been proposed for stiff adherends that does not have this disadvantage. It is sketched in Figure 24. Two plates are adhered together partway along their narrow edges and the unbonded portions are twisted by a load P applied at one end point of the common interface. As the debond is forced to propagate, the debonded portions of the plates increase in length and in torsional compliance, in direct proportion to the distance c debonded. This feature leads to a fracture force P that is, in principle, independent of the distance c debonded (161):

$$P^2 = 2G_a t / C' \quad (27)$$

where C' denotes the torsional compliance of a unit length of the debonded portions of the adhering plates and t is the thickness of the bond itself. Note that the value of C' can be determined from the slope of the linear relation between deflection and applied load before the initial debond starts to propagate. This test technique has also been modified using a pulley arrangement to apply torsional deflections of much greater magnitude (162).

Because the fracture force P is, in principle, constant, it will only fluctuate if the bond strength itself is variable. Thus variations in the fracture force can be directly associated with variations in the strength of adhesion.

Both of the test techniques considered in this section depend on the adherends being linearly elastic. If this is not the case, then the relations given (eq. 26 and 27) no longer apply. (This is the case for all of the relations given in this chapter: the adherends are assumed to be perfectly elastic so that energy expended in deforming them is available for fracture.) However, it is sometimes possible to bond fully elastic backing plates (eg, of spring steel) to the adherends under study and thus to convert plastic or yielding adherends into effectively elastic ones.

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ADHESIVE COMPOUNDS

Introduction

An adhesive is a material that is used to join two objects through nonmechanical means. It is placed between the objects, which usually are called *adherends* when part of a test piece or *substrates* when part of an assembly, to create an adhesive joint. Although some adhesives form joints that nearly immediately are as strong as they will be in actual use, other adhesives require further operations for the adhesive joint to reach its full strength. Adhesives can be made in several

different physical forms, and the form of a given adhesive will define the possible methods of its application to the substrate.

An adhesive is comprised of a base chemical or a combination of chemicals which define its general chemical class. Most adhesives contain a curing agent or catalyst that will cause an increase in the molecular weight of the system and frequently the formation of a polymeric network. Nearly all adhesives also contain additives or modifiers which fine tune the adhesive and may significantly influence its behavior before and after formation of the adhesive joint. These additives include solvents, plasticizers, tackifiers, fillers, pigments, toughening agents, coupling agents, stabilizers, and so on. Additives or modifiers increasingly are chosen for their ability to provide more than one benefit, for example, a pigment may not only color but may also reinforce an adhesive. In some cases, the process used to combine these diverse ingredients will strongly influence the properties of an adhesive. Although inorganic adhesives do exist, this article will be restricted to organic polymeric adhesives.

Consumers, designers, and engineers generally choose between adhesive bonding and mechanical or thermal methods when deciding how to join one object to another. Mechanical methods utilize bolts, screws, and rivets. Thermal methods include welding, soldering, and brazing. Adhesive bonding is the obvious choice for joining in cases in which the substrate is thin and relatively weak, for example, paper, or strong but relatively brittle, for example, glass. Use of adhesives in these situations avoids formation of stress concentration points and possible damage to the substrates. Even where the substrates will bear mechanical fastening, the geometry of certain parts sometimes makes welding or bolting more costly if not entirely impossible, as in the case of the aluminum honeycombs used in aerospace structures or tube-to-tube joining used in motor vehicle frame construction. Because they are usually applied so as to cover the entire joined surface in a continuous rather than point-by-point fashion, adhesives can provide a measure of environmental protection and mechanical reinforcement or stiffening well beyond the capabilities of mechanical fasteners. Stresses in adhesive joints are distributed over a relatively large area, which generally increases the mechanical and cosmetic integrity of joined parts. The energy damping capability of many polymeric adhesives contributes a mechanical damping component to joints that can increase their toughness and impact resistance. Adhesives are a great help in reducing the weight of structures because they add little weight and can facilitate the use of thinner substrates. Joining of dissimilar materials for reasons of economics, weight, or performance is frequently accomplished using adhesive bonding, providing properties already mentioned as well as electrical and thermal insulation, protection against galvanic corrosion, and acoustic damping. In some cases, adhesives are used in conjunction with joining methods such as welding and riveting, via weld bonding and rivet bonding, respectively, in order to maximize stiffness, strength, and fatigue resistance of joints.

Where an adhesive is the obvious choice, it is often the least expensive choice as well. In industrial situations where the performance expected of the adhesive is high and broad and its cost is that of a specialty rather than a commodity material, it is common to see users take a systems approach to make the best choice of joining method or the best choice of adhesive, if adhesive bonding is seen to be the best joining method. The systems approach to choosing adhesives goes well

beyond comparing the cost per gallon of adhesives. It considers the number of parts to be joined, the time and cost constraints of assembly, spatial limitations, the need for substrate surface cleaning or preparation, the cost of all application, fixturing, and curing equipment, environmental and safety requirements, disposal costs, and, finally, part performance and lifetime.

Market Economics

In 1996, the global adhesive and sealant industry was estimated to have a size of about 7.5 million metric tons. The monetary value of this volume was considered to be about US\$20.0 billion (1). The value of the market was estimated to be \$28.0 billion in 1998 led by North America with a 33% share followed by Europe (30%), the Far East (19%), and the rest of the world (18%) (2). By 2002, the same marketplace is expected to grow to 16.7 million metric tons (3). Adhesives make up over 80% of the adhesives and sealants market. It has been estimated that the global use of adhesives will continue to grow annually by 3–4% from 2000 through 2005, but for some types of adhesives and for some markets, the growth could be much larger.

In the United States, the adhesive and sealants business was producing about US\$1 billion from sales in 1972. By 1999, the U.S. adhesive business was estimated to be nearly 6.9 million tons in size with an approximate value of US\$9.5 billion. The size of the U.S. adhesive market is anticipated to grow to 7.9 million tons by 2004 (4). The largest markets for adhesives in the United States are construction, primary wood bonding, textiles, and packaging. Markets that command some of the highest prices for adhesives include dental, aerospace, and microelectronics.

The late 1990s were marked by significant numbers of consolidations and partnerships in the adhesive industry that are expected to continue into the twenty-first century. In 1999, only seven companies produced 49% of the adhesives sold in the world (5). The remainder of the adhesive industry is highly fragmented; in the United States alone, there are about 500 adhesive companies. North American and European adhesive companies have partnered to serve the global operations of automotive OEMs expecting worldwide service. Several companies have formed joint ventures in the People's Republic of China (6) in anticipation of large market growth in that country. Such arrangements are expected to increase in number as makers of adhesives accelerate their pursuit of greater market share and opportunities in the most lucrative markets. Concurrently with these changes, many large resin suppliers have spun off their adhesive resin operations into new companies or sold off their adhesive raw materials divisions to established companies. An active adhesive formulator must keep track of raw materials sources and be prepared to trace older materials to their new sources.

The adhesives industry has been affected by environmental and regulatory concerns regarding health and safety issues of adhesive ingredients, use of solvents, and other issues. Less than 5% of the adhesives used in the United States in 1999 contained organic solvents. The use of adhesives with solvents is decreasing by about 2% annually. All other adhesives are waterborne or contain

no carrier solvent. Recycling of adhesives has become more important as paper recycling has become very common, and the quality of recycled paper depends in part on the nature of adhesive residues present in recycle feedstock (7). Historically, certain adhesives have been based on natural products such as starch, natural rubber, and animal glue, and many adhesives still use as modifiers various tree-based rosins and terpenes, but there has been a strong shift away from naturally derived adhesives. Between 1972 and projected out to 2003, the value of U.S. adhesives made of synthetic resin and rubbers will have increased almost eight times while the value of U.S. adhesives made from natural bases will have increased only about five times (8). In the 1920s, nearly all primary wood bonding was done with adhesives produced from natural products (9). By the 1970s, that need was filled almost entirely by synthetic adhesives. As the price of crude oil rises and oil reserves dwindle, there is increasing interest in making more adhesives from renewable resources (10).

Principles of Adhesives and Adhesive Formulation

An adhesive is designed to perform certain functions. These functions are common to all adhesives, but the details as they relate to a given ultimate use can vary considerably.

First, the adhesive must be able to be conveniently applied to the substrate using a manual or mechanized method of application. Second, the adhesive must wet the surface to which it is applied. Third, the adhesive must achieve a permanently solid state via evaporation of a solvent, removal of pressure, a drop in temperature, or the occurrence of chemical reaction. The conversion must occur within a time period amenable to the use of the bonded part. Fourth, before it is put into service, the adhesively bonded part must have been provided with a bond that is strong enough to resist normally imposed stresses. The stresses normally imposed on a sealed envelope are very different from those imposed on a tiled wall or a bonded vehicle frame. Fifth, the adhesive must maintain the bond through the joint's functional lifetime, withstanding all environments to which the joint is normally exposed.

Methods of Adhesive Application. Until the twentieth century, adhesives and sealants were applied by hand using fingers, sticks, trowels, brushes, spatulas, shovels, and similar implements. These tools are still used by many do-it-yourselfers, craftspeople, and construction workers. Other relatively simple means of applying adhesives involve the use of squeeze bottles, spray cans, rollers, and squeeze tubes. Manual and pneumatic guns are often used to dispense adhesives, sealants, and caulks. For this type of application, the adhesive is supplied in a plastic cartridge to which can be affixed a tip or applicator to help control the shape and size of the adhesive bead as it is expelled. The adhesive is expressed from the cartridge by pressurization of a sealing piston. Such guns can be used to dispense two-part adhesive systems as well as one-parts, which are commonly called 2K and 1K adhesives, respectively, probably in reference to the German *komponent*. In the case of 2K adhesives, a mixing nozzle will be attached to the cartridge. This device consists of a tube and an inserted mixing element through which the two parts of the adhesive flow in a tortuous

path, folding over on each other and becoming well mixed. For low volume applications in the industrial sector, 2K epoxy adhesives are often supplied in double-barreled plastic cartridges for application using manual or pneumatic dispensing guns.

High volume applications of adhesives generally dispense adhesives out of containers having volumes up to at least 1135 L (300 gal). Through proper choice of pump design and material choice, bulk dispensing is possible for both liquid and high viscosity paste adhesives whether 1K or 2K (11,12). For some industries, dispensing guns will be handheld and manually operated. In the automotive industry, hem flange adhesives, cosmetic sealers, antifatigue sealants, gap-filling adhesives, and other viscous materials are dispensed in high volumes using computer-controlled guns mounted on robot arms which zip about a part in a few seconds to lay down dollops or linear beads of adhesive or sealant. Gun-robot coordination must be precise. To lay down enough but not too much adhesive in a well-defined area in a controlled fashion, adhesive dispensing companies provide extrusion, spray, streaming, and swirling patterns of adhesive delivery. The adhesive is sometimes heated to lower its viscosity.

Hot-melt adhesives are also dispensed using guns. Hobbyists and do-it-yourselfers use small electric handheld guns into which they insert the adhesive sticks. The gun heats the adhesive, and the operator squeezes a trigger to dispense it. High volume dispensing systems for hot-melts generally include a stirred melting tank and a hot pumping system that delivers the adhesive to the application device, which may be a spray gun, a roller, a brush, or a film die. Application methods include rotating pick-up wheels, transfer from a hot bar, and release from extrusion heads facilitated by spring ball valves (13).

The invention of pressure-sensitive tapes in the early 1930s provided a novel means of delivering an adhesive where it was needed. Adhesive tapes were first sold as rolls in boxes or cans and were unrolled by hand to be cut with scissors or a blade. This was followed by the design of tape dispensers that range from single-use, all-plastic disposables, to sand-weighted desk-top models fitted with metal blades, and on to the semiautomated dispensers used at large packing plants. Recent advances include dispensers of pre-cut adhesive strips that can be worn on one's wrist and the development of hand-tearable tapes. Solid curable adhesive films are available in roll, strip, and pre-cut forms of various shapes and thicknesses, with or without liners. These are typically somewhat tacky and are generally hand-applied.

Bond Formation. Adhesion science has established several mechanisms by which adhesion will occur. These are sometimes referred to as theories of adhesion, and they represent a means of explaining adhesion phenomena and increasingly provide guiding principles by which adhesion can be predicted to some extent and controlled to a larger extent. These theories are covered in most general texts on adhesives and adhesion science, many of which point out specific examples relevant to the scope of the text, for example, aerospace aluminum bonding or wood bonding. The theories of adhesion include the following:

- (1) Electrostatic theory
- (2) Diffusion theory
- (3) Mechanical interlocking theory

- (4) Acid–base theory or specific adhesion/interaction theory
- (5) Covalent bonding theory

Regardless of which theory or theories are manifest in an adhesive bond, establishing an adhesive bond requires that first there be sufficient contact between the adhesive and the substrate. This can be accomplished only if the adhesive intimately wets the substrate. Although there are many types of adhesives, in order to form this necessary contact each must flow under the influence of gravity, pressure, heat, or presence of a solvent to wet any asperities on the substrate surface. This wetting is necessary for establishment of a bond, but it is ordinarily insufficient for establishment of the strongest or most durable bond. (Conversely, the area of contact may be controlled to minimize adhesion.) Adhesion science, one of the most interdisciplinary of all sciences, has established several tenets for wettability which are applicable to adhesives, coatings, and other substances whose adherability is of interest. The first is that the surface energy of the wetting material will ideally be lower than that of the substrate. Methods for establishing surface energies of liquids are well established, and tabulations of such data are readily available. Obtaining the surface energy of a solid is somewhat more problematic, but methods do exist, most based on the determination of critical surface tension from measurement of contact angles made by various liquids, and these have been shown to have merit on a fundamental basis. Any surface roughness or surface contaminants will greatly influence the results of such measurements; however, the methods used are valuable in characterizing the wettability of ceramics and polymers, which generally have smooth surfaces.

The bulk properties of the adhesive and its ability to effect the transfer of stress across the adhesive–adherend interface will strongly dictate the measured strength of the bond, often described in terms of *practical adhesion*. The durability of the bond will be governed by the physical and chemical nature of the interfacial region formed, aptly called the *interphase*. The failure of a bond is usually characterized as being *adhesive* in the case where the failure is between the adhesive and the substrate and *cohesive* where the failure is within the adhesive. Failure may also be *mixed* mode, and other subtleties of the failure mode should be noted during testing or in the field. If surface analysis will be carried out to determine details of failure, failed bonds should be closed until that analysis can be performed.

Ideally the adhesive formulator will have at least a rudimentary knowledge about substrates, be they metals, ceramics, or polymeric materials. Whenever possible, testing of adhesives should be done on the same material being used in practice. If this is not possible, a nominally identical substitute should be used. The surface of the substrate should be what it will be in use. The state of that surface will affect adhesive wet-out, interfacial area, stress distribution, and the likelihood of chemical reaction. It is highly recommended that surfaces be as clean as possible, and it is often recommended that surface treatments be used. The most basic of all surface treatments is cleaning.

Simple cleaning methods include blowing away debris with canned or filtered air, wiping with a dry cloth or a cloth wet with ethanol, cleaning with a water-based citrus cleaner and rinsing with distilled water, and dipping in methyl ethyl ketone or petroleum ether and drying with a clean cloth. Vapor degreasing is used when the volume of parts to be cleaned can justify its installation. Until the

early 1990s, chlorinated solvents were used widely for degreasing, but health and environmental concerns have shifted interest to other organic solvents and aqueous degreasers. Other environmentally acceptable cleaning methods that have been investigated include grit blasting, ultrahigh water jetting (14), and excimer laser treatments (15–17).

In some cases, cleaning of a surface is not sufficient for adequate bond formation. For metal bonding, this is especially true in situations where the adhesive joint will undergo exposure to severe environmental conditions such as moisture, salt spray, and high temperatures. The coupling of these environments with mechanical stresses can lead to failures at loads much lower than those at which the same joint would fail in a milder environment. In these situations, it is common to use a wet chemical surface treatment which removes all surface contamination as well as any poorly adhering oxides and converts the newly exposed surface to a durable oxide, preferably with a texture that encourages mechanical interlocking with an applied adhesive. Pretreatments for aluminum have been the subject of considerable research (18). In partnership with adhesive suppliers, aerospace users of aluminum have advanced the state of the aluminum-bonding art on a continuous basis for many years and often use the steps of alkaline cleaning, phosphoric acid anodizing, and application of epoxy–phenolic primers to prepare aluminum for bonding. For industries in which failure may have less devastating results, organosilanes, sol–gel coatings, and gas plasmas have become the basis of a number of surface treatments.

Polymeric materials often present significant challenges to adhesive bonding. This is particularly true when bonding polymers with low surface energies such as polyethylene, polypropylene, and polytetrafluoroethylene; however, it is also true for bonding high surface energy polymers such as poly(ethylene terephthalate). Reliable wet chemical treatments continue to be used for plastics, but dry chemical treatments are well established as primers for adhesive bonding. These treatments include corona discharge, plasma, flame, and excimer laser.

Cleaning methods chosen should remove rather than redistribute contamination. Some methods which are ostensibly meant to clean may also contribute something in the way of a surface treatment via chemical or physical changes of a substrate. Methods which treat a surface chemically often also change surface texture, coupling roughness and chemical surface modification and making it difficult to separate their independent effects. Microscopic surface texturing can favorably enhance adhesion.

Adhesive users should not assume that meticulous cleaning and costly surface treatments will always be needed to ensure reliable adhesive bonding; however, as in all adhesive applications, the better the user understands what the adhesive must do, the more readily the need for cleaning and surface treatments can be assessed. Cleaning and surface treatment of substrates is not always economically feasible nor is it necessarily environmentally desirable. There have been considerable advances with respect to pressure-sensitive and structural adhesives which form strong durable bonds on oily metals and untreated plastics.

Adhesive Testing. The lifetime of an adhesive includes shipping and compounding of its components, storage and shipping of the adhesive in its final form, application to a surface or surfaces, service use, and a number of methods of disposal along the way and at its end. Adhesive raw materials are tested for

certain characteristics at their source and then tested to some minimum standard by the adhesive manufacturer at the manufacturing site. The manufacture of adhesives is either a bulk or continuous process, as appropriate to the form and type of adhesive. After manufacture, there is testing to known standards based on customer and manufacturer requirements. Tests done on the as-manufactured adhesive include both bulk tests of the adhesive which are relevant to its handling and dispensing and tests of the adhesive as a bonding agent. Even before any of this testing occurs, there will often have been extensive laboratory testing of the adhesive to customer specifications, only a very small part of which is repeated on each lot subsequent to manufacturing. In bulk testing of both cured and uncured adhesives, attention to detail is of paramount importance. Consistency of preparation and test conditions can have a profound effect on final results, which are increasingly subjected to statistical analysis during development and through various manufacturing processes.

A variety of standardized tests have been published for adhesive testing. The American Society for Testing and Materials (ASTM), the Technical Association of the Pulp and Paper Industry (TAPPI), the Society of Automotive Engineers (SAE), the Pressure Sensitive Tape Council (PSTC), and the International Organization for Standardization (ISO) have developed and published many different tests of interest to the technical community. Many academic and corporate libraries have bound collections of these standards. One can search the standard titles at each organization's website, respectively: www.astm.org, www.tappi.org, www.sae.org, www.pstc.org, and www.iso.ch. These organizations and their volunteer working committees actively update existing methods, standardize new methods, and obsolete older methods no longer in wide use. Additional standards are also published by or available from other professional organizations as well as specific companies and institutions. One will find that similar tests have been published by more than one organization or by the same organization; it is therefore useful to consult the source closest to one's interests and to review all applicable methods to find the one closest to one's needs. Variation from these standard methods, which is not uncommon, should be noted whenever reporting results from a given test. In cases where a specific test has not been published, these standards often provide help in developing needed tests. Numerous tests are also described in the open technical literature.

Bulk Testing. The chemical fingerprint, identity of, or contaminants present in bulk uncured adhesives can be obtained by any of the chemical tests routinely performed on other chemicals, including Fourier-transform infrared spectroscopy, mass spectrometry, and elemental analysis. Many adhesives are tested for their water or solvent content using weight loss or expansion tests or one of the analytical methods available. Percent solids are sometimes determined using mass measurements made before and after treatment in an ashing furnace. Volatile organic content is measured using weight loss tests done under relevant conditions. Measurement of the flow properties of adhesives is very important. Rheological tests include simple empirical tests that measure quantities such as the time needed to flow a certain volume a certain distance down an inclined plane or through a pressurized orifice, rotating-spindle tests that determine the relative viscosity of a liquid, and more advanced methods using cone-and-plate and parallel-plate methods that directly measure viscosity, yield

stress, and flow activation energy at a variety of shear rates and temperatures. Density of paste adhesives can be measured using calibrated pycnometers. Thicknesses of solid adhesives, tapes, and related products can be measured manually or with methods such as x-ray fluorescence. Qualitative tests performed on adhesives include those addressing color, odor, consistency, foreign particulates, separation, and skinning. Shelf-life tests of bulk adhesives generally track how one or more of these many adhesive characteristics changes with time and temperature.

Testing of cured adhesives in the bulk state has become more widespread because of increasing use of adhesives in engineered structures. Concurrently, modelling of adhesive joints has become more commonplace, and for such work, measurement of the bulk mechanical and solid fracture properties in a variety of modes is essential. Developers of adhesives are also increasingly aware that testing of cured adhesives in the bulk state can provide information relevant to their performance in bonded joints.

Tests in common use for bulk characterization of adhesives include ASTM D816, *Standard Test Methods for Rubber Cements*; SAE J1524, *Method of Viscosity Test for Automotive Type Adhesives, Sealers, and Deadeners*; ASTM D638, *Standard Test Method for Tensile Properties of Plastics*; ASTM D3983, *Standard Test Method for Measuring Strength and Shear Modulus of Nonrigid Adhesives by the Thick-Adherend Tensile-Lap Specimen*; and ASTM D2979, *Standard Test Method for Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine*.

Adhesive Bond Testing. Practical adhesion is quantified in terms of the force or energy per unit area needed to separate a bonded joint. The most commonly used bonded joint configurations are the asymmetric and symmetric overlap shear and 90° and 180° peel. Many special or use-specific adhesive joint tests are also done. Adhesive tests based on fracture mechanics are increasingly used for their relevance to engineering design. Commonly used adhesive bond tests include ASTM D1002, *Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)*; ASTM D2095, *Standard Test Method for Tensile Strength of Adhesives by Means of Bar and Rod Specimen*; ASTM D950, *Standard Test Method for Impact Strength of Adhesive Bonds*; ASTM D1780, *Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives*; ASTM D2294-96, *Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)*; ASTM D1876, *Standard Test Method for Peel Resistance of Adhesives (T-Peel Test)*; and ASTM D3330/D3330M, *Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape*.

The testing of adhesives for their initial bonding characteristics makes up but one portion of adhesive testing. Testing of adhesive bonds under sustained mechanical loads and aggressive environments (moisture, heat, salt spray, saline soaks, solvent soaks, etc) comprises a significant part of testing. Repeated cycling of adhesive bonds through three or more environments, with or without a sustained load, is widely used although there is not always as much a strong scientific basis for the design of such test regimens as there is an experience base that suggests that such tests are predictive. Impact and dynamic or fatigue testing of adhesive bonds have become important components of adhesive testing.

Classification of Adhesives

There are many ways to classify adhesives. These include chemical class, joint strength, bulk modulus, physical form, ultimate use, general market, method of application, and price. Another classification scheme involves considering the activation of an adhesive and the driving force for its change from a liquid-like system to a solid-like system. Each of these methods of classification provides a framework within which to understand adhesives.

The primary chemical classes from which adhesives are made include epoxies, acrylics, phenolics, urethanes, natural and synthetic elastomers, amino resins, silicones, polyesters, polyamides, aromatic polyheterocyclics, and the various natural products such as carbohydrates and their derivatives as well as plant- and animal-based proteins. Chemical class was once a relatively clean differentiator of adhesives, but so many adhesives now are hybrids, designed to take advantage of specific attributes of more than one chemical class or type of material. Hybridization can be accomplished by incorporating into an adhesive a nonreactive resin of a different chemical class; adding another type of reactive monomer, oligomer, or polymer; or chemically modifying an oligomer or polymer prior to adhesive compounding.

The measured overlap shear strength or peel strength of an adhesive joint is sometimes used to classify adhesives. The choice of substrate is a key element of such a comparison, certain aluminums or steels being most commonly chosen as standards, but glass, polyolefins, and other substrates are also used. Pressure-sensitive adhesives will be found at the low end of the bond strength spectrum, and structural adhesives will be found at the high end. In the middle will be found materials that are strong but not necessarily structural in nature; these are often called semistructural adhesives. Many sealants are strongly adherent, and some of these are referred to as adhesive sealants.

Market is a useful category for those interested in the buying and selling of adhesives, but market-based categories can be very broad. Construction adhesives, for example, include joint compound, carpet glues, ceramic and vinyl tile adhesives, a variety of wood-bonding adhesives, and double-sided foam tapes for hanging architectural glass. Although the adhesives used in some of these product categories are relatively standardized, there are many choices in other product categories. Similar breadth and depth would be encountered among adhesives used in the automotive, medical, and electronics industries. Within each of these market areas and most other market areas there will be found both commodity and specialty adhesives.

Most of those who develop adhesive compositions consider the form and ultimate use of an adhesive to be the most useful categories because these guide and direct adhesive development. The ability of the adhesive formulator to satisfy an end use will be very much related to the completeness of the information available concerning performance attributes required or expected. Price is a category of immense interest to the adhesive developer as it helps to define the raw materials from which the formulator may choose. The adhesive development team often must work closely with the customer to learn what is really needed from an adhesive.

Forms and Types of Adhesives

As supplied, adhesives can be found in the form of low viscosity liquids, viscous pastes, thin or thick films, semisolids, or solids. Before application to a substrate, an adhesive need not be sticky or otherwise particularly adherent. A distinct exception is the pressure-sensitive adhesive (PSA), which is inherently tacky when first made. Such an adhesive is applied as a thin film with or without a backing, the combination of the adhesive and the backing defining an adhesive tape. The PSA remains throughout its useful lifetime essentially the same material it was when first made. All other forms and types of adhesives undergo a transformation which is central to their function as an adhesive. This transformation is usually carried out through imposition of time, heat, or radiation, either actively or passively.

By loss of liquid, an adhesive applied as a true solution or a dispersion of solids will dry through loss of water or another solvent, leaving behind a film of adhesive. A reactive adhesive system will form internal chemical bonds through the process of cross-linking, chemical reaction that joins dissimilar long-chain molecules, or polymerization, chemical reaction that joins similar monomer units. Solid adhesives are heated in order to be applied and then on cooling become functional adhesives. The transformation from a liquid, paste, or semi-solid to a functional adhesive is loosely termed *curing*. Additional general terms that refer to this transformation include *setting up* and *hardening*. Adhesives may also cure in stages. The first stage of curing is sometimes referred to as the B stage, and adhesives which have undergone some level of precure in their manufacture are often said to have been *B-staged*. For many adhesive applications, the ability of an adhesive to gel, precure, or develop green strength or handling strength is a key characteristic, being most important for parts which will be bonded and then transported to the next step in their processing. *Adhesives* are referred to as such before and after cure.

Pressure-Sensitive Adhesives. Pressure-sensitive adhesives (PSAs) are inherently and permanently soft, sticky materials that exhibit instant adhesion or tack with very little pressure to surfaces to which they are applied. The level of adhesion may build with time and be surprisingly high. PSAs generally have a high cohesive strength and often can be removed from substrates without leaving a residue. Some applications take advantage of a PSA's ability to quickly form a strong bond and under stress, force failure elsewhere in a system, an attribute used to advantage in tamper-proof packaging and price stickers. At the other end of the spectrum lie PSAs that can be repeatedly repositioned. The primary characteristics used to describe the performance of PSAs are tack, adhesion strength in peel, and resistance to shear forces.

PSAs can be sold in bulk or solution for later coating by product manufacturers. Most PSAs, however, are sold as components of tapes or labels. PSAs are also used to make protective or masking films, some of which also function as conventional tape products. PSAs are sold in the form of aerosol sprays for graphic arts work. Tape products join one object to another, as when one wraps a gift, seals a box, or puts up a notice. They consist of a film or web carrier coated on one or both sides with a PSA. The carrier is usually a paper or synthetic polymer

made in the form of a solid or a foamed film. It is a key component of the tape. Such a construction is usually slit and wrapped on itself to form rolls of adhesive tape from which sections of the desired length can be removed. A release coating is sometimes added to the backside of the tape backing so that the tape can be removed from the roll cleanly, easily, and quietly without splitting the adhesive from the backing. Double-sided tapes that have no release liner effect release through opposite pairing of chemically different adhesives which are chemically incompatible or through use of adhesives of different levels of cross-linking which are physically incompatible. There also may be a primer on one or both sides of the tape carrier to ensure better adhesion of the PSA or the release coating. Some tapes are sold with release liners that must be removed after the tape is taken off its roll. Tapes can be applied manually or via mechanized tape dispensers for packaging, splicing, and other applications. Labels are sold with the PSA already present for their attachment to a variety of surfaces. Transfer tapes are PSAs that are provided on a liner from which the adhesive film can be transferred to another surface. PSAs that are effectively sticky hot-melt adhesives can be applied in discrete lines, dots, or other shapes using manual and automated equipment. The convenience and adaptability of PSAs has gained them wide use in diverse applications in virtually every market served by adhesives.

Many PSA compositions contain a base elastomeric resin and a tackifier, which enhances the ability of the adhesive to instantly bond as well as its bond strength. The elastomer may be useful without cross-linking but will often require either chemical or physical cross-linking for establishment of sufficient cohesive strength. Heat or uv or radiation is usually the activator of the cross-linking, and suitable catalysts are used, their choice depending on the base resin. Small amounts of epoxy or hydroxy functionality are sometimes added to allow uv cures if the base resins are not themselves uv-curable. Electron beam curing has received attention but tends to be more costly than uv curing. Elastomers used as the primary or base resin in tackified multicomponent PSAs include natural rubber, polybutadiene, polyorganosiloxanes, styrene-butadiene rubber, carboxylated styrene-butadiene rubber, polyisobutylene, butyl rubber, halogenated butyl rubber, and block polymers based on styrene with isoprene, butadiene, ethylene-propylene, or ethylene-butylene. Any of these resins may be blended with each other to alter or optimize properties. Polychloroprene, *cis*-polyisoprene, and some waxes are rarely used as the main components in PSAs but have found some use as modifiers. Natural rubber grafted with methyl methacrylate, styrene-acrylonitrile copolymers, and other elastomers have been found useful as components of primers for PSA products. Polymers which can be useful as PSAs without tackification but may be modified beneficially with their addition include poly(alkyl acrylate) homopolymers and copolymers, polyvinylethers, and amorphous polyolefins. Comonomers useful for acrylate PSAs include acrylic acid, methacrylic acid, lauryl acrylate, and itaconic acid.

Much of the art of making PSAs rests in the choice of tackifier and the balance between base resins and tackifiers, of which there are numerous choices (19). Tackifiers commonly used with natural rubber, butyl rubber, and polyacrylates include rosins and rosin derivatives manufactured from pine tree gums. The styrenic block polymer base resins respond well to tackification with aliphatic and

partially aromatic materials miscible with their continuous nonstyrenic phase or phases. Materials useful as PSA tackifiers have a lower molecular weight than the base resin. They are useful because they lower the modulus of the bulk adhesive in the rubbery region of the modulus–temperature spectrum, that is, above the glass-transition temperature. Tackifiers also tend to raise the glass-transition temperature of the system. Tackifiers which react with PSA resins have been introduced to counteract tendencies of tackifiers to migrate, bloom, or volatilize; these kinds of tackifiers are based on isocyanato-reactive or vinyl functional groups (20). Plasticizers are mentioned somewhat synonymously with tackifiers as modifiers for PSAs, but their use is recommended cautiously as any improvements they provide in tack can be quickly offset by losses in strength if the glass-transition temperature of the material is lowered too much.

Silicone PSAs are blends or reaction products of the combination of a poly-organosiloxane, such as poly(dimethyl siloxane) or its copolymers with diphenylsiloxane or methylphenyl siloxane, with a polysiloxane resin, which is largely inorganic. Pendant vinyl groups may also be incorporated into silicone PSAs, making cross-linking possible with peroxide and other kinds of cures. These kinds of PSAs are most often tackified with additional silicone gums and siloxane resins of varying molecular weight. The silicone PSAs are unique in their resistance of temperatures up to 400°C; performance at elevated temperatures can be optimized using the siloxane resins and rare earth or transition-metal esters (21) (see PRESSURE SENSITIVE ADHESIVES).

The large bulk of PSAs are coated onto continuous webs or films to make pressure-sensitive tapes, labels, and so on. While many PSAs continue to be coated out of organic solvents, many have been converted to water-based formulations or are extruded as hot-melt adhesives, which upon cooling retain their tack. Aqueous emulsions of carboxylated styrene–butadiene and various acrylate copolymers are among the most useful as bases for water-based PSAs. The complexity of latex chemistry introduces additives such as chain-transfer agents and defoamers (22) into some emulsion-based PSAs. Proper coating of these kinds of PSAs can require addition of thickening agents based on water-soluble polymers. Other additives that may be found in PSAs include cross-linking agents, catalysts, heat stabilizers, antioxidants, photoinitiators, depolymerizers (or peptizers), and various fillers. Reinforcing agents such as phenolics and higher molecular weight relatives of the tackifiers are sometimes added to improve cohesive strength. As made, PSAs are generally colorless or off-white in appearance but are sometimes pigmented for color adjustment or become pigmented through addition of a colored filler such as titanium dioxide, talc, or silver.

Hot-Melt Adhesives. Hot-melt adhesives are solid adhesives that are heated to a molten liquid state for application to substrates, applied hot, and then cooled, quickly setting up a bond. The largest uses of hot-melt adhesives are in packaging, bookbinding, disposable paper products, wood bonding, shoemaking, and textile binding. The advantages of hot-melt adhesives include their easy handling in solid form, almost indefinite shelf life, generally nonvolatile nature, and, most importantly, ability to form bonds quickly without supplementary processing. They are considered friendly to the environment and are expected to see expanded use on a worldwide basis as the market continues to move away from

solvent-based adhesives. The disadvantages of hot-melts lie in their tendency to damage substrates which cannot withstand their application temperatures, limited high temperature properties, and only moderate strength.

Application temperatures typically used for hot-melts range from about 65–220°C. Although the industry still refers to most temperature-sensitive adhesives as hot-melts, one will see references to warm-melt adhesives that soften at about 121°C and cool-melt adhesives that soften below about 100°C, but these terms are somewhat arbitrarily applied. Decreases in the application temperatures for hot-melts have lessened safety concerns associated with this type of adhesive. While most hot-melts are supplied as sticks or pellets, they are also produced as flat films or sheets, rolls, fibrous nonwovens, powders, strings, bulk masses, or dots or lines on liners.

Hot-melts generally are based on one or more thermoplastic resins. The largest portion of commercial hot-melt adhesives has for many years been based on ethylene–vinyl acetate copolymers having a vinyl acetate content of about 20–40%. The styrenic block polymers which are thermoplastic elastomers also make up a large portion of hot-melts. Other resins that have been found useful as bases for hot-melts are synthetic elastomers, ethylene–ethyl acrylate copolymers, amorphous polyolefins, branched polyethylenes, polypropylene, polybutene-1, phenoxy resins, polyamides, polyesters, and polyurethanes. Combinations of these resins allows for property and cost adjustments. Tackifiers and plasticizers are commonly added to hot-melts to improve their flow and adhesion to substrates. Examples include synthetic hydrocarbons, natural terpenes, rosins, and various phthalates. Polybutene is occasionally used as the base resin for hot-melts having good cold flow and high wet-out characteristics, but it may also be used as a flexibilizer or plasticizer. Waxes are important hot-melt ingredients, lowering melt viscosity and improving wet out of the substrate. Reactive tackifiers exist to address migration. The polyamide, polyester, and polyurethane hot-melts are often classed separately from the other resins on which hot-melts are based. All are the result of condensation reactions, and they are frequently used with few additives, their properties instead being adjusted by changing the starting ingredients of the polymers. They may, however, contain additives that make them better suited to specific uses. Adhesives based on these polymers are considered to deliver higher performance by virtue of better high temperature resistance and higher strength and may provide better adhesion to polar substrates than the other largely hydrocarbon hot-melt adhesives (23).

Conventional hot-melt adhesives cool to set and do not chemically cross-link. Such systems have an open time of a few seconds to a few minutes. The need for more heat-stable adhesives and stronger bond strengths has driven the development of reactive hot-melts which undergo cross-linking. These are primarily based on polyurethane hot-melts with residual isocyanate groups that react with water after application to form a thermoset adhesive material. Water is provided by the surrounding air and substrate. Cure of these hot-melts is nearly complete within 24 h, but time for full cure will depend on temperature and ambient and substrate moisture content. An extension of the water-activated isocyanate cross-linking reaction is found in the use of polyurethanes which have been silylated to provide active hydrogens for reaction with residual isocyanates in polyurethanes (24). The acceptance of reactive polyurethane hot-melts has led to development

of reactive block polymer and acrylate hot-melts which rely on radiation cure through activation of epoxy or vinyl groups (25,26); these are used primarily as PSAs.

Hot-melt adhesives are usually clear, off-white, white, or amber. Colored versions are available for nonbonding decorative use, for example, arts and crafts. Good color retention with heat aging is an important feature of a heat-stable hot-melt system, and antioxidants and heat-stabilizers are common ingredients in hot-melt adhesives. Photoinitiators are frequently present when uv or other radiation curing will be used. Other useful additives include fillers and reinforcing agents. When there is some lack of cohesiveness in blends of base resins, compatibilizers may be used to improve the apparent miscibility of these resins (27). Hot-melts can be based on either amorphous or semicrystalline resins. Particularly in the case of semicrystalline resins, the rate of cooling can dramatically affect adhesion to a substrate (28). To control the development of crystallinity, nucleating agents may be added to formulations based on crystallizable polymers such as polyesters.

Solution Adhesives. Adhesives delivered out of solutions are typically used for joining large areas destined for nonstructural or semistructural service. The solution may be made with an organic solvent or with water or may be an aqueous dispersion. It is important that the liquid carrier have some means of escaping from the bondline in order for the proper bond strength to develop. It should be appreciated that many PSAs are made by casting out of liquids, but when put into use as components of tapes or labels, these adhesives are soft solids containing virtually no liquid.

Solvent-Based Solution Adhesives. Contact adhesives, activatable dry-film adhesives, and solvent-weld adhesives make up the solvent-based adhesives. Contact adhesives are solutions of high polymers which are applied to all surfaces to be joined via spray or brush, allowed to dry partially, and then given time under pressure to allow the adhesive layers to fuse. Heat is sometimes used to increase tack or accelerate drying. These adhesives are commonly used to join wood veneers to wood bases, synthetic laminates to particleboard countertops, and paper products to other materials. The major dry-film adhesive is solvent-applied natural rubber, which is unique in its ability to adhere to itself without tackification and useful for self-sealing envelopes and similar employment. After being coated on to paper or another substrate, dry-film adhesives must be wiped or sprayed with a liquid to regain their adhesiveness; the activating liquid now is nearly always water. Solvent-weld adhesives are used to join plastic parts such as PVC piping. The adhesive is usually a solution of PVC or chlorinated PVC that is applied to the outer surface of the pipe and the inner surface of a connector piece that are joined firmly together before the solvent has evaporated.

The most widely used contact adhesive is a solution of polychloroprene or modified polychloroprene in solvent blends of aromatic hydrocarbons, aliphatic hydrocarbons, esters, or ketones, for example, toluene–hexane–acetone. Viscosity, dry time needed before bonding, bond strength, and price are affected by the solvent. Using various combinations of the isomeric forms of polymerized 2-chlorobutadiene permits a fine-tuning of the crystallization rate of the dissolved polymer as the solvent evaporates. The polychloroprene may also be modified by the incorporation of methacrylic acid or mercaptans. Metal oxides (MgO

and ZnO) that scavenge acids are often part of polychloroprene adhesives and also may act as cross-linking agents. Oxygen scavengers such as butylated hydroxytoluene (BHT) [128-37-0] or naphthylamines [25168-10-9] are added to prevent dehydrochlorination. To build initial handling strength, the solvent-based polychloroprene contact adhesives may be modified with alkyl phenolics, terpene phenolics, or phenolic-modified rosin esters, the first of these being the most effective and least deleterious (29). Chlorinated rubbers are sometimes added to these adhesives to improve their adhesion to plasticized PVC and other plastics. Added just before adhesive application, isocyanates are useful in modification of polychloroprene contact adhesives, reacting perhaps through hydrolysis of the pendant allylic groups present from the small number of 1,2 isomeric segments (30). The remainder of the solvent-based contact adhesives are comprised of polyurethane, SBR, styrene-butadiene-styrene block polymers, butadiene-acrylonitrile rubber, natural rubber, or various acrylic or vinyl resins in suitable solvents.

Water-Based Solution Adhesives. Solution adhesives based on water dispersions and aqueous emulsions are steadily gaining in use largely at the expense of solvent-based adhesives. These are rarely true solutions, with the exception of the viscosity modifiers often used to adjust flow characteristics. Dispersions of polyurethanes in water find use in bonding of plastic sheets and films, cloth, shoe parts, foams, PVC veneers, and carpets. Other water-dispersible resins can be added to the polyurethane dispersion to lower costs and modify performance characteristics. The largest group of water-dispersed or water-dissolved adhesives are made of natural products, which are covered separately. At one time, vegetable gums were used widely as water-activatable adhesives, but poly(vinyl alcohol) has replaced them in envelope sealing and similar areas.

Poly(vinyl acetate) emulsions, the basis of the ubiquitous household white glues, are among the most familiar water-based adhesives. These are widely used for paper and wood bonding. They contain a substantial percentage of vinyl alcohol content, formed via partial hydrolysis from the vinyl acetate homopolymer as vinyl alcohol itself is not a stable molecule. Such latices are stabilized through the use of surfactants, one choice being well-hydrolyzed poly(vinyl acetate). After application to the substrate, latex adhesives cure by the evaporation of water accompanied by the coalescence of the latex particles. On the porous substrates with which these are most frequently used, the water exits the bondline through the substrate as well as the adhesive, preventing voiding or foaming which might weaken the bond. Subtle changes in properties can be engineered through the use of other comonomers or the use of liquid plasticizers. Glyoxal [107-22-2] or other cross-linking agents can be added to poly(vinyl acetate) latex adhesives to combat creep (31).

Polychloroprene latex adhesives have been available for many years. They are stable at pH values between about 10 and 12. The latex particles are usually lightly cross-linked. Except for the substitution of water for the organic solvent, the ingredients in these kinds of adhesives are similar to those found in their solvent-based counterparts. Terpene-phenolics are particularly effective as tackifiers for contact adhesives based on polychloroprene latices but rosin acids, rosin esters, hydrocarbons, and coumarone-indenes are also useful, particularly where heat-assisted bonding is not possible. Dehydrochlorination leading

to acid generation is particularly possible with the water-based polychloroprene adhesives. Like other water-based adhesives, these may require addition of biocides or preservatives to prevent the breeding of microorganisms (32).

Structural Adhesives. Structural adhesives are designed to bond structural materials. Nearly any adhesive giving shear strengths in excess of about 7 MPa (about 1000 psi) may be called a structural adhesive. Structural adhesives are generally the first choice when bonding metal, wood, and high strength composites to construct a load-bearing structure. Bonds formed with structural adhesives cannot be reversed without damaging one or the other substrate. They are the only kind of adhesive that might be expected to be able to sustain a significant percentage of its initial failure load in a hot and humid or hot and dry environment. Any one of these descriptors names structural adhesives the strongest and most permanent type of adhesive. For good reason, they are sometimes referred to as engineering adhesives. The strength and permanence of structural adhesives is largely achieved using reactive adhesives, a term which has become something of a synonym for structural adhesives. Epoxies are the most widely used class of structural adhesive chemistry, but acrylates, urethanes, phenolics, and other classes have been used to great advantage, and the combination of these different chemical classes to create hybrid adhesives propagates the best virtues of each. Reactive adhesive systems which are arguably not always considered structural adhesives but are conveniently grouped here are also reviewed in this section.

Epoxy Resins. Epoxy resins have a long and distinguished record as structural adhesives. Their use dates to 1950 or earlier, and their utility for adhesives was recognized upon their development. Most epoxy adhesives are resins based on what is commonly known as the diglycidyl ether of bisphenol A (DGEBA). These resins are based on the reaction of 4,4'-isopropylidene diphenol (bisphenol A) [80-05-7], $C_{15}H_{16}O_2$, and epichlorohydrin [106-89-8], C_3H_5ClO . The molecular weight of the commercial difunctional resins formed by this reaction will vary with the molar ratio of the reactants. At a molecular weight of about 400 or less, these resins are viscous liquids which are immensely useful in epoxy adhesives. Commercially viable solid resins based on DGEBA have molecular weights ranging up to about 4000. Many epoxy adhesives will also contain a small amount of an epoxy diluent having low viscosity and a more flexible structure; this resin adjusts the flow of the system and also helps to wet out the fillers that are usually present.

A wide variety of epoxy resins are commercially available: monofunctional or polyfunctional, aliphatic, cyclic, or aromatic. Brominated epoxies may be useful where flammability is a concern. An oxirane functionality is all that is needed to make an epoxy resin, and structural adhesives are only one of over a dozen different uses for epoxy resins. Many epoxy resins on the market will not necessarily be suitable for adhesives, but their availability does expand the choices available for adhesive formulators. The specialty epoxy resins developed specifically for adhesive use sometimes will be more costly than the DGEBA resins but may provide the basis for a specialty adhesive that can meet a unique need and therefore command a proportionally higher price. Examples of these are epoxy-functional dimer acids, urethanes, and various elastomers.

Epoxy resins based on DGEBA usually are quite stable at temperatures up to 200°C. Curing agents, sometimes called hardeners, must be added to the epoxy so as to cause cross-linking and chain extension to occur and a bond to form. Certain types of curing agents will be favored over others for each of the three types of epoxy structural adhesives: one-part (1K) epoxy paste adhesives, 2K epoxy paste adhesives, and 1K epoxy film adhesives. The strained oxirane ring is reactive with functional groups having either nucleophilic (basic) or electrophilic (acidic) character. Acid anhydrides, carboxylic groups, and hydroxyl groups react very slowly with the oxirane ring and are usually used with catalysts that accelerate their reaction with epoxies. Those groups which readily react without catalysts but often benefit from their use include amines and mercaptans. Both the epoxy resin and the curative package (curing agent plus catalyst) will influence final cure speed.

One-part (1K) paste adhesives usually consist of a DGEBA resin, a reactive diluent, and latent curing agents that are insoluble with the resin at room temperature but dissolve at elevated temperatures to trigger cure. These kinds of adhesives are in use in the aerospace, automotive, and electronics industries. Dicyanodiamide or dicyandiamide [461-58-5], $C_2H_4N_4$, is the most frequently mentioned latent curing agent for cures occurring in the range of 170–180°C; practitioners refer to this material as *dicy*. Also useful in this range are metal-complexed imidazoles, complexes of Lewis acids (eg, boron trifluoride with amines), and diaminodiphenylsulfone. Cure temperature can be lowered by using micronized dicyanodiamide ground to a particle size of 5–15 μm . Cure can be accelerated by use of aromatic tertiary amines, imidazole derivatives, and epoxy resin adducts with tertiary and other amines. Substituted ureas such as Monuron [150-68-5], $C_9H_{11}ClN_2O$, and nonchlorinated substituted ureas such as 3-phenyl-1,1-dimethylurea [101-42-8], $C_9H_{12}N_2O$, have also found use as accelerators in 1K epoxy adhesives. Dihydrazides offer a range of melting points depending on structure, their cure temperatures with epoxies beginning as low as 100–110°C. Adducts of dicyanodiamide which melt at temperatures in the 115–120°C range are available. Accelerated 1K epoxies show faster cures once heated but suffer from decreased shelf lives; after manufacture, they are usually stored in refrigerators or preferably freezers although this is usually impractical for drum quantities. For these same reasons, their manufacture is carried out at temperatures well below their activation temperatures and at low shear rates to avoid viscous heating.

The low viscosity two-part (2K) epoxy adhesives sold in hardware stores as 5-min epoxies are based on cure with polymercaptans regulated with amines to control worklife. The human nose can sense some mercaptans in air at the ppb level, making them valuable as gas odorants, but they are tremendously useful as curing agents, particularly when used in thin films as for adhesives. Their low toxicity is also an advantage. Capcure 3-800 [101359-87-9] is a commonly found polymercaptan. Low odor polymercaptans have been developed which combine strategies of odor masking, odor counteracting, and absorbency to stabilize polymercaptans, reducing the level of odor by about 75% (33). Higher molecular weight versions of the polymercaptans are useful as the base resins of polysulfide sealants, which are sometimes categorized as adhesives. In full formulation, the

polysulfide base resins are blended with curing agents such as manganese dioxide or sodium perborate, accelerators or retarders, fillers, plasticizers, thixotropes, adhesion promoters, and pigments (34). These materials are used primarily in the construction and aerospace industries.

Many useful 2K epoxies utilize curing agents that are the reaction products of amines of low molecular weight with fatty acids. These are variously known as polyamidoamines, polyamides, and amidoamines and sold in a range of molecular weights under trade names such as Versamid and Ancamide. The fatty acid portion of these amines gives them larger bulk than the lower molecular weight amine curing agents, which facilitates formulation of adhesives having mix ratios closer to 1:1 by volume, which is of benefit for both packaging and off-ratio tolerance. Curing with polyamidoamines generally produces relatively flexible adhesives having good chemical resistance. Because they typically cure slowly, they are frequently used in combination with other amines such as diethylenetriamine (DETA), triethylenetriamine (TETA), tetraethylenepentamine, aminoethylpiperazine, modified imidazolines, and oligomeric amine-terminated polyethers. Some of the amines in this group are used as sole curing agents, and others, such as DETA and TETA, are used as epoxy adducts to reduce toxicity and increase stability. Aromatic amines, although useful for epoxy resin composite matrices, find little use in epoxy adhesives.

Another family of curing agents is based on substituted phenols such as tris(dimethylamino)phenol [31194-38-4], $C_{12}H_{21}N_3O$, and tris[(dimethylamino)methyl]phenol [90-72-2], $C_{15}H_{27}N_3O$. These tertiary amines can produce rather brittle adhesives if used as sole curing agents, but are valuable as accelerators for other amines. They act as catalysts for dicarboxylic acid anhydride cures. Amines are also useful as accelerators for the oxirane-alcohol reaction, which is sluggish at room temperature but with catalysis will proceed above 120°C. Imidazoles are also generally useful as catalysts or cocuring accelerators for epoxy reactions with amines, hydroxyls, and thiols. Organic and inorganic salts sometimes find use in epoxy adhesives, coatings, and encapsulating compounds. Acid catalysts such as boron trifluoride-amine complexes find some use in epoxy adhesives but tend to require long cures, even at elevated temperatures, which normally works against their use in adhesives. Epoxy resins react slowly with acid anhydride curing agents but can be accelerated with acids or bases, imidazoles being used most often; however, anhydrides are not often used as curing agents in epoxy adhesives.

Epoxy film adhesives are 1K adhesives in film form. They are formulated much like 1K paste adhesives but often contain solid epoxy resins and additional resins that provide binding properties. These may be partially cured (B-staged) to provide a more dimensionally stable film. Epoxy film adhesives have been widely used in the aerospace industry where their relative stability accommodates the long build times needed for aircraft manufacture. Their cured properties can be outstanding in terms of strength, toughness, and durability. They can be supplied in film form and cut to size or provided as tapes in convenient slit widths. They may be made to be tacky using rubber resins and other mild tackifiers or they may be dry. Film adhesives of a more aggressive pressure-sensitive character have been developed by coating or laminating with pressure-sensitive formulations or

formulating such that the bulk adhesive (35) is a PSA in its own right but can be cured to a semistructural or structural strength. Epoxy film adhesives based on thermoplastic polyamide resins are very tough when cured but can be susceptible to moisture absorption.

In addition to resins and curing agents, epoxy adhesives will contain many functional additives and modifiers. Flexibilizers and tougheners such as polysulfides, epoxidized fatty acids, epoxidized polybutadiene, and amine- and carboxy-terminated acrylonitrile butadiene polymers react with the epoxy network. Flexibilizers remain in phase with the epoxy while tougheners typically phase separate to form domains, the result producing a tougher adhesive with more or less strength reduction relative to an unmodified system. Particulate tougheners may also be added to epoxy adhesives. These include core-shell resins, functionalized elastomeric particles, and ground reclaimed rubber. Positive aspects of structural adhesives based on epoxy resins include good adhesion to many substrates, no emission of volatiles upon cure, low shrinkage, and a broad formulating range based on a history of use dating to the 1940s. The lack of outgassing allows most curing to be done at ambient pressure although clamping till cure is standard protocol for any adhesive bonding operation. Shrinkage can be further decreased with use of appropriate fillers, harder fillers by some reports providing the lowest shrinkage.

Acrylics. Historically, acrylics offer several useful characteristics as structural adhesives. Most well known is their relatively high speed of reaction via free-radical polymerization. The details of their reaction provide a useful division of the different classes of acrylic structural adhesives into redox-activated adhesives, encompassing both anaerobic acrylics and nonaerobic structural acrylics, and Polycyanoacrylates. These will be considered in turn.

Oxygen inhibits the polymerization of acrylic monomers to a useful extent, and its exclusion kicks off polymerization of monomeric acrylates. Early versions of anaerobic acrylics relied solely on this mode of initiation and polymerization, containing little besides acrylate monomers and diacrylic esters (36). Later it was found that if hydroperoxides were incorporated into the acrylic monomer, small amounts of free metal ions from metal substrates could help to create free radicals that initiated polymerization of the acrylate monomers. Only small amounts of metal ions are needed, iron, nickel, zinc, and copper being some of those of major industrial interest. Even though a major alloying element, for example, aluminum, may not be capable of helping to generate free radicals via the redox reaction, minor alloying elements, such as copper, may be available which can act in this capacity. The speed of reaction is limited by the ability of the metal ion to reduce the peroxide. Free-radical initiators used in anaerobic acrylics have included cumene hydroperoxide, *t*-butyl hydroperoxide, and potassium persulfate [7727-21-1], $K_2S_2O_8$. Other useful initiators for this cure are combinations of saccharin [81-07-2] with aromatic amines such as *N,N'*-diisopropyl-*p*-toluidine [24544-09-0] or 1-acetyl-2-phenylhydrazine [114-83-0]; such combinations were originally thought to be accelerators useful only with peroxide initiators until it was found that they were themselves initiators (37). Various accelerators can be used with initiators to hasten cure of these adhesives; classes of compounds useful as accelerators include cyclic peroxides, amine oxides, sulfonamides, and triazines (38).

A key ingredient in anaerobic acrylic adhesives is the acrylate monomer or monomers. These include primarily acrylic acid and methacrylic acid and their many and various esters such as lauryl acrylate, cyclohexyl methacrylate, methyl methacrylate, hydroxyalkyl methacrylates, and tetrahydrofurfuryl methacrylate. These monomers vary in their volatility, reactivity, and cost, the less volatile monomers forming the basis of low odor acrylic adhesives. In addition to the monomer acrylates, there generally is also present a diacrylate which acts as a cross-linker, the alkyl glycol dimethacrylates being widely used in this function. Other ingredients used in these adhesives include stabilizers or polymerization inhibitors such as phenols or quinones, chelating agents that snatch up trace metals to prolong shelf life, and various modifiers such as inert fillers, inorganic and polymeric thickeners, elastomers to improve toughness, and bismaleimides that improve high temperature performance (39).

The low viscosities and good wetting properties of these adhesives allow them to penetrate and flow in tight spaces. This is taken advantage of in many of their uses. Threadlocking and sealing are primary applications. When applied to the threads of bolts or pipes, to flanges, and to other tight-fitting machine parts which are later screwed into or pressed against a mating surface, the adhesive cures because of the exclusion of air and the formation of free radicals via the reaction of metal ions with the initiator. Other applications include bonding of optical fibers, impregnation of porous parts, crimp-bonding of electrical parts, and fastening of press-fit parts. Anaerobic adhesives are one-part adhesives, usually packaged in small oxygen-permeable plastic containers which have not been entirely filled, this arrangement providing a sufficient supply polymerization-inhibiting oxygen to ensure good shelf life.

The non-aerobic structural acrylic adhesives are two-part adhesive systems. They are generally less oxygen-inhibited than the non-aerobic acrylics and do not rely on metal surface activation in the same way as the anaerobics. These adhesives are very similar in formulation to the non-aerobics, each borrowing technology from the other as it has developed. Lower oxygen sensitivity is accomplished through higher concentrations of accelerators and initiators. The accelerators and initiators are usually redox couples such as the commonly used hydroperoxide/amine-aldehyde condensates (oxidant/reductant), which react to form alkoxy radicals. The most widely used condensate is a polymeric resin [9003-37-6]. Produced by reaction of *n*-butyraldehyde [123-72-8] with aniline [62-53-3]. This material has a complex structure, the major component and active ingredient apparently being dihydropyridine [27790-75-6] (40). Another common redox couple is based on hydroperoxide coupled with an alkyl aromatic amine such as *N,N*-dimethylaniline [121-69-7]. A number of 2K acrylic formulations include metals, metal oxides, or metal salts (41).

The 2K non-aerobic acrylic adhesives can be used in any of three ways. The first is as a no-mix two-part, the use of which involves applying a thin layer of accelerator (in dilute solution) to one mating surface, flashing off the solvent, applying the adhesive to the second mating surface, and joining the two surfaces. It is perhaps a poor choice of terms, but the accelerator contains the initiator (eg, peroxide) or may contain a redox couple. As long as the bondline thickness is no more than about 500 μm (0.020 in.) for one-side activation or about 1000 μm for two-side activation, cure is expected to be adequate. 2K acrylics which

are meant to be mixed before application utilize a different kind of accelerator that contains the catalyst system in a carrier resin such as an epoxy and perhaps a diluent. These can be used in a fashion similar to the no-mix adhesives, but this approach may not produce optimal properties. Typically, the 2K acrylics are made by mixing the accelerator into the one-part acrylics and immediately applying this mixture to the substrate. Volume mix ratios will range from about 2:1 to about 20:1. Additional ingredients commonly found in these compositions include various elastomeric polymeric tougheners such as chlorosulfonated polyethylene, butadiene–acrylonitrile elastomers, and polyurethane acrylates. These tougheners are usually incorporated into the adhesives by dissolution in the acrylic monomers, creating adhesives sometimes referred to as second-generation acrylics. Their development by DuPont (42) and others marked the entry of acrylic structural adhesives into a large number of new applications.

Because of their high reactivity, these 2K acrylic adhesives are used in many situations where fast ambient cure is important. Since the incorporation of the redox couple catalysts, acrylic adhesives have advanced their use on metals as well as plastics, woods, and ceramic substrates. As a class, they tend to be fairly accommodating of oily metal and unprepared plastics and composites. Offensive odors often accompany the common forms that use the less expensive lower alkyl acrylates. Colors of these materials are clear, off-white, white, and amber. They are not often intentionally pigmented, although they may be tinted by functional metal additives or aluminum powders.

A very important class of acrylic adhesives, the cyanoacrylates are distinguished by their relative simplicity of formulation and their nearly instant bonding properties. The name recognition of “super glue” surpasses that of nearly any commercial adhesive though it is now known by a variety of other ungenericized trademarks. First discovered in the 1940s during World War II, cyanoacrylates were rediscovered and first truly appreciated in the 1950s and brought to the market in 1958. Then as now they were largely based on ethyl and methyl cyanoacrylate. Other monomers of interest have been the isopropyl, butyl, allyl, ethoxyethyl, methoxyethyl, methoxypropyl, and fluoroalkyl esters (see POLYCYANOACRYLATES).

Cyanoacrylate adhesives cure by polymerizing anionically. They are catalyzed by mild nucleophiles (bases), such as an OH^- ion, which can readily be found in small quantities on many surfaces. Strong acids, found in many woods and acid-treated metals, can inhibit polymerization. As long as the adhesive film thickness is as low as possible, that is, practically zero, sufficient catalyst provided by the substrate will be available, hence the usual directive to apply the adhesive sparingly and to avoid using it as a void filler or to bond porous surfaces. Bond thicknesses higher than about $13\ \mu\text{m}$ (0.005 in.) are not recommended unless appropriate surface activators are used. As the conversion to a cured adhesive is a polymerization, it passes through and is subject to the same stages as any addition polymerization: initiation, propagation, chain transfer, and chain termination. Like the anaerobic adhesives, these adhesives are conveniently initiated by coating onto surfaces suitable initiators such as alcohols, epoxides, various amines, caffeine, and other heterocyclic compounds (43). Compositions may also incorporate accelerators as well as inhibitors, the latter usually being either phenolics designed to inhibit premature polymerization because of heat or

light or anionic polymerization inhibitors consisting of sulfur dioxide, other acid gases, or complexes of sulfur dioxide with organic or inorganic compounds. Normally quite brittle, cyanoacrylate adhesives can be flexibilized using monomers having longer alkyl side chains (2-octyl cyanoacrylate) or by incorporating plasticizers such as acetyl tributyl citrate (44). Various approaches have been taken to toughening the cyanoacrylates (45). As uncross-linked thermoplastic adhesives, the cyanoacrylates begin to soften and flow at about 80°C and will also depolymerize. Their durability in hot moist environments is considered to be poor, especially on metals. This has been addressed through introduction of difunctional or bifunctional cross-linkers, addition of heat-resistant adhesion promoters, and various other strategies aimed at improving moisture resistance. The last important component of the cyanoacrylate adhesive is the thickener, which is usually polymeric in nature.

Cyanoacrylates have long been known to be effective adhesives for human skin and other soft human tissues. They are effective when used for sutureless wound closures and hemorrhage prevention, the butyl cyanoacrylate being most widely used (46) based on a good balance between biodegradability and inflammatory response. Flexibilizers as well as aids to biodegradation are added to make these more suitable for tissue bonding. In everyday use, the outstanding capability of cyanoacrylate adhesives to instantly bond human skin is seen as a negative feature. Skin-adhesion inhibitors that have been found useful include alkanols, carboxylic acid esters (47), and copolymers of maleic acid, vinyl chloride, and vinyl acetate (48). These slow the adhesive's reaction rates against human skin or at least lower adhesion to it.

Urethanes. The core of a urethane adhesive is an isocyanate compound (see POLYURETHANES). Isocyanates react with a variety of functional groups having active hydrogens to generate a variety of linkages which give the resulting polymers their names. These include reaction with alcohols to form urethanes $[R-NH-CO-O-R']$, with amines to form ureas $[R-NH-CO-NH-R']$, with thiols to form thiocarbamates $[R-NH-CO-S-R']$, with amides to form acylureas $[R-NH-CO-N(R')-CO-R'']$, with urethanes to form allophanates $[R-NH-CO-N(R')-CO-O-R'']$, and with ureas to form biurets $[R-NH-CO-N(R')-CO-NH-R']$. Isocyanates can also react with water, generating carbon dioxide through the degradation of the unstable carbamic acid $[R-NH-COOH]$. This last reaction is the basis for the making of polyurethane foams. To a great extent, what is classified as urethane chemistry encompasses the entire chemistry available to isocyanates (see ISOCYANATE-DERIVED POLYMERS).

Most polyurethane structural adhesives are two-part systems based on the reactions of isocyanates and polyisocyanates with oligomers or polymers having at least two hydroxyl groups, which are generically referred to as diols or polyols. Although part of many earlier adhesive formulations, toluene diisocyanate (TDI) is now decreasing in use while use of diphenylmethane diisocyanate (MDI) is growing. Other common diisocyanates include 1,6-hexamethylene diisocyanate (HMDI or HDI) and isophorone diisocyanate (IPDI). Also available are the modified MDIs, multifunctional isocyanates often termed polyisocyanates, polymeric polyisocyanates, and isocyanate-capped oligomers which are often referred to as urethane prepolymers (49). Materials now available which have very low

monomeric isocyanate content are expected to bring about increased use of urethanes in adhesives (50). Hydroxyl-functional materials useful in urethane adhesives have molecular weights between about 500 and 3000 and functionalities between 2 and 3. The base oligomer is usually a polyester, polyether, polycarbonate, or polydiene such as polybutadiene. Cross-linked polyurethanes can be made with the use of trifunctional isocyanates and triols or through reactions of urethanes with urethanes, ureas, or isocyanates to yield the trimer isocyanurate.

In many cases, as polyurethanes are formed, long-chain and short-chain diols alternate along the chain to form segments which are either "soft" or "hard." On a microscope scale, the soft and hard segments coexist in a domain morphology characteristic of what are known as segmented polyurethanes. The very good impact and fatigue resistance of polyurethanes is attributed to this phase-separated microstructure. Because it is the integral component of the soft segment, the particular diol or polyol chosen will greatly influence the rubbery and impact-resistance properties of the polyurethane. Likewise, the isocyanate chosen will strongly influence the strength, modulus, and hardness of the polyurethane. The domain morphology of segmented polyurethanes is most pronounced for systems containing no chemical cross-linking. In contrast to most adhesive systems, low levels of cross-linking tend to degrade the properties of polyurethane adhesives because of disruption of the domain morphology.

Because isocyanates react with so many different organic functional groups and can also react with water, which is found nearly everywhere, catalysts are very important for the control of isocyanate reactions. Many of the catalysts used may push one reaction over another, but they do not necessarily entirely block unwanted reactions. Tertiary amines, principally bis(dimethylaminoethyl)ether, are frequently used to promote the isocyanate–water reaction, producing a blowing or foaming that generally would not be desirable for adhesives. Compounds that drive the isocyanate–hydroxyl action without substantially encouraging the isocyanate–water reaction include organometallic complexes such as dibutyltin dilaurate and stannous octoate. At temperatures higher than 100°C, urethanes and ureas will react with isocyanates to form the allophanates and biurets described previously, but above 130°C, these groups will decompose. Dimerization of isocyanates to form uretidiones is catalyzed by bases such as trialkylphosphines, pyridines, and tertiary amines. Formation of the trimer of isocyanates, isocyanurates, is favored through use of phosphines, amines, and various metal salts such as potassium acetate.

One-part urethane adhesives have been used for many years as high performance sealants. In this capacity they provide a useful combination of strength, flexibility, and elastic recovery. As adhesives, these systems have limited use unless formulated to overcome their inherent disadvantages. One-part polyurethane adhesives are typically moisture-cured and rely on a multistep reaction sequence as follows: isocyanate reacts with water to form carbamic acid, the unstable carbamic acid loses carbon dioxide and generates an amine, the amine reacts with additional isocyanate to form a urea, and the urea reacts with additional isocyanate to form a biuret, which includes a cross-link. Unless it diffuses out of the system, the CO₂ can cause foaming. Formulators learn to minimize the isocyanate content (%NCO) of a system in order to balance cure speed with foam control. Cure speeds—and foaming rates—of these systems decrease

from the outside in and vary with the amount of atmospheric moisture in the air, which changes hourly and seasonally.

A different kind of moisture-activated 1K urethane adhesive utilizes a moisture-activated curing agent such as oxazolidine (51). Oxazolidines are formed by dehydration and subsequent ring closure of aminoalcohols by aldehydes or ketones. When the presence of water causes that reaction to reverse, hydroxyl and amine groups are formed. These react readily and directly with isocyanates. Monooxazolidines are useful primarily as water scavengers, but bisoxazolidines can participate in the curing reactions of urethane adhesives.

More sophisticated 1K urethane adhesives use blocked isocyanates along with polyol curing agents. Useful blocking compounds include phenols, malonates, methylethylketoxime, and caprolactam. These react with isocyanates, but at high temperatures or in the presence of strong nucleophiles, the reaction reverses, freeing the isocyanate. Such systems do not rely on water for reaction, nor do they suffer from the detriments of CO₂ generation, but they do require heat for cure. Another approach to a stable 1K urethane is to use a solid polyol, such as pentaerythritol, that melts at elevated temperatures and then reacts with the isocyanate (52). Other schemes for 1K urethanes have been described (53).

As a class, urethane adhesives have somewhat poorer thermooxidative and moisture resistance than acrylic and epoxy structural adhesives. This has historically limited their expansion into certain areas of use. A 2K adhesive having the ability to survive automotive paint oven temperatures, which run as high as 205°C, uses polyols with high percentages of hydroxyl groups, an acrylonitrile-grafted triol, a phosphorus adhesion promoter, and a DABCO trimerization catalyst (54). 1K adhesives made with blocked isocyanates tend to be unable to withstand high temperatures because of volatility of the blocking agents, and other approaches are also unsatisfactory for high temperature stability. Use of micronized dicyanodiamide as a latent catalyst and curing agent for isocyanates has produced 1K urethane adhesives showing some capability to tolerate heating to well over 250°C while bonding well to fiber-reinforced plastic (FRP) (55). Sensitivity to hydrolysis has been another of the historic disadvantages of traditional urethane structural adhesives.

Two-part polyurethane adhesives will usually contain fillers and may contain pigments that facilitate visual qualitative off-ratio mixing detection. To increase cure speed, polyamines are sometimes added to the polyol curative, which also contains the catalysts. In addition to their primary ingredients, one-part moisture-curing urethane adhesives will typically contain fillers and perhaps pigments. Arguably the largest user of urethane structural adhesives is the transportation industry, which uses urethane structural adhesives for bonding of automotive parts made of sheet molding compound, FRP, and reinforced reaction injection molding composites and plastics. One-part urethanes are widely used for bonding of windshields to automotive vehicle frames. Although 1K urethanes are not conventionally considered to be structural in nature, automotive engineers hold that the windshield is part of the primary structure of the vehicle, conferring on these one-part urethanes the status of a structural adhesive. Wood bonding is another significant market for polyurethane structural adhesives.

As a group, polyurethane structural adhesives produce bond strengths on the lower end of the strength scale for structural adhesives, but their high flexibility, usually strong peel strength, and generally good impact and fatigue

resistance recommend their use when these characteristics are important. A variety of adhesives have been developed which incorporate polyurethanes into acrylic or epoxy structural adhesives (56–59). Inclusion is done through use of isocyanate-functional ingredients or polyurethanes end-capped with a nonisocyanato functional group. The broad reactivity of isocyanates offers many other options for hybridization.

Phenolics. Phenolic Resins were the basis of the first synthetic structural adhesives. They are formed by the reaction of phenol [108-95-2], C_6H_6O , and formaldehyde [50-00-0], CH_2O . There are two types of phenolic resins, resoles and novolaks (or novolacs), the former being comprised of methylol-terminated resins and the latter of phenol-terminated resins. Resoles result from use of basic reaction conditions and an excess of formaldehyde and will cure via self-condensation at 100–200°C with loss of water. Novolaks are produced using acidic reaction conditions and formaldehyde/phenol molar ratios of 0.5–0.8, and they require addition of a curing agent for cure. Hexamethylenetetramine [100-97-0], $C_6H_{12}N_4$, is a widely used novolak curing agent. Resoles and novolaks are sometimes referred to as one-step and two-step resins, respectively.

Formulators can choose from a variety of commercially available phenolic compounds, including, in addition to phenol itself, the isomers of cresol, the isomers of xylene, resorcinol, catechol, hydroquinone, bisphenol A, and various alkylphenols. Formaldehyde is usually used as the second major component, but acetaldehyde, furfuraldehyde, and paraformaldehyde (the polymer of formaldehyde) have been used sometimes alone and sometimes along with formaldehyde. The reactions of these various components are complex but have been elucidated by painstaking research (60).

Like epoxies, the phenolics are very brittle unless modified by tougheners. The first successful tougheners were poly(vinyl formal) resins which were added as a powder sprinkled over a layer of resole phenolic applied out of solution. These ReduxTM adhesives were the first toughened thermoset adhesives and were the basis of the first durable adhesive bonding technology for aerospace aluminum in the 1940s and 1950s. These were superseded in the 1960s by film adhesives formed from liquid phenolics filled with poly(vinyl formal) powders. Other tougheners followed: poly(vinyl butyral), nitrile rubbers, polyamides, acrylics, neoprenes, and urethanes. Epoxy–phenolics are important hybrid adhesives and offer an immensely useful combination of strength, toughness, durability, and heat resistance. Phenolic structural adhesives as a class of materials are highly resistant to most chemicals.

Phenolic adhesives are found as powders, liquids, pastes, and supported and unsupported films. Among the pastes, both 1K and 2K systems are available. Fillers are commonly used in paste adhesives. Support of film adhesives is provided by glass, cotton fabric, nylon, or polyester scrim. The novolaks are almost exclusively powders in pure form, but the resoles often are found as liquids. The resole systems are usually cured at temperatures exceeding 170°C. The condensation cure of the resole phenolics systems requires that they be cured under high pressures to minimize evolution of bubbles from water vapor. This is usually done in autoclaves or hot presses at pressures of about 200 to nearly 1400 kPa (29–203 psi) (61). Cure times range from 1 to 4 h depending on temperature. The cure conditions required for the resole phenolic adhesives have limited their use, and to a great extent they as well as the relatively brittle novolak phenolics have been

displaced by epoxies for aerospace aluminum bonding applications for which they were once the first choice. Nitrile–phenolic adhesives have a long history of use not only in aerospace applications but also in automotive applications such as the bonding of brake linings and the friction materials used in transmissions. Resole phenolic resin adhesives are widely used in the making of plywood and particleboard as both binders and for laminating of veneers; resorcinol is frequently used along with phenol or as the sole hydroxyl compound. In wood bonding, the porosity of the wood allows escape of the water vapor generated during curing of the adhesive and is believed to facilitate mechanical anchoring of the adhesive in the wood. Phenolics are also widely used as foundry resins for making sand-shell molds.

Urea–Formaldehyde and Related Adhesives. Urea–formaldehydes (UF) are the most significant members of the class of materials known as the Amino Resins or aminopolymers. These are the polymeric condensation products of the reaction of aldehydes with amines or amides. A molar excess of formaldehyde is used, and this along with the temperature and the pH dictate the properties of the final product. The initial reactions of urea and formaldehyde to form mono- and dimethylolureas can be catalyzed by either acids or bases, but the final condensation reactions will proceed only under acid conditions. These adhesives are widely used to make plywood and particleboard in processes utilizing heated hydraulic presses with multiple outlets for water vapor release. Temperatures up to 200°C may be used. UF adhesives in the first use contain hardeners composed of ammonium chloride or ammonium sulfate solutions or mixtures of urea and ammonium chloride plus fillers such as grain and wood flours. Particleboard adhesives, which are really binders, contain similar hardening agents, a worklife extender (ammonia solution), insecticides, wax emulsions, and fire-retarders. The slow hydrolysis of the methylenebisurea [13547-17-6], $\text{NH}_2\text{CONHCH}_2\text{NHCONH}_2$, has been linked to the slow release of formaldehyde from UF adhesives (62). The wood industry has been under increasing pressure to reduce and eliminate unreacted and evolved formaldehyde from these products and has made great efforts to do so. Melamine–formaldehyde (MF) and the less expensive melamine–urea–formaldehyde (MUF) resins are the bases of high performing wood-bonding adhesives. Their resistance to water is superior to that of the UF resins, but their higher cost has limited their use. The urea in the MUF resins decreases the cost of the MF resins. Uses of these are similar to those for the UF resins with the addition of paper-laminates for wood panels. Melamine reacts more easily with formaldehyde than does urea, making possible full methylation of melamine (63). Condensation of methylolated melamine with formaldehyde does occur under both acidic and slightly alkaline conditions, but acid catalysts or compounds generating acids are usually used in MF adhesives. Compounds such as acetoguanamine, ϵ -caprolactam, and *p*-toluenesulfonamide are often added to combat inherent brittleness and decrease stiffness. Ammonium salts are useful in making bulk wood products, but laminates can be adversely affected by these compounds; a complex of morpholine and *p*-toluenesulfonic acid is one hardener employed for this particular kind of MUF or MF adhesive. Defoamers and judicious amounts of release or wetting agents may also be used.

High Performance Adhesives. A number of adhesive needs exist which require resistance to very high temperatures and other environmental stressors such as certain gases, solvents, radiation, and mechanical loads. The upper

temperature limits of the most durable epoxy and phenolic adhesives lie between about 200 and 250°C. The aerospace industry requires adhesives that are resistant to temperatures of nearly 400°C for hundreds of hours or about 150°C for much longer times. Heterocyclic polymers such as polyimides and polyquinoxalines have been the basis of most heat-resistant adhesives. Microelectronics adhesives sometimes also must deal with high heat, but they must also conduct heat away from heat-sensitive parts. This has been the inevitable result of increasing miniaturization. Epoxies continue to be the basis of many microelectronics adhesives, but adhesives based on stiff-chained thermoplastic resins such as polyethersulfone and polyetheretherketone have made some inroads. Electrical conductivity is most commonly enhanced with silver flake or powder, but nickel, copper, and metal-coated metals are also being used in this function (64). Thermal conductivity is usually adjusted through incorporation of aluminum, aluminum nitride, or other metals or ceramics (65).

Adhesives made from Natural Products. The first adhesives developed by humans were based on naturally available materials such as bone, blood, milk, minerals, and vegetable matter. Beginning with the commercial development of Baekeland's phenolic resin adhesives by the General Bakelite Co. around 1910, synthetic adhesives began to replace natural product adhesives for existing applications. The use of adhesives by industry began to grow and diversify over the ensuing decades. In certain industries, among them furniture, food, book-binding, and textiles, adhesives based on natural products continue to be used to a significant extent. These adhesives can be divided into those based on proteins, carbohydrates, and natural rubbers or oils. Historically, *glue* is a term used to refer to adhesives made from animal matter or vegetable-based protein.

Protein-Based Adhesives. The protein sources for these adhesives include mammals, fish, milk, soybeans, and blood. Animal and fish parts that yield useful proteins include hides, skins, bones, and collagen from cartilage and connective tissues. Most animal proteins are extracted using water and vary considerably in molecular weight, amino acid sequence, and inorganic impurities. For those proteins that are not already soluble in water, such as collagen, solubilization is accomplished by imposition of heat, pressure, or, most commonly, addition of acids or alkalis. Final molecular weights are in the range of 10,000–250,000 (66). Following solubilization, the protein solution is boiled down and dried to a final moisture content of 10–15%. Milk and cheese yield the relatively simple mixture of proteins called casein [9000-71-9]. Proteins are extracted from milk through direct acidification following de creaming and may also be generated through fermentation of lactose by bacteria to create lactic acid. Blood is almost entirely made up of proteins and after spray drying to remove water, can be stored for an extended period of time. Soybeans are important sources of both proteins and triglyceride oils. Proteins for adhesives are obtained from harvested soybeans by extracting or pressing out oils and then heating the remaining matter no higher than 70°C lest its alkaline solubility be compromised. Soybean meal is approximately 45–55% protein, the balance consisting of carbohydrates (~30%) and ash (67).

Proteins are highly susceptible to changes in their structure through changes in pH, and the process of denaturation used when necessary to unfold protein molecules and break down their molecular weight to effect solubilization must only go far enough to obtain those effects but not deteriorate

their adhesive qualities. Additional acids and bases are used in preparation of working adhesives made from proteins. Formulations of protein-based adhesives, in general, include the dried protein, water, an alkali compound which helps dispersion, and a hydrocarbon oil defoamer. Hydrated lime and sodium silicate solutions are usually added to modulate viscosity and to improve water resistance. Plasticizers are sometimes added as are fillers, biocides, preservatives, and fungicides. Protein-based adhesives are widely used for bonding of porous substrates such as wood, and as water is removed from the adhesive by absorption, air drying, and the optional application of heat, the proteins become fully denatured and the adhesive is set. A variety of denaturing and curing agents or cross-linkers can be used with protein-based adhesives, including hexamethylenetetramine, carbon disulfide [75-15-0], thiourea [62-56-6], dimethylolurea, and various metal salts. Blood glues may contain aldehydes and alkaline phenol-formaldehydes as cross-linkers. Although very strong, protein-based adhesives have been largely restricted to nonstructural interior wood-bonding applications and other uses where their susceptibility to water and moisture do not jeopardize their stability, and the use of the various cross-linkers is targeted primarily at improving their water resistance. The most water-resistant protein-based adhesives are the blood or blood-soybean blends, but even they are not fully weatherproof. Casein or casein-soybean blends are next in line, and soybean and animal hide glues exhibit the least water resistance. The use of blood and casein adhesives is limited by the low yield of adhesive-grade dried blood from drying processes and the lack of appreciable suppliers of casein in the United States alongside a large number of diverse global sources. There has been a strong push from the soybean industry to have soy products more widely accepted in various industrial uses, but considerable work remains to be done in this area. Protein-based fibrin sealants have been the subject of considerable interest as medical adhesives and are considered by some to have many advantages when compared to cyanoacrylates and other types of adhesives (68), but their development has been limited because of human blood contamination issues.

Carbohydrate-Based Adhesives. Carbohydrates are available from a wide variety of plants, the shells of marine crustaceans, and bacteria. The raw adhesive materials obtained from these sources include cellulose, starch, and gum. Cellulose [9004-34-6] is a semicrystalline polymeric form of glucose having a molecular weight of less than 1000 to nearly 30,000. It is present in plant matter at a level between about 30 and 90%. Like some of the naturally occurring proteins, cellulose must be chemically treated in order to be used as an adhesive. Reaction of its hydroxyl groups is used to convert cellulose to cellulose esters and ethers. Important cellulose esters include cellulose nitrate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, and cellulose acetate butyrate (69). The most important cellulose ethers include carboxymethylcellulose, ethylcellulose, methylcellulose, and hydroxyethylcellulose. The cellulose adhesives are film formers having a thermoplastic nature. A typical adhesive formulation includes a few percent of the cellulose, less than a percent each of a plasticizer and a natural protein, and the great balance of water or another solvent. Methylcellulose is the basis of a common nonstaining water-based wallpaper adhesive. Celluloses are very effective aqueous solution thickeners and are sometimes used in that capacity, so their solubility is limited by viscosity increases. Starches are

the most significant class of carbohydrate adhesives. The source of the basic materials is broad and includes corn, wheat, rice, and potatoes as well as seeds, fruits, and roots from which starch is isolated by hot water leaching. Starch is a naturally occurring polymer of glucose. It occurs for the most part in either of two forms or something intermediate between the forms: amylose [9005-82-7], which is highly linear and has a degree of polymerization of 500–700, and amylopectin [9037-22-3], which is branched and has a degree of polymerization of about 1500–2000. Starch is also semicrystalline in nature, and its tightly packed granules must be opened to make it suitable for adhesive use. This is accomplished through heating, oxidation, or alkali or acid treatment. Colloidal suspensions of starches can be made by heating in water, but these have a tendency to solidify on cooling. Treatment with an alkali such as sodium hydroxide can lower the gelation temperature. Treatment with a mineral acid plus heat followed by neutralization with a base degrades the amorphous regions of the starch granule but does not disturb the crystalline regions, allowing a higher percentage of solids to be used in making an aqueous solution called a thin-boiling starch. Oxidation with alkaline hypochlorite produces a material similar to acid-treated starch but having better tack and adhesive properties. Dry roasting of starch in the presence of an acid catalyst produces dextrin [9004-53-9], which ranges in color from white to yellow to dark brown and shows different tendencies to repolymerize depending on the temperatures, times, and catalyst concentrations used. Additives used in dextrin adhesives include tackifiers such as borax [1303-96-4], viscosity stabilizers, fillers, plasticizers, defoamers, and preservatives. Formaldehyde-precondensates and other compounds are added to improve water resistance. Starch-based adhesives are used in corrugated cardboard, paper bags, paper or paperboard laminates, carton sealing, tube winding, and remoistenable adhesives. Gums are naturally occurring polysaccharides obtained from various plants or microorganisms and usually prepared as adhesives by dispersion in either hot or cold water. Although they find use in applications similar to those mentioned for starches, they are more often found as additives in synthetic adhesives in which they act as rheology modifiers.

Other Nature-Based Adhesives. The use of natural rubber, an important adhesive component obtained from the rubber tree, is discussed under the section on Pressure-Sensitive Adhesives. Tannins are polymeric polyphenols isolated as one of two products from the bark of conifers and deciduous trees. Lignin is widely available as a waste material from pulp mills and has a complex structure. Tannin-based adhesives have attained some level of success in the marketplace. Despite considerable interest in and work toward more commercial use of lignins in adhesives for wood bonding, they have not yet succeeded in capturing market share. A vinyl-functionalized sugar has been developed for use in products including, most prominently, adhesives (70). Modification of sugars to make liquid epoxy resins has also been accomplished (71). Use of whey and whey by-products as adhesive components has been investigated (72). Modification of natural materials to make polyols and diisocyanates has been pursued in both the United States and the United Kingdom (73,74). It can be expected that additional plant-based monomers and polymers will be developed as the chemical industry comes to terms with the limited supply and rising costs of petrochemicals, making “green adhesives” a not-uncommon reality in the not-too-distant future (75).

Direct Bonding

Strictly speaking, direct bonding does not include the use of conventional adhesives or seemingly any adhesive at all. However, the joining of two extremely smooth solid surfaces into a spontaneous bond requires careful preparation and surface treatment which reflect the sophisticated use of chemistry, physics, and engineering. Practitioners of direct bonding consider its gluelessness to be a considerable benefit within its primary areas of applications, optics, electronics, and semiconductors, which benefit from minimal or no contamination (76). Such bonds are also considered jointless because of the atomic distances between the joined surfaces. The most prominent use of direct bonding may be wafer bonding, a key part of the silicon-on-insulator technology behind the making of integrated circuits, that is, computer chips (77). Another important use of direct bonding is construction of waveguides for optical devices.

The inclusion of direct bonding among a list of adhesive types reflects the supposition that conventional adhesives of any composition are useful because they compensate for the shortcomings of most surfaces one might wish to join. Indeed, if smooth enough, even polytetrafluoroethylene will adhere to itself. In the case of what is called stiction, direct bonding is not seen as desirable, and steps are taken to prevent it from occurring (78). Redesign can be used to avoid material contact altogether. Surfaces can be roughened on a fine scale using chemical treatments.

Adhesive Formulation and Design

A 1999 compilation of chemicals used in adhesives listed 6300 materials (79), but the total number of compounds available for adhesive formulating is well in excess of this figure. Formulators of adhesives are in constant search of unique adhesive ingredients and their unusual combinations in order to satisfy the ever-increasing needs of their customers. In the interests of competition, many vendors of adhesive raw materials continue to protect the proprietary nature of their products by providing coded product names, a practice which though entirely understandable runs contrary to the need for the educated formulator to know the chemistry and structure of raw materials rather than relying on vague descriptions of the effects of a raw material in some standard formulation on some standard substrate.

Formulating adhesives is both a skill and an art. The novice formulator will find it invaluable to seek out other formulators in the same organization and learn from them as much as possible or at least whatever their time and patience allow. Maintaining such relationships over time can provide great benefit to the beginner as well as the veteran formulator, who will soon start learning from the former novice. The written and electronic literature of many vendors of adhesive raw materials includes information on formulating, including starting formulations. To the extent possible, one can also consult with vendor technical staff. The open technical literature, encompassing technical and trade journals, conference proceedings, and patents, provides considerable information on formulations, and its age should not discourage one from reading it as there is much to be learned from the older literature. The literature on nonadhesive polymer-based products,

such as coatings, molding plastics, and composite matrix materials, may prove helpful in describing interesting raw materials not commonly used in adhesives. Likewise, components commonly used in one class of adhesives may be found to be useful in modifying adhesives of another class. The best teacher of formulating is experience, that is, trial and error.

Adhesive formulation involves more than the combining of various raw materials. The formulator must be a multidimensional technical professional able to juggle several different fields of science and engineering, legal issues, environmental considerations, computer hardware and software, and business concerns. It is not unusual to create a remarkable adhesive only to find that a key ingredient is unstable or too expensive for the intended market or poses unacceptable health and safety risks. Some customers have lists of ingredients which will not be allowed in items sold to them. Government entities require increasingly stricter labeling of adhesives and other chemical products, the requirements varying from country to country.

Better tools for adhesive formulation have been developed with the onset of the personal computer and computer workstations. These include software for design of experiments, databases used to track endless variations in adhesive recipes, mixtures design software for faster product optimization, and simple and complex spreadsheets used to determine cost at the front end of development. On-line searching of and access to the scientific and patent literature as well as the information on business trends and supplier's products available on the Internet have made information gathering easier. Adhesive development accelerates more each year, and the savvy formulator must keep pace.

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ADSORPTION

Introduction

When a multicomponent system is exposed to an interface, there is a change in the concentration profile at the interfacial region. If the concentration of one or more of the components at interface increases, then these components are said to

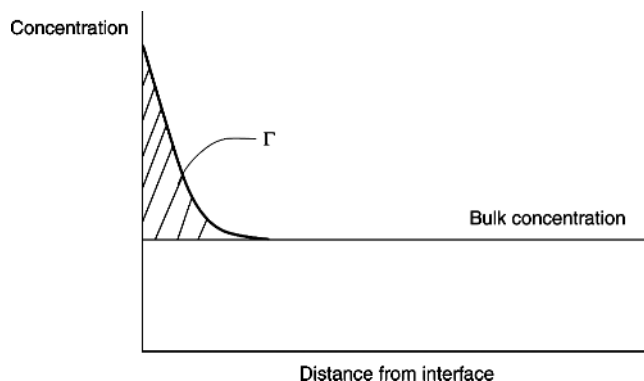


Fig. 1. Concentration profile of an adsorbed layer.

adsorb at that interface and the phenomenon is known as *adsorption*. The extent of adsorption is quantified by the term *surface excess* or *amount adsorbed*, which has dimensions of mass/unit area. Figure 1 illustrates the concentration of the adsorbed species as a function of distance from the interface. The shaded area is defined as surface excess (or amount adsorbed) Γ , which can be mathematically defined as follows:

$$\Gamma = \int_0^{\infty} [c(z) - c(\infty)] dz \quad (1)$$

where $c(z)$ is the concentration at a distance z from the interface and $c(\infty)$ is the bulk concentration. Surface excess can be positive, zero, or negative.

With some similarities, adsorption of macromolecules differs fundamentally from adsorption of small molecules. Although in both cases adsorption is often driven by the enthalpic interactions (such as hydrogen bonding, van der Waals, or electrostatic attractions), entropic contributions to the adsorption free energy are more commonly seen in the adsorption of polymers. Examples include adsorption of polymers from aqueous solutions at hydrophobic substrates, as well as adsorption of polyelectrolytes at charged surfaces, where hydration entropy of surface and small ions, as well as an increase in entropy due to release of counterions caused by the formation of polymer–surface ionic pairs might become significant. Adsorption of linear polymer chains and biological molecules at interfaces is also accompanied by the significant loss in conformational entropy of linear polymers or changes in the three-dimensional (3D) structure of biomacromolecules, both contributing to the resultant values of Γ and $c(z)$ in the equation 1.

Probably, the most distinct feature in polymer adsorption is stronger binding of polymer chains as compared to that of small molecules. This is the result of a multiplicity of contacts of individual macromolecules with surfaces, which causes amplification of molecular binding even when the interaction between a monomeric unit and the interface is weak. For example, if there are 100 segment–surface contacts per chain, each interaction with a weak segmental binding energy of $\sim kT$ such as in the case of polyethylene oxide (PEO) adsorbed on silica

(1), the net binding energy will be ~ 100 kT, giving the effective equilibrium partition constant between adsorbed and free chains larger than 10^{50} M (2). Therefore, unlike small molecules whose adsorption is usually described by the classical Langmuir, Freundlich and Temkin models, polymers typically exhibit high affinity isotherms, which saturate at very small solution concentrations. One consequence of such strong binding is that once adsorbed, a polymer chain cannot easily desorb from the surface due to the prohibitively high energetic barrier for desorption, which requires simultaneous detachment of all monomeric units. The desorption rate of adsorbed chains into pure solvent is extremely slow, and for sufficiently long chains polymer adsorption is irreversible toward dilution with a solvent.

When a polymer chain adsorbs at the interface, its conformation drastically alters from that in solution. Specific conformations adopted by polymer chains at interfaces are determined by many parameters, including the strength of polymer segment–surface interactions, chain flexibility, solvent quality, the concentration of the polymer solution, and the degree of crowding of polymer chains at the interface. Typically, at extremely low coverages, an isolated polymer chain adopts flat, pancake-like conformation (Fig. 2a), but at higher coverages the fraction of polymer segments contacting the surface decreases (3) (Fig. 2b). Conformation of polymer chains attached to the surfaces is usually described by “trains,” “loops,” and “tails” (4, pp. 113–118) (Fig. 2b). The segments of the chain that are in physical contact with the interface are called trains. Loops and tails are the parts of the chain that are not in contiguous contact with the interface. Loops are the portions of the chain between two trains, whereas tails are the parts that incorporate the chain ends. The presence of a train segment increases the enthalpic gain upon adsorption, and the loops and tails reduce the entropic penalties upon adsorption. The bound fraction (or the fraction of segments in trains) is defined as $p = \Gamma_{\text{tr}}/\Gamma$, where Γ_{tr} is the surface excess of polymer in physical contact with the substrate. The bound fraction, an important parameter that, along with surface excess Γ and segmental distribution $c(z)$, is central to theoretical and experimental studies of polymer adsorption.

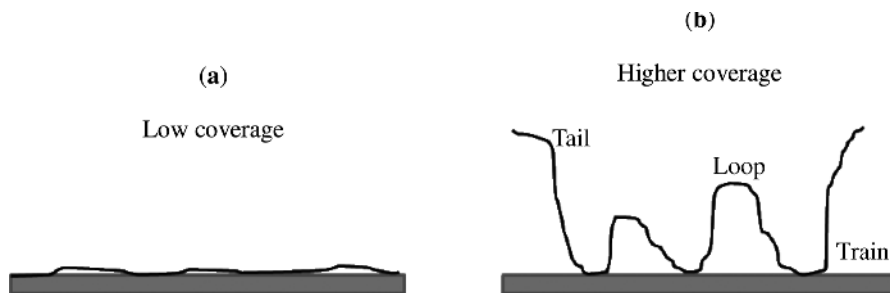


Fig. 2. Conformation of a polymer chain at extremely low (a), and at higher (b) surface coverage.

Adsorption at Solid–Liquid Interfaces

Adsorption of Homopolymers.

Adsorption of Neutral Polymers.

Adsorption Isotherms. Specific shape of high affinity type adsorption isotherms of polymer chains depends on the strength of polymer–surface interactions, polymer molecular weight and molecular weight distribution, solvent quality, as well as on equilibration of polymer chains in the adsorbed layer. Figure 3a illustrates the adsorption isotherms for polymer chains in a good solvent as a function of concentration. The surface excess saturates with an increase in the concentration of polymer chains in solution. The value of the saturated surface excess and its dependence on the molecular weight are functions of the solvent quality. In a good solvent, the surface excess increases with molecular weight for shorter chains but becomes independent of molecular weight for longer chains (Fig. 3b). The surface excess is higher in the case of a theta solvent (in which the Flory-Huggins parameter χ is 0.5) as compared to a good solvent because of weakened interactions between polymer segments in the adsorbed layer, and Γ at equilibrium increases as a function of molecular weight, following a logarithmic behavior $\Gamma = a + b \log N$, where a and b are constants, and N is the number of segments in a polymer chain (5, p. 468; 4, pp. 264–270).

In addition to the average molecular weight, the shape of the isotherm is also influenced by the molecular weight distribution of the adsorbing polymer. For polymers with a broad molecular weight distribution, adsorption isotherms have more rounded profiles, reflecting competition of shorter and longer chains in the adsorbed layer. Indeed, shorter polymer chains diffuse faster and arrive at the surface first. On the other hand, longer polymer chains lose less translational entropy per unit mass upon adsorption and have higher binding enthalpy per polymer chain. Therefore, shorter chains adsorb at the surface at extremely small solution concentrations, when unsaturated surfaces are capable of accommodating chains of all lengths, but can be displaced by longer chains at high bulk concentrations when the surface becomes saturated (6). According to Scheutjens–Fleer theory, complete preferential adsorption occurs when the polymer chains differ in length by the factor of 2 or more. Indeed, in the case of nonionic polymers of two different molecular weights, the higher molecular weight polymer was shown to displace the lower molecular weight polymer at the surface (7).

Because of slower motions of polymer chains in adsorbed layers compared to that of small molecules, adsorption isotherms might also reflect slow equilibration of polymer chains at the surface, especially for longer polymer chains and stronger segment-surface interactions.

Structure of Adsorbed Polymer Layers. The Scheutjens–Fleer theory (4, pp. 240–248) predicts a detailed structure of adsorbed polymer layers as a function of several parameters. For example, as an adsorbed layer saturates with an increase in the bulk concentration, the fraction of segments in loops increases at the expense segments in trains. Another prediction of the theory is that the average length of tails increases with molecular weight, and that this dependence becomes stronger at higher solution concentrations. The fraction of loops

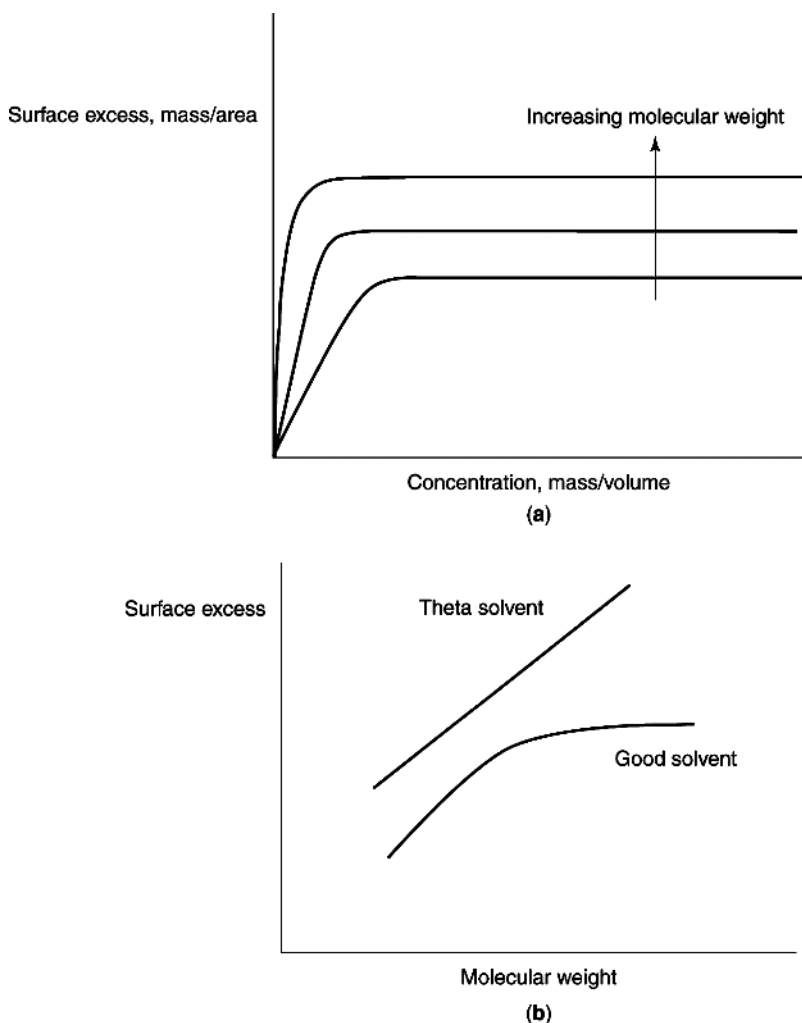


Fig. 3. (a) High affinity adsorption isotherm; (b) molecular weight dependence of the surface excess.

increases continuously with the length of the chain, whereas the fraction of tails remains almost constant after an initial increase. Experimental verification of these predictions is challenging, however, as segments in loops and tails are not distinguishable by most experimental techniques.

The surface excess Γ , the bound fraction of polymer segments p , and the segmental profile $c(z)$ can be measured, however, enabling comparison with theoretical predictions. It was confirmed experimentally, for example, that trains dominate the adsorbed layers for low molecular weight polymers, and that the fraction of loops and tails increases at the expense of trains with an increase in molecular weight (8,9). The bound fraction p is dependent on the strength of polymer-surface interactions, solvent quality, solution concentration, and surface coverage. A broad range of p from 0.02 to 0.97 was reported for various systems

(2,10,11). In a good solvent, the bound fraction remains constant for adsorption from dilute solutions and decreases with surface crowding for concentrated solutions, suggesting conformational changes of the adsorbed chains. A decrease in p with the surface coverage was observed with nonionic and weakly ionic homopolymers in measurements of differential adsorption enthalpies (12) and NMR relaxation times (1). The bound fraction also increases as adsorption energy of a polymer to a surface increases, and as the solvent quality deteriorates.

For adsorbed homopolymers, the average density (or concentration of chain segments) decays monotonically with the distance (z) from the surface. Neutron reflectivity and small-angle neutron scattering have determined the segmental density profiles in the adsorbed layer. Scaling arguments suggest that the segment density scales as $z^{-4/3}$ (13) in good solvents, whereas mean field calculations predict that the segment density scales as z^{-2} (4, pp. 145–146) in the limit of long polymer chains. Experimental results obtained so far are in qualitative agreement with these predictions. While there seems to be no agreement on the specific value of the exponent (14,15), experiments involving measurements of the structure of adsorbed polymer layers using small-angle neutron scattering (SANS) with the contrast variation method confirmed the $z^{-4/3}$ scaling prediction (16). While original scaling of the segmental density was based on the assumption that the polymer layers are equilibrated, the same form of the density profile also follows from theoretical considerations of nonequilibrated layers of irreversibly adsorbed polymers (17).

Thickness of Adsorbed Layers. Since the adsorbed layers are heterogeneous in the distribution of segments, the experimentally measured extension of the adsorbed layer into a solvent depends upon the technique used. For example, hydrodynamic techniques are sensitive to the contributions from tails, whereas ellipsometry to the contributions from the trains and loops. As the tails are much longer than the loops, the layer thicknesses obtained with hydrodynamic techniques are usually larger than those measured by optical techniques. In addition, complementary application of hydrodynamic and optical techniques provides clues about conformational changes of polymers in the adsorbed layer as a function of the solvent quality, surface coverage, and length of polymer chains. For example, the hydrodynamic thickness shows a stronger dependence on the molecular weight as compared to the thickness obtained by ellipsometry, indicating that for longer polymer chains a larger fraction of segments is included in the entropically favored polymer tails. The hydrodynamic thickness also increases with surface coverage, reflecting changes in the chain conformations from predominantly flat to those more extended into solution (4, pp. 240–248).

Experimentally, the thickness of the adsorbed layer was found to exhibit a power law dependence on the molecular weight, with the value of the exponent varying from 0.4 to 0.7, depending upon the technique and the polymer–solvent system (4, pp. 260–264). In the case of adsorption from theta solvent, the thickness of the adsorbed layer varies as $M^{0.5}$ (18).

Dynamics of Adsorbed Polymer Layers. In solution, conformation interconversions in a polymer chain occur on microsecond time scales. At a surface, due to adsorption of train segments, the time frame for conformational rearrangements of adsorbed macromolecules can be dramatically longer. Specific time scale for relaxation of polymers at surfaces depends on the energy of polymer–surface

interactions, the polymer molecular weight, and the surface coverage. Lateral diffusion of adsorbed polymer chains, along the surface with diffusion coefficients D being 2–4 orders slower than those for polymer diffusion in solution, was found in the case of low molecular weight PEO adsorbed onto a hydrophobic surface (19). At another extreme, chain dynamics can be sluggish, with no rearrangements observed in hours (20). Dynamic behavior of adsorbed polymers is also controlled by surfaces coverage (21).

While self-desorption of polymer chains in a pure solvent usually does not occur, the adsorbed polymers can be exchanged for another polymer supplied from solution. Two possible scenarios include the following: removal of the shorter chain by longer one of the chemically identical polymers, called *self-exchange*, or *displacement* of weakly adsorbing polymers by strongly adsorbing ones for two chemically different polymers. The driving force for self-exchange of polymers at surfaces include stronger adsorption enthalpy of longer chains, which form larger number of polymer–surface contacts, and an entropy gain resulting from release of shorter chains from the adsorbed layers to solution (22). An additional significant driving force for polymer displacement is the differential energy in segmental adsorption for the two chemically different polymers (7).

The nonequilibrium nature of the adsorbed layer is strongly evident in the displacement kinetics of protonated polystyrene by deuterated polystyrene molecules (23). The exchange time constants were found to be dependent on the “aging” time of adsorbed layers prior to the displacement experiment. Such “aging” was explained by continuous relaxation of adsorbed chains toward an equilibrium state, which proceeded through an increase in the bound fraction p , as was shown by direct IR measurements in two experimental systems (24,25).

If chain desorption is controlled by surface energetics with a single energy barrier, the surface excess of initially adsorbed polymer decays exponentially with time, following single exponential kinetics, as in the case of self-exchange of polymer chains that are weakly bound at surfaces (26). The time constant for displacement of polymer chains from equilibrated homogeneous layers increased exponentially with the molecular weight. However, this simple dependence is observed only with chemically homogeneous surfaces, and the exchange time constant shows a power law dependence on the molecular weight for chemically heterogeneous surfaces (25).

Deviations from the simple single exponential law in the time evolution of surface excess often arise from strong energetic barriers toward chain rearrangements within adsorbed layers. Such barriers might occur as a result of strong adsorption, chain pinning, osmotic, or electroosmotic barriers and/or entanglements of long polymer chains within adsorbed layers. Chain pinning and entanglements are more pronounced with polymers of higher molecular weight. One example includes pinning of weakly adsorbing chains to a surface by a stronger adsorbing polymer (27). In these cases, kinetics obeys a stretched–exponential behavior $\Gamma(t) = \Gamma(0) \exp[-(t/\tau_{\text{off}})^\beta]$ for the originally adsorbed polymer, and the exchange is governed by diffusion away from the surface (28). The value of the exponent β can vary between 0 and 1, depending on the rate of readsorption and the bulk diffusion rates (29). If diffusion is slow and the chain exhibits a strong tendency to readsorb, β assumes a small value ($\beta < 1/2$). The time constant for exchange in

this case scales as D^{-1} , where D is the diffusion coefficient of the polymer chain in the matrix of adsorbed chains.

It has been shown experimentally that temperature variations can switch the relaxation regime from diffusion controlled to adsorption controlled (28). Similar switching was also achieved by varying the length of adsorbed polystyrene being displaced with polyisoprene (30).

Role of Surface Charge. The presence of charge at the surface or in the polymer chain has a drastic effect on polymer adsorption. When the polymer is uncharged but the surface is charged, the driving force for polymer binding is nonelectrostatic in its origin. Yet, the surface charge can significantly affect adsorption of neutral polymers. For example, many polymers form hydrogen bonds with oxygen or silanol groups at surfaces of oxidized metal or oxidized silicon, respectively (29), and their adsorption is strongly dependent on the acidity of the surface hydroxyl groups and the surface pH. Adsorption of PEO at the silica surface, for example, was completely suppressed at high pH values (31). While surface counterions and small ions might affect adsorption of neutral polymers, these effects are usually not very significant.

Adsorption of Polyelectrolytes. In the adsorption of polyelectrolytes, a crucial role is played by columbic interactions between polymer segments and the surface, as well as between charges in polymer chains. As a result of repulsions between charged polymer segments, the fraction of segments included in trains is usually higher for adsorbed strongly charged polyelectrolytes than that for nonionic polymers. Another distinctive feature of adsorption of strongly charged polyelectrolytes is a weak dependence of train fraction on surface coverage (1,32).

The estimated sticking energy of polyelectrolyte segments to charged surfaces is usually higher than those of nonionic polymers. For example, adsorption energies of $\sim 4 k_B T$ and $\sim 7 k_B T$ per segment were estimated or experimentally determined (1,33). Therefore, in addition to the repulsive potential built by earlier adsorbed polyelectrolyte chains for incoming chains, equilibration of adsorbed polyelectrolyte layers is impeded by strong energetic barriers to chain rearrangements within the adsorbed layers. Polyelectrolyte adsorbed layers often do not reach thermodynamic equilibrium and are strongly history dependent even in solutions with high concentrations of small ions (34).

Surface Charge. The effect of surface charge on polyelectrolyte adsorption depends on the type and strength of the polymer-surface interactions, the solvent quality for the polymer backbone, as well as on the concentration of polyelectrolytes and small ions in solutions (35,36). Recent molecular dynamic simulations show that for hydrophobic polyelectrolytes adsorbed on hydrophilic surfaces, the thickness of the adsorbed layer decreases monotonically with the surface charge density (37). For adsorption of hydrophobic polyelectrolytes on hydrophobic surfaces, however, the layer thickness shows nonmonotonic dependence on the surface charge density. After an initial decrease with increasing the surface charge density, indicating the flattening of the adsorbed polyelectrolyte chains, the layer thickness begins to increase at sufficiently high surface charge densities (35). Nonmonotonic dependence of the layer thickness on the surface charge density is in agreement with the predictions of a scaling theory for necklace-like hydrophobic polyelectrolytes adsorbed at oppositely charged

surfaces (38). Similar nonmonotonic dependence of the layer thickness is also expected for adsorption of hydrophilic polyelectrolytes at hydrophilic charged surfaces (25,39). Experimentally, it is common to observe a gradual increase in polymer-adsorbed amount for strong polyelectrolytes with increasing the surface charge density (40). However, a nonmonotonic variation in polymer-adsorbed amount was also observed for adsorption of poly(acrylic acid) at a positively charged surface with varied surface charge density (41). The dependence was qualitatively explained in the framework of a simple free energy model of polyelectrolyte adsorption (41).

Polyelectrolyte Charge Density. While conformations of adsorbed strongly charged polyelectrolytes are predominantly flat, the chains adopt more loopy 3D conformations as the charge density in the polyelectrolyte chains decreases. Experimentally, this was confirmed for random copolymers composed of different fractions of uncharged and positively charged monomers (42), which showed an increase in the amount adsorbed with decreasing polymer charge density. However, for chains with very low charge density, electrostatic attraction between the chains and the surface weakens resulting in a maximum in the dependence of the amount adsorbed on the polyelectrolyte charge density (43).

Adsorption of Weak Polyelectrolytes. Charge density of weak polyelectrolytes is dependent on the solution pH. When weak polyelectrolytes adsorb, their ionization is additionally adjusted to a local electric field in the adsorbed layer, and it consequently can no longer be described by their solution pK_a s (44). Moreover, ionization of weak polyelectrolytes is dependent on the surface coverage and constantly readjusts as adsorbed layers become more populated with polyelectrolyte chains (45).

Salt Concentration. An electrical double layer and charge screening play an important role in polyelectrolyte adsorption. Small ions screen polymer-polymer and polymer surface electrostatic interactions, disrupt segment-surface binding, and can also influence the polymer-solvent interactions. Depending on the nature of polyelectrolyte-surface interactions, the polymer and surface charge density, and the solvent quality for the polymer backbone, enhanced salt concentrations can result in an increase or a decrease in the polymer surface excess (*screening-enhanced* and *screening-reduced* regimes, respectively). When polyelectrolytes adsorb at uncharged surfaces, the polymer adsorbed amount increases with an increase in the salt concentration (32). At low salt concentrations, the strong electrostatic interactions between chains lead to low polymer surface coverage. With increasing salt concentration, the electrostatic interactions between chains are screened, resulting in an increase in polymer surface coverage. In addition to screening of the interchain electrostatic interactions, the salt ions also screen intrachain electrostatic repulsion resulting in a coil-like chain configuration and formation of loops and tails. For adsorption of polyelectrolytes at surfaces of opposite charge, scaling theories predict that the effect of salt on polyelectrolyte adsorption depends on the polymer surface coverage (39). Specifically, at low polymer surface coverage, when polyelectrolytes form two-dimensional adsorbed layers, the addition of salt results in an increase in the polymer amount adsorbed. In contrast, at high polymer surface coverage when polyelectrolytes form 3D adsorbed layers the polymer-adsorbed amount decreases with

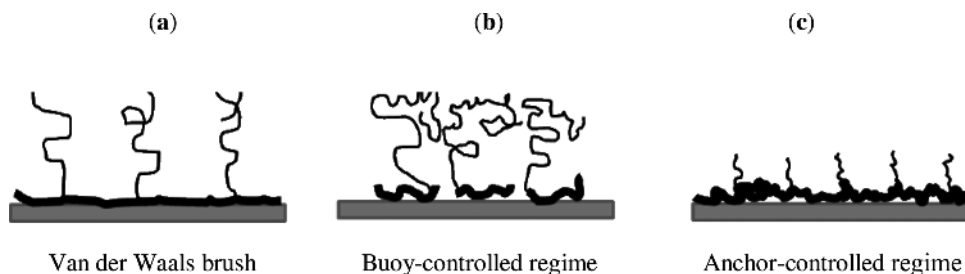


Fig. 4. Adsorption of block copolymers at a surface.

increasing salt concentration (39). Experimentally, both *screening-enhanced* (33, 46) and *screening-reduced* adsorption (47,48) was observed. For the *salt-enhanced* regime, the polymer surface coverage was found to increase as the square root of salt concentration ($\Gamma \sim \sqrt{c_{\text{salt}}}$) (46). Addition of salt could also worsen the polymer–solvent affinity, resulting in an increase in polymer surface coverage. A self-consistent mean-field theory predicts that unlike adsorption from θ and good solvents, polyelectrolyte adsorption from poor solvent results in polyelectrolyte layers that undercompensate the surface charge, and the polymer surface coverage in this case decreases with increasing the salt concentration in high salt concentration regime (49).

Another important variable determining the effect of salt on polyelectrolyte adsorption is the charge density on the polyelectrolyte backbone. In studies of adsorption of cationic polyacrylamides with different fraction of charged groups f at the surface of montmorillonite, the polymer surface coverage was found to decrease with an increase in the salt concentration at small fraction of charged monomers f , whereas it increased with the salt concentration for strongly charged chains with large values of f (42). This peculiar dependence of the polymer surface coverage on the polyelectrolyte charge density was explained in the framework of a scaling theory of polyelectrolyte adsorption (39).

Adsorption of Copolymers

Figure 4 shows surface structures that adsorbed copolymers might adopt. In the case of block copolymers, the block that is preferentially adsorbed is called the anchor whereas the nonadsorbing block is called the buoy. The structure of the adsorbed layer depends on the nature of the solvent and the relative sizes of the blocks. In a solvent that selectively solubilizes one of the blocks, the anchor block is collapsed and forms a dense layer, whereas the buoy stretches out to form a brush-like structure. For one possible case in this regime, referred to as the “van der Waals brush regime” (50), chain conformation and structure of the adsorbed layer are determined by the competition between van der Waals attraction between the anchor and the substrate and repulsive interactions inside the brush (Fig. 4a).

If the solvent is nonselective, the anchor swells and has a structure similar to that of an adsorbed homopolymer. In the case of adsorption of a diblock copolymer from nonselective solvents, there are two possible cases (51): (a) the “buoy” regime (Fig. 4b), in which the anchor is small and adsorption is dominated by repulsive interactions between the buoys, and (b) the “anchor” regime (Fig. 2c), in which the anchor is large and adsorption is determined by the saturation of the anchor layer.

A major difference between adsorption of homopolymers and block copolymers is that in the case of block copolymers, the fractions of trains and loops are smaller than that of the tails. Consequently, the volume profile in block copolymers exhibits a parabolic decay with distance (52,53). In the case of random copolymers, in addition to the solvent quality and the copolymer chain length, adsorption is also strongly affected by the composition and distribution of the monomers along the chain. For a truly statistical copolymer, the adsorption behavior can be expected to be between the behaviors of the two homopolymers (31).

Adsorption of Biomacromolecules

The characteristic features of adsorption of proteins are their propensity to adsorb to a variety of surfaces, as well as their vulnerability to denaturation (54). Protein adsorption is strongly dependent on the nature of a protein, the surfaces chemistry and nanotopography (roughness, curvature), and adsorption conditions (55–57). Patterned surfaces engineered by lithography or microprinting permits spatial control over biomolecule attachment (58,59). Selective patterning of biomolecules at surfaces can also be achieved by creating adhesive surface patches of polyelectrolytes or self-assembled monolayers (60). The density of the adsorbed proteins layers depends on the protein type, the solvent quality, the hydrophobic/hydrophilic properties of the surfaces, and on the surrounding conditions. Usually, denser adsorbed layers result from adsorption of smaller proteins (61).

Conformational Changes. Unlike global unfolding of proteins induced by changes of pH, pressure and by the presence of denaturing molecules, protein unfolding upon adsorption is initiated by the local interactions of proteins with surfaces. The extent of protein conformational changes depends on the protein type with “soft” proteins being more prone to conformational changes than “hard” ones (62), surface hydrophilicity (with hydrophobic surfaces usually causing greater protein denaturation), surface charge (with stronger denaturing capability of stronger charged surfaces), as well as temperature and ionic strength. In addition, surface coverage plays an important role. Proteins adsorbed at low surface coverage have sufficient space to flatten and change their conformation, whereas later adsorbing proteins greatly preserve their native structure because of the surface crowding (63). Because conformational changes of proteins at surfaces trigger a series of biochemical reactions, including coagulation, control of cell adhesion and proliferation, significant efforts were made to create non-fouling surfaces that resist protein adsorption. Most common approaches include decorating surfaces with poly(ethylene glycol) coatings (59) or modification of surfaces with zwitterionic headgroups (64).

From Adsorbed Monolayers to Multilayers

Substrates covered with adsorbed polymer monolayers can be used for further deposition of polymer layers. Sequential adsorption of anionic and cationic polyelectrolytes, or hydrogen-bonding neutral polymers led to formation of layer-by-layer (LbL) films (65). Importantly, trends observed for adsorption of polymer monolayers at solid substrates can also be usually seen with LbL films. One example is that in the case of strong polyelectrolytes, amount of polymers deposited within the film during a single adsorption cycle usually increases with an increase in the concentration of small ions in the deposition solution (66). Another example is the observation of the critical degree of polyelectrolyte charge density required for the deposition of stable LbL films (67). Construction of polymer multilayers also facilitates experimental observation of changes in ionization of weak polyelectrolytes upon adsorption (68). In spite of the many similarities with adsorption of polymer monolayers at solid surfaces, LbL films demonstrate additional complex features, such as facilitated exchange of polymer chains between the film and solution (67), as well as interdiffusion of polymer chains in the direction normal to the surface (69).

Adsorption at Liquid–Liquid and Air–Liquid Interfaces

The driving force for polymer adsorption at the oil–water interface is the minimization of the interfacial tension between the two interfaces. Typically, random copolymers or block copolymers, in which the monomeric units are preferentially solvated in either of the two phases, adsorb readily at the interface. In the case of homopolymers, adsorption occurs either if the polymer is soluble in both phases or if the polymer has functional groups that can reduce the interfacial tension, such as in the cases of PEO and poly(methyl methacrylate) (PMMA) adsorbing at the toluene–water interface, respectively. In contrast, because of its hydrophobic nature, polystyrene does not adsorb at the same interface (70).

Studies of the thickness of adsorbed layers of copolymers at liquid interfaces using neutron reflectivity showed strong dependence of the structure of adsorbed polymer layer on the distribution of monomeric units within polymer chains (71). In the case of a diblock copolymer with both blocks selectively solvated by water and oil phases, the chains stretch at the interface forming thick adsorbed layers. With a random copolymer having the same composition as the diblock copolymer, the interfacial thickness is significantly smaller as a result of the localization of the polymer chains at the interface caused by unfavorable interactions between insoluble copolymer units with the two phases.

The structure of polymer adsorbed layers at the air–liquid interface is similar to that at the solid–liquid interface. Adsorption at air–liquid interface has been studied by ellipsometry (72), X-ray and neutron reflectivity (73,74), surface tension measurements (75), X-ray evanescent wave-induced fluorescence (76), and Langmuir trough techniques (73). Neutron reflectivity measurements indicate that in the case of homopolymers the segment density decreases as $z^{-4/3}$, in good agreement with scaling predictions for homopolymers at the solid–liquid interface (73).

Techniques to Study Polymer Adsorption

Techniques applied to study polymer adsorption have to be sensitive enough to detect small mass ($\sim 1\text{--}5\text{ mg/m}^2$) included within adsorbed polymer monolayers. One way to increase the sensitivity of the measurements is to study polymer adsorption using dispersed particles. Sensitive techniques are also now available to study thin adsorbed polymer layers at planar surfaces.

Measurements on Dispersions.

Concentration Measurements. For a polymer adsorbed onto dispersed particles, adsorbed amount Γ can be calculated from the change in polymer concentration (ΔC) in a supernatant solution before and after adsorption, that is usually measured by UV-vis and IR spectroscopy:

$$\Gamma = \frac{\Delta CV}{A}$$

where V is a known volume, and A is the surface area of the adsorbent.

Scattering Techniques. The thickness of adsorbed layers on dispersed particles can be determined using light, X-ray, or neutron scattering techniques (4, pp. 67–71). Quasi-elastic light scattering determines the hydrodynamic layer thickness by measuring the diffusion coefficients using dispersions with and without the adsorbed polymer and by calculating the particle sizes from the diffusion coefficient using the Stokes–Einstein equation.

In X-ray and neutron scattering measurements, the scattering intensity is measured as a function of the scattering angle, and the data are modeled to determine thickness and volume profiles of adsorbed polymers. A “contrast matching” or “contrast variation” technique, achieved by varying the isotopic or atomic composition of the solvent or the polymer in neutron scattering and X-ray scattering experiments, respectively, affords selective observation of adsorbed polymer chains.

Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR). The NMR technique (77) can be used to determine the bound fraction of polymer segments from an increase in the spin–spin relaxation time (T_2) of polymer segments when they are included into the trains, from the changes in the solvent relaxation time, or from the chemical shifts due to changes in the electronic environment of the chain segments bound to the interface.

The ESR technique (78) can also be applied to determine the fraction of bound segments by measuring the differences in the rotational correlation time of the mobile and immobile segments. However, the polymer labeling required by this technique can affect the adsorption behavior of the polymer chains, and the bound fraction determined with ESR is often higher than that obtained with other techniques (79).

Measurements on Flat Surfaces. Using planar substrates, polymer adsorption can be studied under well-defined conditions of surface energies and known surface area. These measurements provide important insights into the structure and dynamics of adsorbed polymers, which are often not experimentally achievable using dispersed particles.

Quartz Crystal Microbalance (QCM) and Direct Microbalance Techniques provide measurements of the adsorbed mass. In the QCM technique, adsorbed mass is determined from the shifts of vibration frequency of a quartz single crystal to lower values as a result of polymer adsorption (80). In the microbalance technique, microbalances with sensitivity of 10^{-4} mg are used to determine the change in mass of a substrate due to adsorption (81).

Evanescent Wave/Spectroscopic Techniques probe adsorbed polymer monolayers using the exponentially decaying evanescent electric field, which is formed upon *total internal reflection* of radiation propagating within a higher refractive index medium. One example is attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), which enables *in situ* measurements of a polymer adsorption as a function of adsorption time (82). In addition to the adsorbed amount, ATR-FTIR can also be used to measure the bound fraction of adsorbed chains. The latter is possible only in those cases when there is a change in the absorption bands of functional groups upon binding of polymer chains to a substrate, such as in the case of PMMA adsorbing at the oxidized silicon crystal (83). ATR-FTIR was also used to obtain structural information on the adsorbed layer based on the dichroic ratio of functional groups in the adsorbed polymer layer (84). The ATR principle can also be applied to quantify the surface excess using fluorescence intensities of a labeled polymer chain (85).

Both ATR-FTIR and ATR-fluorescence techniques (86) were used to study exchange kinetics of the adsorbed polymers. In the case of IR spectroscopy, competition between chemically different chains, or between deuterated and hydrogenated polymer chains at the surface, can be studied as a function of time (23). Similarly, ATR fluorescence spectroscopy can be used to study adsorption kinetics using mixtures of fluorescently labeled and unlabeled chains.

Ellipsometry is an optical technique that measures the changes in amplitude and phase of polarized light upon reflection (87). These changes are related to the refractive index of the substrate and the thickness and refractive index of the adsorbed polymer layer. By measuring these changes for different wavelengths of light and/or at different incident angles, one can also determine the segmental concentration profile in the adsorbed layer. *In situ* ellipsometry can also be used to study kinetics of polymer adsorption (88).

Reflectometry. Optical reflectivity is sensitive to changes in the refractive index, X-ray reflectivity—to changes in electron density, and neutron reflectivity—to the variation in the scattering length density in the adsorbed layer. In the case of X-ray and neutron methods, the reflectivity is measured as a function of incident angle, and the reflectivity data are modeled to determine the concentration profile (89). In neutron reflectivity, additional contrast can be provided by using deuterated solvents or deuterated polymer layers.

Surface Force Measurements. Another method to measure the thickness of adsorbed layers is by the surface force apparatus (SFA) (90). In SFA, two freshly cleaved mica sheets carrying adsorbed polymer chains are brought together, and forces between surfaces are measured as a function of separation. The thickness of the adsorbed layer is estimated from the onset of the repulsive force as the adsorbed layers overlap.

Measurements at Liquid–Liquid and Liquid–Air Interfaces. One of the simplest methods to study adsorption at the oil–water interface is to measure

the variation of interfacial tension as a function of concentration. The surface excess can be correctly estimated from the interfacial tension measurements only in the case of monodisperse polymers (91). Other techniques such as total internal reflection fluorescence microscopy (92) and scintillation measurements (93) were also used to study polymer adsorption at the liquid–liquid interface. The thickness of adsorbed layers at liquid interfaces is often experimentally evaluated using neutron reflectivity (71).

Applications of Polymer Adsorption

Polymer adsorption plays an important role in colloidal stabilization and flocculation, adhesion and lubrication, and chromatographic separations. Moreover, polymer monolayers and multilayers at surfaces are increasingly used for designing bioactive surfaces, which controlled biocompatibility and cellular adhesion at surfaces. Recent progress in the area LbL films has demonstrated strong potential of such coatings as drug-releasing or antifogging coatings. Recent developments in designing polymer surfaces that can switch between extended and collapsed conformations (94) in response to external stimuli such as pH, ionic strength, temperature, or light, further broaden the possibilities in using polymer-modified surfaces in biomedical applications. Here, some recent applications of adsorbed polymers are summarized.

Flocculation and Stabilization of Colloids. When two surfaces covered with adsorbed polymers are brought in contact, repulsive and/or attractive forces arise whose magnitude, sign, and range depend on the solvent quality, segment–surface interactions, and the surface coverage. In poor solvents or on sparsely coated surfaces, the force is attractive and polymer chains bridge between surfaces. Such bridging-induced flocculation is useful for the removal of suspended fine solids in wastewater treatment. At high surface coverage and in a good solvent, repulsive forces occur as a result of steric stabilization with adsorbed polymer layers. Polymers are often added, therefore, to stabilize colloidal particles, which are prone to coagulation in inks, cosmetics, and in processed food (95).

Friction and Lubrication. Surfaces carrying extended, brush-like adsorbed polymer layers experience steric repulsive forces when brought together. Interestingly, while brush-coated surfaces can sustain large normal forces upon approach, their friction coefficient remains very low (96). This phenomenon lies in the heart of using polymers as friction modifiers and lubricants in mineral processing, paper industries, and other applications.

Biomedical Applications. Tuning composition and hydrophobic/hydrophilic balance of surface-bound copolymers can be used to improve surface biocompatibility (97) (see BIOMOLECULES AT INTERFACES). Control over binding of biomolecules with surfaces are also key in regulating cellular and bacterial adhesion and proliferation at surfaces (98,99), as well in the development of advanced sensors used for drug screening, bioseparation and diagnostics (100). Moreover, interactions between proteins and inorganic materials are central to the performance of important natural biocomposites such as enamel and nacre, and artificial self-assemblies mimicking such biocomposites.

Another type of polymer/inorganic composite material useful for biosensing and drug delivery applications is obtained by linking polymers to nanoparticles by physical adsorption or by “grafting-to”/“grafting-from” techniques. The polymer shell can be made highly functional, being able to entrap and release drugs and biomolecules (such as DNA and enzymes) in response to environmental stimuli (101).

Finally, extension of the adsorption process to multilayers offers greater versatility in controlling properties of the polymer layers, and enables high loading capacity of polymer films to functional molecules, and controlled release of functional molecules from surfaces (102,103), including delivery of multiple therapeutic agents (104).

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AGING, PHYSICAL

Introduction

All glasses, including polymeric glasses, undergo a process known as physical aging or structural recovery. The origin of physical aging can be understood on a macroscopic level by examining the volume versus temperature path of an amorphous polymer, as shown in Figure 1. On cooling from the liquid state, the amorphous material does not crystallize because of kinetic or steric constraints and its volume decreases along the equilibrium density line. As the volume decreases, the molecular mobility also decreases. At the glass temperature or glass-transition temperature (T_g), the molecular mobility is such that the material can no longer maintain equilibrium density on the time scale of cooling and the material deviates from the equilibrium line onto the glass line. Although the glass temperature is often reported as a single number, its value depends on the cooling rate; faster cooling rates giving higher T_g values and higher glass lines. Independent of which glass line the material is on, the glass is not at equilibrium. Physical aging, which is also called structural recovery particularly when the evolution of thermodynamic variables is being referred to, is shown by the downward arrow in Figure 1 at aging temperature T_a .

The driving force for physical aging is the attempt to achieve equilibrium density through configurational rearrangements on a molecular scale. Corresponding to these changes on the molecular scale, we observe a decrease in volume, a decrease in enthalpy, an increase in modulus, and an increase in brittleness. The time scale for physical aging (ie, the time required to reach equilibrium) can be as short as several hundred seconds at aging temperatures in the vicinity of the nominal T_g and increases to years or millennia as the temperature decreases. According to the Gibbs and DiMarzio theory of the glass temperature (1–3), there is an underlying thermodynamic transition, often associated with the Kauzmann temperature 52°C below T_g (4).

Physical aging and structural recovery are reversible phenomena. There is no change in chemical structure during physical aging. The changes in physical and mechanical properties that accompany structural recovery are caused by the densification associated with the approach to equilibrium. The changes can be erased by heating the material above the glass temperature to a temperature

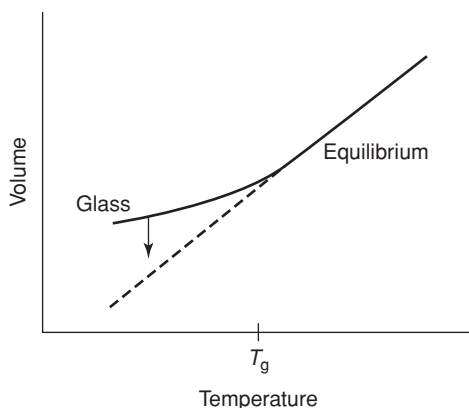


Fig. 1. Schematic of volume vs temperature for an amorphous glass-forming material. The arrow shows the evolution of volume from the nonequilibrium glass line to the equilibrium line during structural recovery.

where the material is again at equilibrium. Cooling the material from the equilibrium state will result in reestablishment of the glass. This reversibility is often exploited in physical aging research as is mentioned later in this article.

The importance of structural recovery and physical aging lies in the changes in material properties that accompany the phenomena. These changes can in many instances adversely affect performance and lifetime. Consequently, structural recovery and physical aging impact the design, processing, and performance of polymers in many applications, including, but not limited to, aerospace and automotive applications, xerographic applications, and glass-to-metal seals (5). In addition to the practical effects of physical aging, an understanding of glasses and the effects associated with structural recovery is important from a fundamental scientific viewpoint. In fact, Nobel laureate P. W. Anderson claimed that the glass transition was one of the greatest unsolved problems of condensed matter physics (6). Although the basic phenomenology associated with glasses is known and models exist which describe structural recovery and physical aging, researchers are not yet able to predict a priori experimental observations.

In this article on physical aging, the phenomena associated with structural recovery and physical aging are described, starting with discussion of volume recovery, enthalpy recovery, viscoelastic properties, and failure. There are more in-depth reviews of the phenomena and models associated with the glass transition (7) and enthalpy recovery (8). See also GLASS TRANSITION, AMORPHOUS POLYMERS, and VISCOELASTICITY.

Volume Recovery

The decrease in volume during physical aging is specifically known as *volume recovery* or *volume relaxation*. Volume recovery experiments include down-jump, up-jump, and memory experiments. The results of these experiments, which are

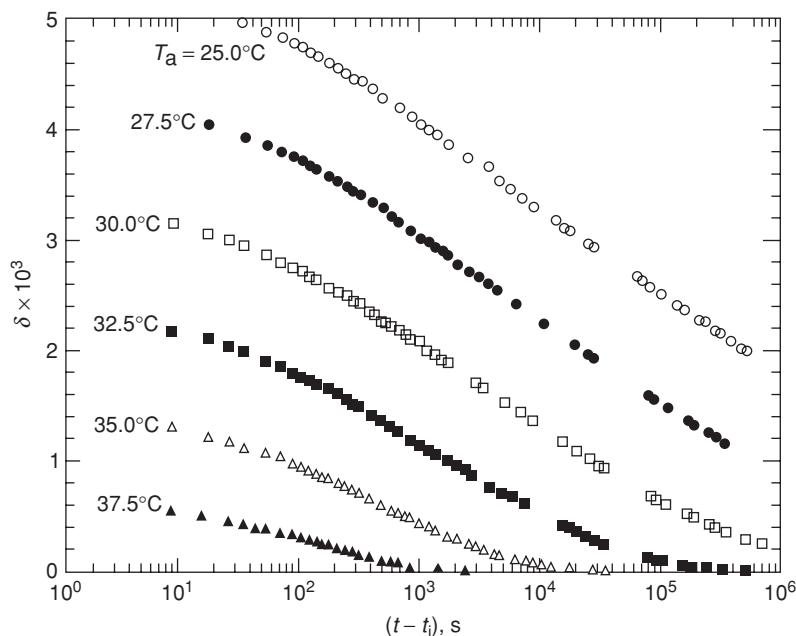


Fig. 2. Intrinsic isotherms for poly(vinyl acetate) from the data sets of Kovacs (replotted after Ref. 9). The departure from equilibrium is plotted vs time after thermal equilibration. Down-jumps were performed from 40°C to various isothermal aging temperatures ranging from 37.5 to 25°C.

shown and discussed later, demonstrate that structural recovery is both nonlinear, nonexponential and path-dependent.

The simplest volume recovery experiment performed is the down-jump. In this experiment, a material initially above T_g and at equilibrium is subjected to a temperature down-jump to an aging temperature T_a below T_g . The isothermal evolution of volume at T_a , as indicated by the downward arrow in Figure 1, is monitored with time via length or volume dilatometry. Figure 2 shows typical data replotted from Kovacs data (9) for a series of aging temperatures for poly(vinyl acetate). These curves, called intrinsic isotherms, are plotted as the relative departure from equilibrium δ versus the logarithm of time, with δ defined as

$$\delta = \frac{v - v_\infty}{v_\infty} \quad (1)$$

where v is the volume at a specific aging time and v_∞ is the volume at equilibrium density. The relative departure from equilibrium has a nonexponential shape and approaches zero asymptotically at long times as equilibrium is attained. As might be expected, the times required to reach equilibrium increase as the aging temperature decreases.

The total change in delta during aging depends on the magnitude of the temperature jump and is related to the initial departure from equilibrium (δ_0):

$$\delta_0 = \Delta\alpha (T_{f_0} - T_a) \quad (2)$$

where $\Delta\alpha$ is the difference in thermal expansivities between the liquid and glass ($=\alpha_l - \alpha_g$, where subscripts l and g refer to the liquid or equilibrium and glassy regimes, respectively). T_{f_0} is the initial fictive temperature and it equals the value of the glass temperature associated with the rate of the quench to T_a . A more general definition of T_f is given later. For a perfect quench, T_{f_0} is equal to the temperature at which the quench was made, although experimentally this is never the case. Although Figure 2 shows that Kovacs plotted his original data versus $(t - t_i)$ where t_i is the time at which the quench was initiated, modeling work (10) has indicated that this is incorrect. For capillary dilatometers (10), taking time zero at the beginning of the quench resulted in insignificant error in the data on a logarithmic time scale compared to the results of a perfect quench for times greater than approximately two times the thermal equilibration time. Hence, data should be plotted versus time, with time zero being the time at which the quench is initiated. This is in agreement to Struik's earlier suggestion (11).

The total change of volume during volume recovery is small, generally being smaller than 1%, ie, the change in δ is generally less than 10×10^{-3} . For example, for the data shown in Figure 2, the volume changed approximately 0.05% at the highest temperature and 0.5% at the lowest temperature. These changes, in themselves, are not significant for dimensional stability in most applications. However, the associated changes in mechanical properties, and in particular in failure modes, can be significant in practical applications as is discussed later. It is noted that measurement of volume changes of this order indicates the need for high precision in the measurements. Resolution to 2×10^{-5} cm³/g is desired and can be achieved with both traditional and automated capillary dilatometers. One source of noise in the measurements is the temperature fluctuations in the bath; preferably these fluctuations should be of the order of ± 0.01 K or less.

In addition to the down-jump volume recovery experiments, up-jumps can also be performed. In the up-jump experiment, the material is first equilibrated at a temperature T_i below T_g . It is then subjected to an up-jump in temperature to an aging temperature which may or may not be below the nominal glass temperature. During aging, the volume now increases with time as the material attempts to achieve equilibrium density. Kovacs' data (published originally in Ref. 12) for an up-jump to a single aging temperature after equilibration at the temperatures indicated are shown in Figure 3 for poly(vinyl acetate). Also shown in Figure 3 are the results of down-jumps to the same aging temperature from several initial temperatures.

The data in Figure 3 demonstrate what is known as the asymmetry of approach. For the same magnitude jump, the up-jump response is delayed relative to the down-jump and the time required to reach equilibrium is longer. The asymmetry of approach is considered to be a manifestation of the nonlinearity of the relaxation process as was first recognized by Tool (13). In other words, the rate of volume recovery depends on some characteristic relaxation time (τ), which in turn depends on the instantaneous volume, which in turn depends on the rate of

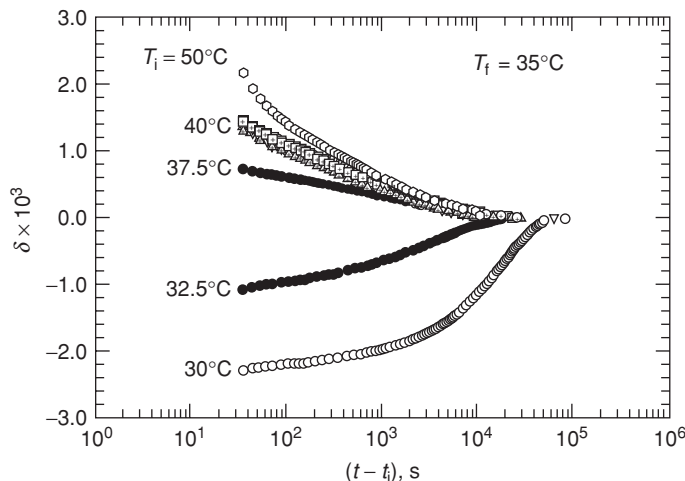


Fig. 3. The asymmetry of approach for poly(vinyl acetate) from the data sets of Kovacs and first published in Reference 12. The isothermal aging temperature is 35°C. Down-jumps and up-jumps were initiated at the temperatures T_i as shown.

volume change (after Ref. 14):

$$\begin{array}{c} v \rightarrow \tau \rightarrow \left(\frac{\partial v}{\partial t} \right)_{T_a} \\ \uparrow \\ \text{ } \end{array} \quad (3)$$

Hence, the down-jump response is autoretarded on a logarithmic time scale with the characteristic relaxation time increasing with the time of aging, whereas the up-jump response is autoaccelerated with the characteristic relaxation time decreasing with the time of aging. For a small enough temperature jump, the response would be linear. In the linear case, the relaxation time would not change during the recovery, and the down-jump and up-jump responses would be mirror images.

The third type of volume recovery experiment, termed the memory or crossover experiment, demonstrates that the relaxation behavior is dependent on the prior thermal history of the material. In this experiment, the material is aged partially into equilibrium at temperature T_1 and then heated to a temperature T_a where the volume initially lies on the equilibrium line. Because the volume departure from equilibrium at T_a is initially zero, no evolution of volume might be expected. However, the observation is that the volume increases away from equilibrium and then decreases back to equilibrium. The thermal history involved in the memory experiment is depicted schematically in Figure 4. The experimental results of Kovacs for poly(vinyl acetate) (PVAc) (9) are shown in Figure 5 for several T_1 , in addition to the down-jump response. The memory experiment is attributable to a distribution of relaxation times; for example, if at T_1 the fastest relaxing regions reached equilibrium density by the time the jump to T_a was made whereas the slowest regions had not, then at T_a the fast regions would expand to get to their equilibrium volume at this higher temperature resulting in the increase in volume away from equilibrium, and at longer times,

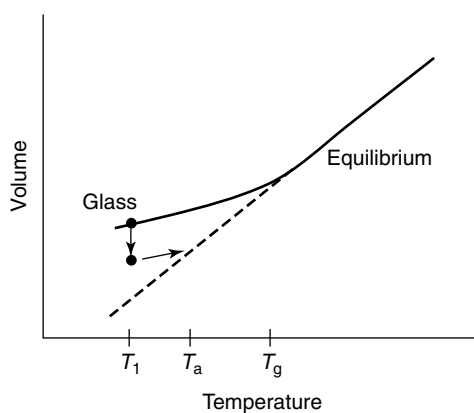


Fig. 4. Schematic of the memory experiment for volume (or enthalpy). The material is aged at T_1 such that the material is initially at equilibrium at T_a following an up-jump from T_1 to the final aging temperature T_a .

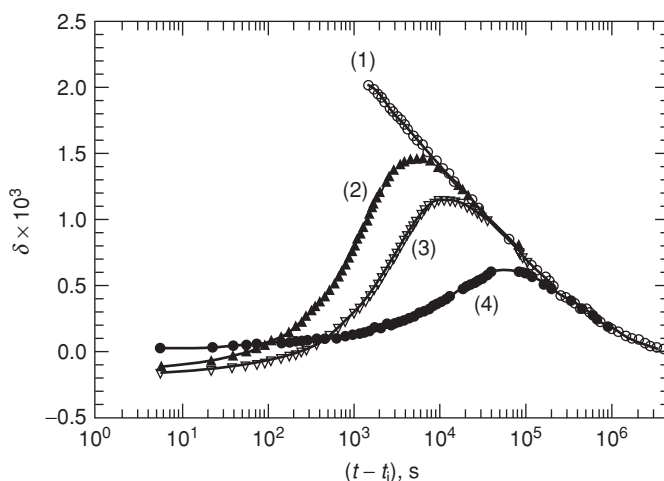


Fig. 5. Isothermal volume relaxation of poly(vinyl acetate) data of Kovacs (replotted after Ref. 9) showing the results of memory experiments. Sample 1 shows the response at 30°C after a quench from 40°C. For samples 2, 3, and 4, the material was initially quenched from 40°C and held at T_1 for a time t_1 before jumping up to T_a of 30°C. Sample 2: $T_1 = 10^\circ\text{C}$ for $t_1 = 160$ h; Sample 3: $T_1 = 15^\circ\text{C}$ for $t_1 = 140$ h; Sample 4: $T_1 = 25^\circ\text{C}$ for $t_1 = 90$ h.

the slowest regions would finally contract to their equilibrium density returning the material to equilibrium volume. Whether this picture is physically correct or not is unclear. However, it is clear that a single exponential relaxation function cannot reproduce the memory effect.

The majority of volume recovery experiments performed to date have been carried out close to the glass transition. The temperature range near T_g is convenient because the entire relaxation is accessible and equilibrium is attainable

in reasonable times. However, glass-forming materials are often used deep in the glassy state. It is unclear whether extrapolation of volume recovery rates to temperatures far below T_g is valid. Recent work (15) on polycarbonate (PC) suggests otherwise. At low aging temperatures, volume recovery appeared to be higher than expected (15). In addition, there was a sharp transition from a slow rate of volume recovery to a much faster aging rate at 10^7 s. The observations have been confirmed qualitatively for polycarbonate but not for polystyrene (PS) (16). The significance of these results and whether current models of structural recovery can predict them is not yet clear.

Enthalpy Recovery

The decrease in enthalpy during physical aging is specifically called *enthalpy recovery* or *enthalpy relaxation*. The enthalpic response of a glass is similar to the volumetric response in that the enthalpy decreases after a down-jump in temperature. The most common way to measure enthalpy relaxation is with differential scanning calorimetry (dsc). However, the evolution of enthalpy cannot be measured *in situ* using dsc because of the small amount of heat given off and the long time scales over which the relaxation occurs. Consequently, the change in enthalpy because of aging is measured after aging for specified times. An explanation of the approach is shown schematically in Figures 6a and b. Enthalpy versus temperature is shown in Figure 6a. The diagram looks similar to that of volume versus temperature. At high temperatures the material is at equilibrium. During cooling from equilibrium, the enthalpy decreases and the molecular mobility of the material decreases. At the glass temperature (T_g), the material is no longer able to maintain equilibrium within the time scale of cooling, and the enthalpy departs from the equilibrium line and moves onto the glass line. The solid curve shows the behavior on cooling. On heating, the dashed curve is observed for an unaged glass, ie, a glass in which no relaxation occurred isothermally in the glassy state or during heating. Some small hysteresis in the vicinity of T_g is observed between the cooling and heating traces. On the other hand, the dash-dot line shows the behavior on heating of an aged glass. Since the aged glass has lower molecular mobility (corresponding to its increased density), the enthalpy often overshoots the equilibrium line during heating such that the rapid increase to equilibrium occurs at a temperature considerably above the glass temperature, as shown. The corresponding heat flow (P) or apparent heat capacity (C_p) for the aged and unaged glasses is shown in Figure 6b. For the unaged material, there is an endothermic step change in the heat flow at T_g (often with a small degree of overshoot). For the aged glass, on the other hand, a significant annealing peak or endothermic overshoot is observed. The difference between the area under the unaged and aged materials is the difference in enthalpy between the glass lines for the unaged and aged glasses (ΔH_a). In traditional dsc, ΔH_a is obtained by performing a temperature scan for an aged glass to obtain the aged response, then quenching the material at a given rate (generally the same rate that was used during the down-jump to T_a), and performing a second temperature scan without aging the material to obtain the unaged response (17). Early suggestions that ΔH_a could also be obtained from the nonreversing heat flow using one heating

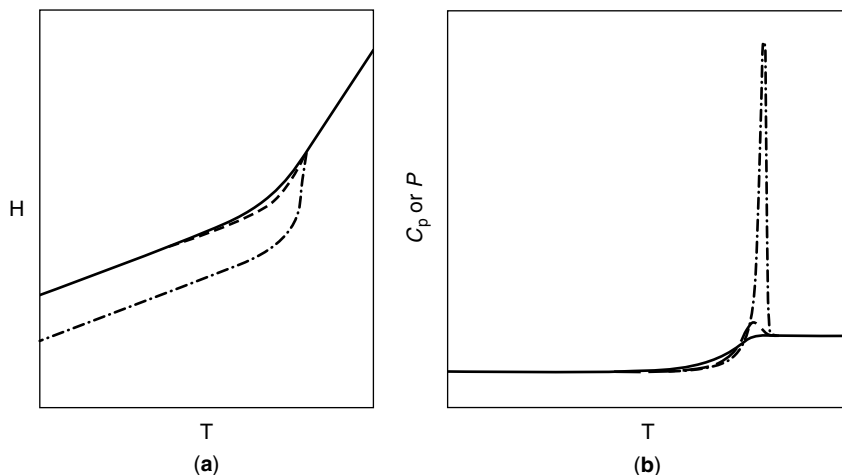


Fig. 6. (a) Schematic of enthalpy vs temperature. The solid line shows the response on cooling from the equilibrium state, whereas the dashed line shows the heating curve for an “unaged” glass in which there is a small hysteresis effect. The dash-dot line shows the heating curve for an “aged” glass; (b) Schematic of heat capacity vs temperature. The solid line shows the response on cooling from the equilibrium state, whereas the dashed line shows the heating curve for an “unaged” glass showing a small overshoot at the nominal glass temperature. The dash-dot line shows the large annealing peak observed in the heating curve for an “aged” glass.

scan with temperature-modulated dsc (18–20) have been shown to not be valid (21,22).

The results of typical dsc heating scans after isothermal aging are shown in Figure 7 for poly(ether imide) (PEI) for various aging times (23). In this case, one sample was used for all experiments, and isothermal aging was performed in the dsc itself. It is noted that if isothermal aging is performed in the dsc, isothermal calibration of the instrument must be performed.

As shown in Figure 7, as the time of aging increases, the overshoot peak temperature shifts to higher temperatures because of the increase in the relaxation time with aging. The area under the peak also increases. When equilibrium is reached, both the peak temperatures and the areas under the peaks stop evolving. Figure 8 shows the evolution of the departure of equilibrium for enthalpy versus the logarithm of time for poly(ether imide) for selected aging temperatures replotted from the data presented in Reference 23. The departure from equilibrium for enthalpy is defined as

$$\delta = \Delta H_{a\infty} - \Delta H_a \quad (4)$$

where $\Delta H_{a\infty}$ is the change in enthalpy at equilibrium. Each data point represents the average of three points. The intrinsic isotherms for enthalpy recovery are analogous to those for volume recovery. The times required to reach equilibrium increase as the aging temperature decreases and the initial departure from equilibrium also increases as the aging temperature decreases. For a perfect quench, the initial departure from equilibrium for enthalpy (δ_0) depends on

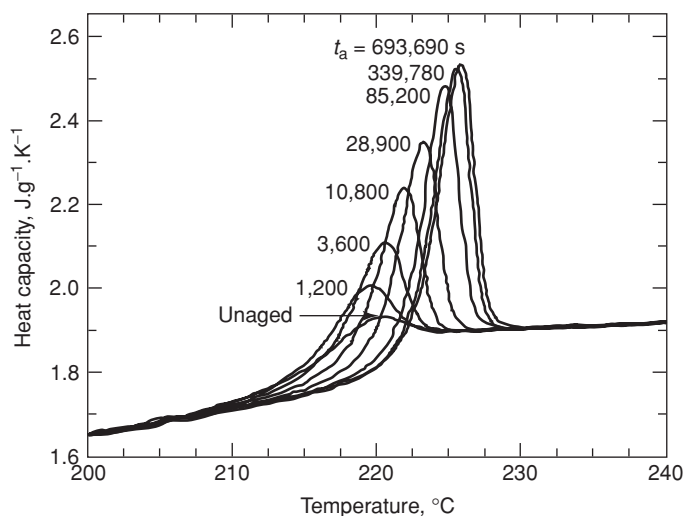


Fig. 7. DSC scans of heat capacity vs temperature for poly(ether imide) after isothermal physical aging at 201.3°C for the various aging times indicated. Scans were made on heating at 10°C/min. The data were corrected to agree with absolute C_p measurements in the liquid state. Data are replotted from Ref. 23.

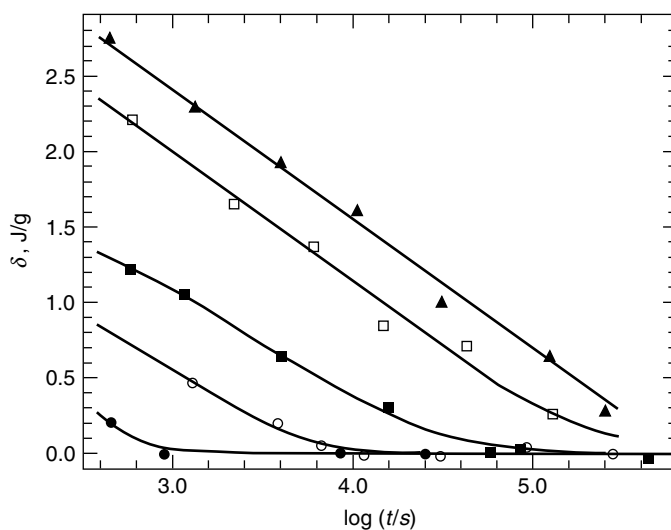


Fig. 8. Relative departure from equilibrium for enthalpy ($\Delta H_\infty - \Delta H_a$) vs the logarithm of aging time for poly(ether imide). Data are replotted from Ref. 23. T_a (°C) = (▲) 201.3, (◻) 202.5, (■) 206.3, (○) 207.5, and (●) 211.3.

the magnitude of the temperature jump through the difference in heat capacity in the liquid $\Delta C_p = C_{pl} - C_{pg}$:

$$\delta_0 = \Delta C_p (T_{i0} - T_a) \quad (5)$$

where T_{f0} is the initial fictive temperature for the enthalpy down-jump and equals the glass temperature associated with the cooling rate used in the quench.

The asymmetry of approach and the memory effect should be observable for enthalpy although the dsc is not convenient for making such measurements. Enthalpy relaxation has been measured *in situ* using an adiabatic calorimeter in isothermal mode and asymmetry of approach data has been obtained by Oguni and co-workers (24,25). An inherent problem with adiabatic calorimetry, however, is the difficulty of the measurements, the large thermal equilibration time, and the drift of the instrument for long-time measurements. It should also be noted that the analysis performed by Oguni et al. on their asymmetry of approach data (24,25) neglected the concept of nonlinearity. The interpretation of their data must be viewed with skepticism for this reason.

Evolution of the Viscoelastic Properties

Corresponding to the changes in volume and enthalpy observed following a temperature down-jump from equilibrium, the viscoelastic properties are also observed to evolve. Changes in the dynamic mechanical properties with time of aging below the glass temperature were first reported in 1963 by Kovacs et al. for poly(vinyl acetate) (26). Subsequently, Struik published his thesis in 1978 in which periodic creep measurements were used to follow the effects of physical aging on the creep compliance (14). Figure 9 is a schematic of the stress, strain, and temperature history for the periodic creep experiment after a down-jump in temperature. The experiment consists of quenching the sample from above T_g to an aging temperature T_a below T_g and applying a load at approximately equal logarithmic increments of aging time (14). Hence, there are two time scales in the experiment: the aging or elapsed time (t_e) which begins at the moment of the quench (but often is taken as the time at which the sample reaches T_a) and the

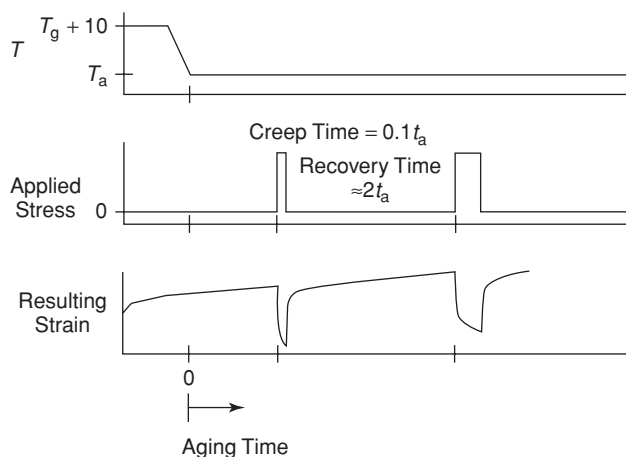


Fig. 9. Schematic of the creep experiment for monitoring physical aging.

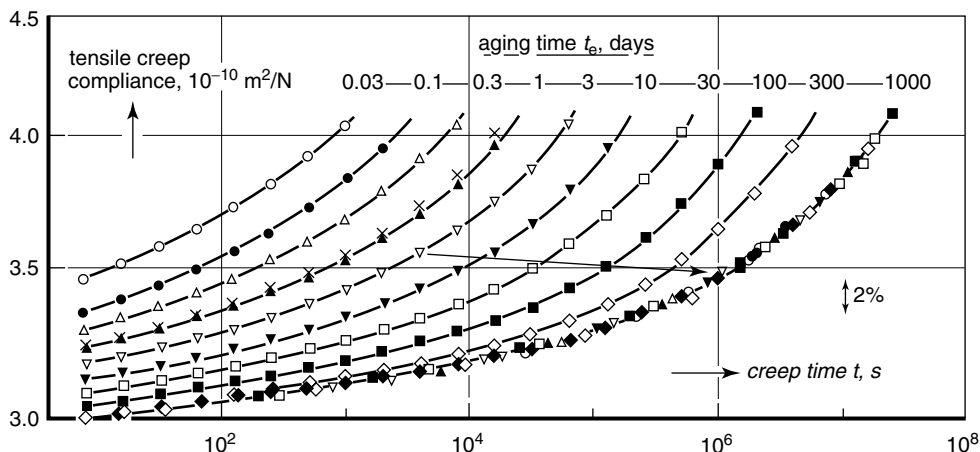


Fig. 10. Small-strain tensile creep curves for rigid poly(vinyl chloride) quenched from 90°C to 20°C and aged at 20 ± 0.1°C for a period of 4 years. The x-axis is the creep time. The times above the curves indicate the aging times at which each individual creep experiment was performed. The reduced curve was obtained by shifting the data to the longest aging time response as indicated by the arrow. The data are from Ref. 14, courtesy of L. C. E. Strvik.

creep time (t) which begins at the moment of loading. Creep times are generally performed for less than 10% of the aging time ($0.1 t_e$) in order to ensure that no appreciable aging occurs during the creep test. Hence, the creep response measured is a “snap shot” of the viscoelastic response at that particular aging time. The time between creep tests generally doubles or triples, allowing sufficient time for creep recovery; the time between measurements should be long enough that the strain change due to creep recovery from one loading is negligible compared to the subsequent loading. The time-dependent viscoelastic response to an up-jump is measured in a similar fashion. Small stresses are used to ensure that the viscoelastic response is linear.

Figure 10 shows the evolution of the creep compliance for poly(vinyl chloride) at 20°C over the course of four years (14). The T_g for poly(vinyl chloride) is around 70°C and so the aging temperature is approximately 50°C below T_g . As the material ages, the creep curves march to longer and longer times, indicating an increase in the characteristic relaxation time as aging progresses. If equilibrium were reached, the response would become independent of aging time (27). In sequential stress relaxation experiments, small strains rather than small stresses can similarly be used to probe the effect of aging on the viscoelastic response. In general, the creep or stress relaxation response due to the applied load or strain is the data analyzed in these experiments as indicated by the creep curves shown in Figure 10. A continuous test data method has recently been suggested, which involves analyzing both load and unload responses for the periodic creep experiment (28). This analysis can potentially yield a more accurate model of the mechanical response (since significantly more data is analyzed); however, the fact that in very few instrumental set-ups the load is actually zero in the unload portion of the experiment must be accounted for.

Time-aging time superposition can generally be used to reduce the curves by shifting them horizontally to superpose. A small vertical shift is sometimes needed as indicated by the slight downward slope of the arrow in Figure 10. The reduced curve is shown at the longest aging time in Figure 10. Struik has maintained that satisfactory time-aging time reduction of data infers that the structural-rheological simplicity is maintained, ie, the retardation spectrum shifts to longer times without a change in shape (14). Time-aging time superpositions have also been performed for poly(vinyl chloride), poly(methyl methacrylate) (PMMA), and polycarbonate creep data obtained by Read and co-workers over fourteen decades in time using several experimental techniques, and the satisfactory reduction of that data in the α -transition region has been interpreted as an indication of structural-rheological simplicity (29–31). On the other hand, Roe and Millman it was found that time-aging time superposition did not work for a polystyrene sample aged for several months at temperatures significantly below T_g and this was attributed to alteration of the shape of the relaxation time spectrum (32). It should be clear that a lack of time-aging time superposition indicates breakdown of structural-rheological simplicity. However, whether time-aging time superposition is sufficient to prove structural-rheological simplicity is less obvious. In order to clarify this point the concepts of time-temperature and time-aging time superpositions are briefly reviewed.

Reduction of linear viscoelastic data is based on the principles of time-temperature and time-aging time superpositions. The principle of time-temperature superposition is widely used to reduce creep or stress relaxation curves obtained at equilibrium density (33,34). The principle implies thermorheological simplicity, ie, the shape of the relaxation time spectrum does not change with temperature although the spectrum shifts to shorter times at higher temperatures. It has been demonstrated, however, that even for what was considered an ideal system, polyisobutylene, time-temperature superposition is not strictly observed (35). In addition, the ability to perform time-temperature superposition should be considered a necessary but not sufficient requirement for thermorheological simplicity because the relatively small experimental time scales over which data is usually obtained, coupled with the uncertainty in the data, leave open the possibility that time-temperature superposition is at best only a good approximation of the behavior over a large time scale. Indeed, it has been shown that although time-temperature superposition appears to be an empirically successful data reduction method for stress relaxation of semicrystalline polypropylene, the reduced stress relaxation curve is not consistent with dynamic mechanical data, and hence cannot be used to predict long-term viscoelastic performance (36). For a more in-depth discussion of time-temperature superposition, the reader is referred to the article on Viscoelasticity.

It is suggested that time-aging time superposition should similarly be considered a necessary but not sufficient requirement for structural-rheological simplicity, particularly since the basis for both shift factors is not well understood. The time-dependent compliance can often be described by

$$J(t) = J_g + J_a \psi(t) + t/\eta \quad (6)$$

where $J(t)$ is the time-dependent creep compliance, J_g refers to the glassy (zero time) compliance, and t is the time of creep. The viscous term (t/η) in equation (6),

where η is viscosity, is generally negligible during physical aging due to the high viscosity of the glass although this is not always the case as is discussed later. J_d in equation (6) is equal to $J_s - J_g$, where J_s is the steady state compliance which is equal to the long-time limiting value of the recoverable compliance for a non-cross-linked system. $\psi(t)$ is the normalized memory function for the compliance, and it goes from $\psi(0) = 0.0$ to $\psi(\infty) = 1.0$. The normalized memory function can often be described using the generalized Kohlrausch–William–Watts (KWW) (37,38) or stretched exponential function:

$$\psi(t) = 1 - e^{-(t/\tau)^\beta} \quad (7)$$

Equation (7) is also only valid for a short-term creep experiment in which the time of creep is short relative to the time scale of aging such that the characteristic relaxation time is constant. It is noted that the relaxation function of equation (7) has the correct limits and differs from the Kohlrausch compliance function ($J = J_s e^{(t/\tau)^\beta}$) which was suggested initially by Struik (14) and which is not physically meaningful at long times (28).

The horizontal and vertical shift factors for reduction of two aging creep curves are defined as

$$\log a_{te} \equiv \log t_{ref} - \log t_1 \quad (8)$$

$$\log b_{te} \equiv \log J(t_{ref}) - \log J(t_1) \quad (9)$$

where $J(t_{ref})$ is the creep compliance at creep time t_{ref} on the reference curve (generally the curve obtained at longest aging times) to which all other curves are being shifted. $J(t_1)$ is the creep compliance at time t_1 which will be shifted to $J(t_{ref})$ and t_{ref} . By definition, the shift factors cannot depend on the creep time at which the shift is performed (ie, on the value of t_{ref}) since for a valid reduced curve the shift factors must be the same for all times along a given creep curve. For structural–rheological simplicity (eg, $\beta = \text{constant}$ in eq. 7), the shift factors are given by those that Struik has reported (14):

$$a_{te} = \tau_{ref}/\tau_1 \quad (10)$$

$$b_{te} = J_{s,ref}/J_{s1} \quad (11)$$

It should be noted that in addition to the criteria of structural–rheological simplicity, equation (11) is valid only when the glassy compliance J_g is negligible relative to the steady-state compliance.

Similarly, the stress relaxation modulus can often be described using the stretched exponential function:

$$G(t) = G_e + (G_g - G_e) e^{-(t/\tau)^\beta} \quad (12)$$

where G_g is the glass (or zero time) value of the modulus and G_e is the equilibrium (long-time) value of the modulus. For viscoelastic liquids, G_e is zero. For structural–rheological simplicity, the horizontal shift factor is given by equation

(10) and the vertical shift factor is given by the following for viscoelastic liquids (39):

$$b_{te} = \frac{G_{gref}}{G_{g1}} \quad (13)$$

When structural–rheological simplicity does not hold and, for example, β in equation (7) changes with physical aging, exact reduction of the creep or stress relaxation curves cannot be accomplished. However, it is estimated by the author that a change in the KWW β parameter of approximately 5–10% would result in a deviation of the logarithm of the aging time shift factor ($\log a_{te}$) of ± 0.05 over two decades in time scale. Scatter in reduced curves of this order of magnitude is often observed because of the scatter in the creep or stress relaxation data (23,39,40). Researchers have not systematically looked for such small deviations in their reduced curves.

In addition, structural–rheological simplicity might not be expected to be perfectly valid since the breadth of the relaxation time distribution is known to change with temperature at equilibrium (41,42) and along the glass line (43). Following a down-jump then, the breadth of the relaxation time distribution at equilibrium may be expected to differ between the initial and final temperatures and part of this change might be expected to occur during physical aging (as opposed to during the quench). A change in β with aging time of the order of 0.01–0.02 for polystyrene close to T_g has been inferred Recently by Ediger et al. (44). Based on the estimation above, such a change appears to be consistent with the majority of creep data in the literature (especially since researchers are not looking for such small deviations from superposition). For example, in a previous work on polycarbonate by McKenna (40) the value of β was observed to be invariant with aging time over the time scales investigated (up to 18 h for temperatures from 111°C below to 6°C below the nominal glass temperature). However, the error in β based on the error in the fit was reported to range from 4 to 7% at 70°C. In addition for two data sets at 135°C, β values equaled 0.47 ± 0.04 and 0.43 ± 0.02 at the longest aging time when a free fit was allowed (45). The point is that small systematic deviations in β may not be easily observable. The ability to obtain time-aging time superposition does not necessarily indicate that the shape of the spectrum is not changing with aging time.

According to equation (11), the vertical shift factor is suggested to be due to changes in the steady-state compliance, J_s , during physical aging. Such changes would arise if the steady-state compliance were temperature-dependent. J_s has been found to be independent of temperature in the range from $1.2 T_g$ to $2.0 T_g$ for several amorphous polymers (46,47). However, in the vicinity of T_g , J_s decreases with decreasing temperature for low molecular weight polystyrenes. (47) In the same work, J_s was predicted to also decrease for polystyrenes of higher molecular weight based on free volume arguments (47). This would suggest that in a down-jump experiment, J_s should decrease with aging time with the result that the vertical shift factors should be negative. Negative vertical shift factors are generally the case although two cases for positive shifts have been reported (14). However, positive vertical shift factors seem not to have a theoretical basis based on all measurements made to date on J_s .

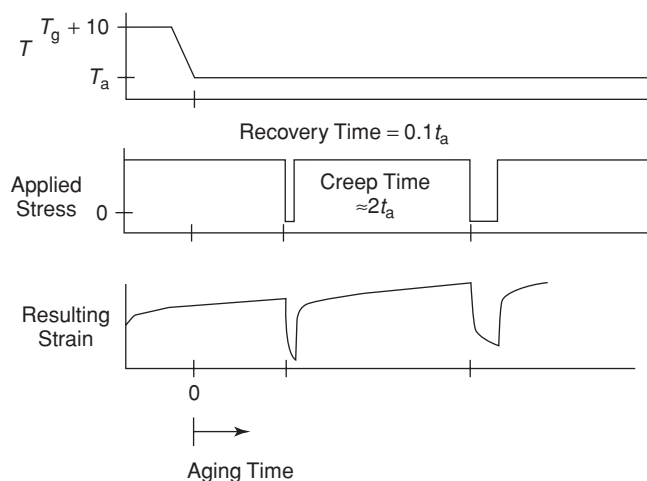


Fig. 11. A schematic of the intermittent creep experiment developed by Bernatz, Giri, Simon, and Plazek (Ref. 48).

In order to measure how the steady-state creep compliance and viscosity evolved during physical aging, a new interrupted creep experiment has been developed by Plazek and co-workers (48). This experiment consists of applying a constant load above T_g for a time long enough to reach steady state. Once in steady state, the material is quenched to the aging temperature T_a while maintaining the constant load. Successive creep-recovery measurements are made at logarithmic time increments. A schematic of the experiment for a temperature down-jump is shown in Figure 11. The rate of creep is monitored until the first creep-recovery measurement when the load is removed. After the first test, the load is reapplied and the creep rate is again monitored to ensure that adequate time has passed before the next measurement. The length of each creep-recovery measurement and the time between subsequent measurements follows the Struik protocol (14) for conventional or periodic creep experiments. The viscosity can be obtained as a function of aging time from the steady-state creep (or quasi steady-state creep for materials in which the steady-state creep compliance is temperature-dependent). The evolution of the steady-state compliance with aging time can be calculated from the horizontal shift factor (assuming β is constant, which should only be considered a first approximation):

$$a_{te} = \frac{\tau_{ref}}{\tau_1} = \frac{\eta_{ref} J_{s_{ref}}}{\eta_1 J_{s_1}} \quad (14)$$

Interpretation of the data from the interrupted creep experiment is based on the assumption that once the material reaches steady-state creep, a change in temperature will not disturb this condition if J_s is independent of temperature. Work by Leaderman on polyisobutylene above T_g (49), as well as Plazek's work on 1,3,5-tri- α -naphthylbenzene (48), indicates this to be the case. Using the interrupted creep test, the evolution of both J_s and η for a polystyrene of 3400

molecular weight have been measured (48). This work confirms that for materials with temperature-dependent J_s , J_s will decrease during physical aging. The interrupted creep experiment may also make it possible to experimentally verify the relationship between the vertical shift factors and J_s .

Effects of Physical Aging on Failure

The most important effect of physical aging, from a practical standpoint, may well be its impact on failure and material lifetime. Physical aging has been found to cause transformation from ductile to brittle failure in many polymers, including poly(ethylene terephthalate) (50–52), polycarbonate (53–55), poly(ether imide) (56), and poly(phenylene oxide) (PPO) (57). In general, physical aging results in a decrease in the time to failure (58), as well as an increase in the yield stress and a decrease in the strain to break (50–57,59–66). A decrease in the impact fracture energy is also generally observed (63,66–69).

The effects of physical aging on craze growth are less clear. It has been found that craze breakdown and ultimate failure are accelerated by physical aging (61) in spite of the fact that the times to craze increase (61,62). However, other researchers found no effect of physical aging on the craze growth rates in polystyrene–polybutadiene diblock copolymers (70) and in polycarbonate (71). Complicating the picture, a transition from a high to low craze growth rate regime at long aging times for low aging temperatures in a styrene–acrylonitrile copolymer has been observed (72). The transition occurred over a narrow aging time window, with craze growth being relatively independent of aging time on either side of the transition. Higher aging temperatures showed only the low craze growth rate regime, leading to speculation that the transition occurred at aging times too short to be measured.

The effects of physical aging on fatigue crack propagation are even less well-documented than the effects on ultimate properties and crazing. Results seem to indicate that fatigue crack propagation depends very little on the degree of physical aging (69,73). The reason for this is suggested to be due to yielding occurring in the plastic zone (73). This is consistent with the fact that the lower yield stress which corresponds to the onset of generalized plastic flow has been observed to also be little affected by physical aging (60).

The Effect of Large Stresses on Physical Aging: Rejuvenation

The effect of large stresses on physical aging are controversial and not completely resolved. The term rejuvenation was coined by McKenna and Kovacs (74) to describe the observation that the aging time shift factor required to superpose large deformation responses was smaller than that required to superpose small deformation responses for the same thermal history. Strvik and others have interpreted this data as erasure of the previous aging by deformation-induced free volume (14,75–79). Other researchers have invoked rejuvenation to explain various observations (64,80). However, McKenna et al. have shown that although mechanical stimuli do induce a short-time volume response, the underlying

volume relaxation is unperturbed by the deformation (81). This is contrary to what would be expected if rejuvenation were the case. In addition, it was found that the time required to reach equilibrium at temperatures near T_g was independent of the applied stress, suggesting that large stresses do not cause erasure of aging (82). It has been argued that the rejuvenation response is simply a result of nonlinear viscoelasticity, ie, the large deformation response is affected less by volume (or enthalpy) changes than in the linear viscoelastic case (83,84). In fact, using the nonlinear viscoelastic Bernstein–Kearsley–Zapas (BKZ) constitutive equation (85) which includes an aging clock that depends upon the deformation magnitude, the rejuvenation response can be reproduced quantitatively without invoking any type of deformation-induced “erasure” effect (86).

There are two alternatives to the rejuvenation hypothesis: mechanical–structural decoupling which much of McKenna’s work suggests (86,87) and the accelerated aging hypothesis suggested some time ago by Sternstein (88). There is some recent evidence of mechanically enhanced aging of polycarbonate (PC) at room temperature (89). Although consistent with Sternstein’s ideas (88), more work is needed to directly test the accelerated aging hypothesis. It is important that this be done, however, in the context of nonlinear viscoelasticity.

Relative Time Scales for Relaxation of Different Properties

There are a number of reports in the literature on the relative time scales of relaxation for different properties (10,23,32,64,65,80,87,90–101) Table 1 summarizes experimental results on polymeric glasses. For nonpolymeric materials, Scherer (102) has summarized the relative values of characteristic equilibrium relaxation times obtained by Moynihan through modeling the relaxation behavior of various properties of low molecular weight glasses, as well as the experimental results of Rekhson on volume and stress relaxation of low molecular weight glasses. The results shown in Table 1 are seemingly contradictory at first glance, with some researchers finding that the time scales are the same for different properties and some groups finding that they differ. The time scale for relaxation is defined differently by different researchers. It has been suggested (10,23,99) that the time required to reach equilibrium may be the best measure of the relaxation time scale in spite of the fact that the relaxation response approaches equilibrium asymptotically. Most of the results reported in Table 1 reflect the relative approach to equilibrium for different properties. The rate of approach can differ for different properties because of differences in thermal history in different measurements and also because of differences in the sensitivity of the properties to the molecular changes associated with physical aging. This is the case even when the time required to reach equilibrium is the same (10,99). Hence, the assertion that the time required to reach equilibrium (rather than some characteristic relaxation time based on the shape of the relaxation response) is the appropriate time scale. McKenna et al. investigated the times required to reach equilibrium, and their results suggested that the relative time scales for stress relaxation and volume recovery depend on the physical aging temperature and the magnitude and direction of the jump from equilibrium to the aging temperature (87,90). On the other hand, the early results of Simon and co-workers on poly(ether imide)

Table 1. Relative Time Scales for Evolution of Various Properties During Structural Recovery for Polymers

Material	Experiments	Findings	Reference
DGEBA ^a /PPO	Volume recovery and evolution of stress relaxation (up- and down-jumps)	Times to reach equilibrium differ: volume is faster in up-jump, slower in down-jump relative to mechanical property.	87,90
DGEBA ^a /DDS ^b	Volume recovery (up- and down-jumps) and creep (equilibrium)	Shift factors for data reduction are the same.	91
PS	Volume and enthalpy recovery	Times to reach equilibrium are the same near T_g ; model calculations predict times to reach equilibrium differ: enthalpy faster than volume.	10
PS	Volume and enthalpy recovery (up- and down-jumps)	Rates of approach to equilibrium are related by a constant for volume and enthalpy.	92
PS	Volume and enthalpy recovery (double temperature jumps)	Times to reach maximum differ: volume is slower than enthalpy.	93
PS	Enthalpy recovery, and room temperature creep evolution (down-jumps)	Times to reach equilibrium differ: enthalpy is faster than mechanical property.	32
PS	Volume and enthalpy recovery (after cooling under pressure)	Times to reach specified percent recovery differ: volume is faster relative to enthalpy.	95
PMMA	Volume and enthalpy recovery (after cooling under pressure)	Times to reach specified percent recovery differ: volume is slower relative to enthalpy.	95
PMMA	Volume and enthalpy recovery, and dynamic mechanical analysis (down-jumps)	Decay functions differ: enthalpy is fastest, followed by volume, followed by mechanical property.	96
PMMA	Enthalpy recovery, and stress relaxation (down-jumps)	Model parameters for enthalpy relaxation comparable to experimental stress relaxation times.	97
PVAc	Volume and enthalpy recovery (down-jumps), dynamic mechanical analysis and dielectric analysis (equilibrium)	Equilibrium relaxation times obtained from modeling data differ: largest for enthalpy, smallest for mechanical property.	94
PVAc	Volume and enthalpy recovery (down-jumps)	Effective retardation times differ: smaller for volume relative to enthalpy.	98

Table 1. (Continued)

Material	Experiments	Findings	Reference
PVAc	Volume and dynamic mechanical analysis (up- and down-jumps)	Relaxation time from fit is smaller for volume than mechanical property on down-jump; activation energy is larger for volume.	80
PVAc	Volume, enthalpy recovery, and stress relaxation (down-jumps)	Mechanical property reaches equilibrium while volume and enthalpy are still evolving.	100,101
PEI	Enthalpy and volume recovery and creep evolution (down-jumps)	Times to reach equilibrium are the same but volume relaxes faster initially relative to enthalpy.	23,99
PC	Enthalpy recovery, creep, and yield (down-jumps)	Rate of change of enthalpy and creep are different; equilibrium is not reached.	64
PI	Enthalpy recovery and creep evolution (down-jumps)	Relaxation times from fit of data are longer for enthalpy than for creep.	65

^aDGEBA: diglycidyl ether of bisphenol A.

^bDDS.: 4,4'-diamino diphenyl sulfone.

indicated that the time required to reach equilibrium for volume, enthalpy, and creep were identical (23,99). Subsequent experiments on polystyrene found that time scales to reach equilibrium were again the same for volume and enthalpy at temperatures where equilibrium was reached (10). However, model extrapolations to lower temperatures indicate that the relaxation times for enthalpy diverge from those of volume, and are shorter. The divergence might be dismissed as being due to problems with the model (see later on the TNM model and problems associated therewith), if it were not for the fact that our most recent data on the glass former selenium appears to show the divergence for temperatures at which equilibrium was reached (103). Figure 12 shows the times required to reach equilibrium as a function of the distance from the glass temperature (with T_g defined at 0.2°C/min) for polystyrene, poly(ether imide), and selenium. The selenium data is offset from the polystyrene and poly(ether imide) data because the temperature dependence of the times required to reach equilibrium differs. The symbols are the measured times required to reach equilibrium, whereas the dashed lines are the times required to reach equilibrium based on extrapolations using the Tool–Narayanaswamy–Moynihan (TNM) model for polystyrene and using a linear extrapolation for selenium (which is expected to give a lower bound for the time required to reach equilibrium). At temperatures in the vicinity of T_g all three properties appear to come to equilibrium at the same time within the scatter of the data. At lower temperatures, the times required to reach equilibrium appear to diverge for the various properties, with enthalpy reaching equilibrium before volume and creep. The divergence appears to occur closer to T_g for selenium than for polystyrene. Although the origin of the divergence in time

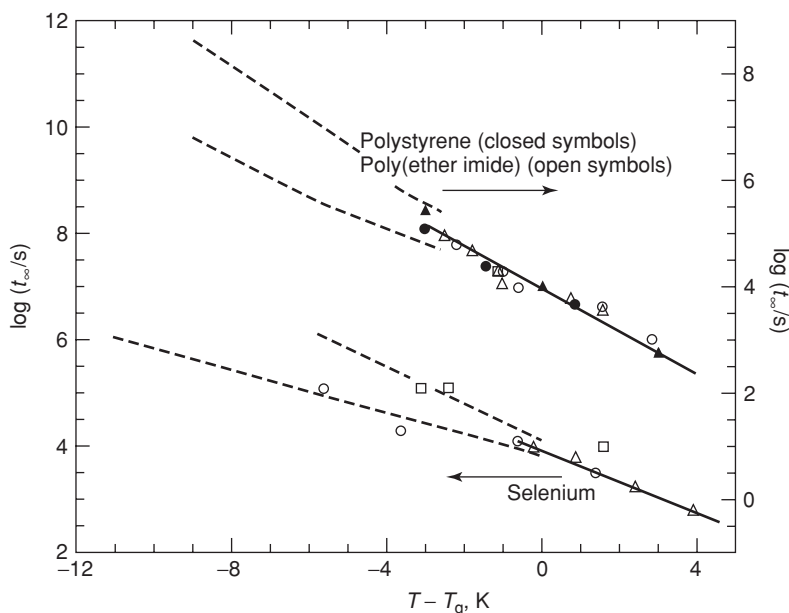


Fig. 12. The times required to reach equilibrium for polystyrene, poly(ether imide), and selenium vs the departure from T_g , where T_g is defined as the value obtained dilatometrically on cooling at $2^\circ\text{C}/\text{min}$. Data are replotted from Refs. 10, 23, 99, and 103 $\blacktriangle$ & $\triangle$ Volume, $\square$ Creep, and $\bullet$ & $\circ$ Enthalpy.

scales is not known, it appears that this general framework is consistent for the three materials which we have studied and with the other data in the literature. We note that other researchers (80) have claimed a difference in activation energies for the characteristic relaxation time obtained from a fit of the stretched exponential to the relaxation data, resulting in a picture similar to what we observe but for the characteristic relaxation time. The two pictures are consistent; the primary difference is that we suggest that the time required to reach equilibrium is a better parameter of the time scale because it is less influenced by magnitude of the temperature jump and the resulting shape of the relaxation response.

Temperature Dependence of the Relaxation Time at Equilibrium

The temperature dependence of the characteristic relaxation time is described by the (Williams–Landell–Ferry) (WLF) equation (104), or the equivalent Vogel–Tammann–Hesse–Fulcher (VTHF) (105–107) expression. These equations are valid from the nominal glass temperature to approximately $100\text{--}150^\circ\text{C}$ above T_g . Far above the glass temperature, the temperature dependence decreases and becomes Arrhenius or follows a different WLF dependence (108). The temperature dependence of the relaxation time along the glass line below T_g is known to

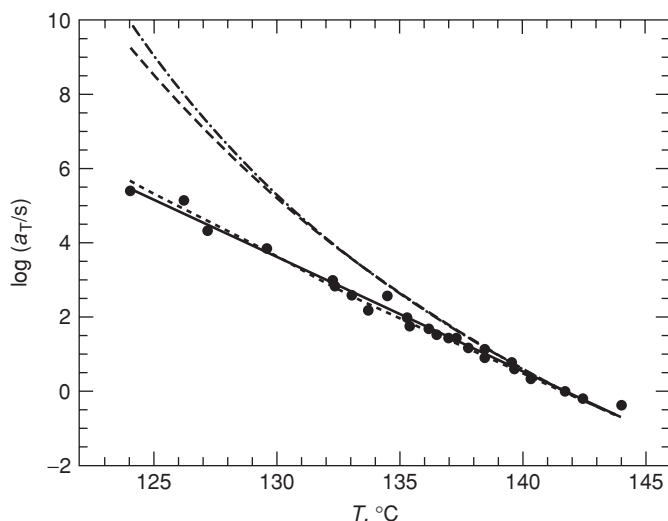


Fig. 13. The temperature dependence of the shift factors for stress relaxation of polycarbonate obtained at equilibrium. The data shows a significant deviation from the expected WLF temperature dependence; the dashed and dash-dot lines are the “universal” WLF temperature dependence and that which fits the polycarbonate data above T_g . The data are replotted from the data of Ref. 39. —●— Experimental data and linear fit, --- WLF ($C_1 = 17.44$, $C_2 = 51.66$ K, $T_{\text{ref}} = 142^\circ\text{C}$), -.-.- WLF ($C_1 = 14.42$, $C_2 = 43.97$ K, $T_{\text{ref}} = 142^\circ\text{C}$), and WLF ($C_1 = 49.71$, $C_2 = 174.6$ K, $T_{\text{ref}} = 142^\circ\text{C}$).

deviate from WLF behavior and follows what appears to be Arrhenius temperature dependence with a very low activation energy (14). What is not as well-known, however, is that below the glass temperature, the temperature dependence of the equilibrium relaxation time also appears to deviate from the WLF relationship with a lower apparent activation energy than expected based on extrapolation of the WLF equation.

The first convincing data depicting the change from WLF to an Arrhenius-type temperature dependence for the equilibrium relaxation time at T_g is the work on polycarbonate by O'Connell and McKenna in which equilibrium was reached at temperatures 17°C below the nominal glass temperature (109). This data is shown in Figure 13. Similar results were found for polystyrene (10). Similar behavior might be interpreted from earlier works on various organic liquids (110,111), although it is not clear in the early work that the measurements reported are all equilibrium measurements or that the reported Vogel fits are correct since in one case (111) T_∞ was very near T_g . Recent theoretical work by Di Marzio and Yang (112) predicts a change in the temperature dependence of the equilibrium relaxation time at T_g from WLF-type dependence to an Arrhenius temperature dependence. The non-WLF temperature dependence below T_g for the equilibrium state has major implications for modeling and predicting the effects of structural recovery, especially for aging deep in the glassy state, since knowledge of the value of the relaxation time at equilibrium is critical for accurate predictions.

Physical Aging in Semicrystalline Polymers

The effects of structural recovery are not limited to fully amorphous materials. In semicrystalline polymers, the amorphous regions physically age in a similar manner to the process in fully amorphous materials. Obviously, however, the change in properties will be only a fraction of that found in fully amorphous materials since the amount of amorphous material makes up only a fraction of the semicrystalline material. One difference between aging in semicrystalline materials and fully amorphous materials, however, is the temperature range over which physical aging is observed. In amorphous materials, aging occurs only below the time or frequency dependent glass temperature, whereas in semicrystalline materials, physical aging has been observed at temperatures above the nominal T_g (14,113–118). The explanation is that the crystalline domains constrain the glass in the vicinity of the crystallite, increasing its T_g , and thereby increasing the temperatures at which physical aging is observed (113–116). However, above T_g secondary crystallization and/or crystal reorganization can take place. Results for physical aging of syndiotactic polystyrene above T_g suggest that in contrast to many semicrystalline polymers, the recrystallization phenomenon is the primary mechanism for physical aging above T_g (118).

Modeling Structural Recovery

Models of structural recovery include the Kovacs–Aklonis–Hutchinson–Ramos (KAHR) model (119), Moynihan's model (120), and Ngai's coupling model (121). These models are based on work done originally by Narayanaswamy (122), incorporating the ideas of Tool (13). The models of structural recovery reflect the nonlinear and nonexponential effects observed experimentally. The historical development of these equations has been detailed (7,8); only a brief description follows. The KAHR formulation (119), which is written in terms of a departure from equilibrium δ rather than in terms of T_f , is conceptually easier to use when the full three-dimensional PVT surface is considered:

$$\delta = \int_0^t \frac{d\delta}{dt} \exp \left[- \left(\int_{t'}^t \frac{dt''}{\tau} \right)^\beta \right] dt' \quad (15)$$

where for volume the departure from equilibrium is given by the definition in equation (1), whereas for enthalpy, the definition in equation (4) is used. τ is known as the characteristic relaxation time (although it is actually a retardation time), β is the nonexponentiality or stretching parameter, and $d\delta/dt$ is the rate of change of δ in arbitrary pressure or temperature histories:

$$\frac{d\delta}{dt} = \left(\frac{\partial \delta}{\partial P} \right)_T \frac{dP}{dt} + \left(\frac{\partial \delta}{\partial T} \right)_P \frac{dT}{dt} \quad (16)$$

For the case of isobaric temperature jumps or isothermal pressure jumps, these equations revert to the KAHR equations for volume recovery using

$(d\delta/dP)_T = -\Delta\kappa$ and $(d\delta/dT)_P = \Delta\alpha$. $\Delta\kappa$ is the difference in the compressibilities of the liquid and glass at T_g . For enthalpy recovery, $(d\delta/dP)_T = VT\Delta\alpha$ and $(d\delta/dT)_P = \Delta C_p$.

The nonexponentiality of the structural recovery process is described by the nonexponentiality parameter β in equation (15); the history dependence is accounted for by the integral of the reduced time (dt/τ) ; and the nonlinearity is incorporated into the model by allowing the characteristic relaxation time τ to be a function of temperature, pressure, and structure, the latter of which is often characterized by the fictive temperature (T_f), the fictive pressure (P_f), or the departure from equilibrium (δ). The fictive temperature is defined as the temperature at which a material would reach equilibrium if heated (or cooled) along the glass line. It is related to δ at constant pressure through the difference between the liquid and glass thermal expansion coefficients ($\Delta\alpha$) for volume and through the difference between the liquid and glass heat capacities (ΔC_p) for enthalpy:

$$T_f = T_a + \frac{\delta}{\Delta\alpha} \quad \text{for volume recovery} \quad (17)$$

$$T_f = T_a + \frac{\delta}{\Delta C_p} \quad \text{for volume recovery} \quad (18)$$

Hence, at equilibrium, the fictive temperature is equal to the aging temperature. The fictive pressure has an analogous definition with respect to glass and liquid lines in pressure space.

Various phenomenological equations have been used to describe the dependence of the characteristic relaxation time on temperature and structure and sometimes pressure, including the TNM equation (120), equations derived by Hodge (123) and Scherer (124), both based on the approach of Adam and Gibbs (125), the KAHR and similar equations (119,126), equations based on free volume, and several others (127,128). The essential idea in all of these equations is that the characteristic relaxation time depends on the instantaneous state of the material (ie, temperature, pressure, and some measure of structure—volume, δ , T_f , and/or P_f). The most widely used form is the TNM equation for isobaric structural recovery:

$$\ln \tau_0 = \ln A + \frac{x\Delta h}{T} - \frac{(1-x)\Delta h^*}{T_f} \quad (19)$$

where x partitions the effects of temperature and structure and determines the degree of nonlinearity, and Δh^* and A are constants. Although this equation is unable to describe the observed WLF (104) or the equivalent VTHF (105–107) temperature dependence in the equilibrium limit when $T_f = T$, it is often thought to be a valid approximation to the narrow range of temperature over which data is modeled. Although this may be the case for modeling isothermal structural relaxation data, this assumption is suspect for modeling dsc temperature scans. To accurately model the poly(ether imide) data shown in Figure 8, the dependence of the characteristic relaxation time is needed as a function of structure and

temperature from 201°C (where aging took place) to 230°C where the enthalpy overshoot returns to the baseline. The linear approximation of equation (19) is not valid over this temperature range above T_g (207°C) where the WLF equation is valid, let alone below T_g where the temperature dependence of the equilibrium relaxation time is expected to change (10,109). Consistent with the fact that equation (19) is not a valid representation over the range of temperatures of interest when modeling dsc temperature scans, Schick and co-workers (129) have recently found that description of the loss and storage heat capacity obtained from slow temperature-modulated dsc cooling scans could only be done well by using an equation based on Adam and Gibbs which is consistent with WLF behavior above T_g .

There are unresolved issues pertaining to the models, including an apparent dependence of model parameters on thermal history and an inability to predict structural recovery for deep quenches (5,7,8,130–138). Simple fixes have been found not to resolve these problems (5,133,136,138,139). To make rational improvements to the models and to determine what “essential ingredients” (140) are needed to predict structural recovery, systematic investigation of model assumptions is now needed. The basic assumptions underlying current models of structural recovery include (1) thermorheological simplicity, (2) structural–rheological simplicity, (3) the assumption that the placement of the relaxation time spectrum on the time scale (ie, the mobility) depends only on the instantaneous state of the glass, and (4) the assumption that the relationship between glassy structure and temperature and pressure history can be described using Boltzmann superposition in a way that is analogous to viscoelasticity.

In contrast to the KAHN, TNM, and Ngai models of structural recovery, which were developed based on extending the formalism developed for viscoelasticity and an understanding of the relationship between the volume (or enthalpy) relaxation kinetics and the volume (or enthalpy), the thermoviscoelastic model developed in Caruthers's group at Purdue (141) is based on Coleman's thermodynamic theory, also known as rational mechanics (142,143). It is one of the first advances in the development of equations to describe structural recovery to appear in about 20 years (144). Caruthers's model begins with a free energy functional which is differentiated to obtain the time- and path-dependent nonequilibrium thermodynamic functions. The thermoviscoelastic constitutive model is the only theory which can qualitatively describe structural recovery, yield in tension and compression, multiaxial yield, nonlinear creep and stress relaxation, and constant rate of cooling isobaric studies with a single set of material parameters which can be independently obtained (145). The model is covered in detail in the Viscoelasticity article of this encyclopedia.

Of particular importance to structural recovery models is the idea that the apparent mobility may depend on the temperature/pressure/stress path rather than on the instantaneous state of the material. This differs from all of the phenomenological equations for the characteristic relaxation time, including equation (19), which are presently used in other models of structural recovery. The dependence of the relaxation on the unique state has been investigated by Strvik (146), and although it was claimed that the relaxation time only appeared to depend on the instantaneous volume, there is considerable scatter in the data and the relationship appears to depend not only on the final aging temperature but

also on the sample history (ie, the magnitude of down- and double-temperature jumps). The scatter may be due to the measurements of volume and relative relaxation time being made in separate instruments such that the thermal history of the samples were not identical. Alternatively, it may be an indication of a more complicated relationship between the characteristic relaxation time and the instantaneous state as Caruther's model suggests.

Current Challenges in Physical Aging Research

One of the greatest unsolved challenges in physical aging research is understanding the relationship between the evolution of various properties, including failure, and the ability to predict time-dependent properties from limited data over, for example, the lifetime of a material. We are not at the point yet where we can predict changes in thermodynamic properties from one another, let alone predict mechanical behavior from thermodynamic variables. Issues such as whether spectral shape changes during physical aging, how to correctly incorporate non-linearity into the models of structural recovery, and how many ordering parameters exist are also not resolved.

Part of our problem lies in the absence of a universally accepted theory of the glass transition itself. For this reason, the interpretation and modeling of experimental results takes place within a weak theoretical framework. It is important that the fundamental questions associated with the glass transition be addressed, including, but not limited to, the assumptions underlying the Adam–Gibbs theory, the ability to calculate the configurational entropy, and the existence or lack thereof of an underlying thermodynamic glass transition.

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ALKYD RESINS

Introduction

Although no longer the largest volume vehicles in coatings, alkyds still are of major importance. Alkyds are prepared from polyols, dibasic acids, and fatty acids. They are polyesters, but in the coatings field the term polyester is reserved for “oil-free polyesters.” The term *alkyd* is derived from *alcohol* and *acid*. Alkyds tend to be lower in cost than most other vehicles and tend to give coatings that exhibit fewer film defects during application. However, durability of alkyd films, especially outdoors, tends to be poorer than films from acrylics, polyesters, and polyurethanes.

There are several types of alkyds. One classification is into *oxidizing* and *nonoxidizing* types. Oxidizing alkyds cross-link by the same mechanism as drying oils. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxy-functional resins, which are cross-linked by melamine–formaldehyde (MF), by urea–formaldehyde (UF) resins, or by isocyanate cross-linkers. A second classification is based on the ratio of monobasic fatty acids to dibasic acids utilized in their preparation. The terminology used was adapted from terminology used to classify varnishes. Varnishes with high ratios of oil to resin were called *long oil varnishes*; those with a lower ratio, *medium oil varnishes*; and those with an even lower ratio, *short oil varnishes*. Oil length of an alkyd is calculated by dividing the amount of “oil” in the final alkyd by the total weight of the alkyd solids, expressed as a percentage, as shown in equation (1). The amount of oil is defined as the triglyceride equivalent to the amount of fatty acids in the alkyd. The 1.04 factor in equation (2) converts the weight of fatty acids to the corresponding weight of triglyceride oil. Alkyds with oil lengths greater than 60 are *long oil alkyds*; those with oil lengths from 40 to 60, *medium oil alkyds*, and those with

oil lengths less than 40, *short oil alkyds*. There is some variation in the dividing lines between these classes in the literature.

$$\text{Oil Length} = \frac{\text{Weight of Oil}}{\text{Weight of Alkyd} - \text{Water Evolved}} \times 100 \quad (1)$$

$$\text{Oil Length} = \frac{1.04 \times \text{Weight of Fatty Acids}}{\text{Weight of Alkyd} - \text{Water Evolved}} \times 100 \quad (2)$$

Another classification is *unmodified* or *modified alkyds*. Modified alkyds contain other monomers in addition to polyols, polybasic acids, and fatty acids. Examples are styrenated alkyds and silicone alkyds. Since they are closely related to alkyd resins, uralkyds and epoxy esters are also discussed.

Oxidizing Alkyds

Oxidizing alkyds can be considered as synthetic drying oils. They are polyesters of one or more polyols, one or more dibasic acids, and fatty acids from one or more drying or semidrying oils.

Film Formation. Most of the studies of the chemistry of cross-linking have been with drying oils and not the alkyds derived from them, but the mechanisms are applicable to both. Films exposed to air undergo autoxidative cross-linking. In nonconjugated unsaturated oils, the active group initiating drying is the diallylic group ($-\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}-$) from esters of (*Z,Z*)-9,12-octadecadienoic acid [60-33-3] (linoleic acid) and (*Z,Z,Z*)-9,12,15-octadecatrienoic acid [463-40-1] (linolenic acid). They have one and two diallylic groups per molecule, respectively. Drying is related to the average number of diallylic groups per molecule. If this number is greater than about 2.2, the oil is a drying oil and if it is moderately below 2.2, the oil is a semidrying oil; there is no sharp dividing line between semidrying oils and nondrying oils. Since diallylic groups are the sites for cross-linking, it is convenient to relate the average number of such groups per molecule to the number average functionality $\bar{f}_n$ of the triglyceride or synthetic drying oil. It is probable that some of the sites are involved in more than one cross-linking reaction.

The methylene groups are activated by their allylic relationship to two double bonds and are much more reactive than methylene groups allylic to only one double bond. The $\bar{f}_n$ of a typical linseed oil is 3.6; it is a drying oil. The $\bar{f}_n$ of a typical soybean oil is 2.07; it is a semidrying oil. The higher the $\bar{f}_n$ of a drying oil, the more rapidly a solvent-resistant, cross-linked film forms on exposure to air.

The reactions taking place during drying are complex. Cross-linked films form from linseed oil in the following stages: (1) an induction period during which naturally present antioxidants (mainly tocopherols) are consumed, (2) a period of rapid oxygen uptake with a weight gain of about 10% (ftir shows an increase in hydroperoxides and appearance of conjugated dienes during this stage), and (3) a complex sequence of autocatalytic reactions in which hydroperoxides are consumed and cross-linked film is formed. In one study, steps 1, 2, and 3 were

far along in 4, 10, and 50 h, respectively, when catalyzed by a drier (1). Cleavage reactions to form low molecular weight by-products also occur during the latter stages of film formation. Slow continuing cleavage and cross-linking reactions through the lifetime of the film lead to embrittlement, discoloration, and slow formation of volatile by-products. Oils with significant quantities of fatty acids with three double bonds, such as linolenic acid, discolor to a particularly marked degree.

When a film is applied, initially naturally present hydroperoxides decompose to form free radicals. At first, these highly reactive free radicals react mainly with the antioxidant, but as the antioxidant is consumed, the free radicals react with other compounds. Hydrogens on methylene groups between double bonds are particularly susceptible to abstraction, yielding a resonance-stabilized free radical that reacts with oxygen to give predominantly conjugated peroxy free radicals. The peroxy free radicals can abstract hydrogens from other methylene groups between double bonds to form additional hydroperoxides and generate free radicals. Thus, a chain reaction is established, resulting in autoxidation. At least part of the cross-linking occurs by radical-radical combination reactions forming C-C, ether, and peroxide bonds. These reactions correspond to termination by combination reactions in free-radical chain-growth polymerization. Reactions analogous to the addition step in chain-growth polymerization could also produce cross-links.

Studies of the reactions of ethyl linoleate with oxygen in the presence of driers by ^1H and ^{13}C nmr showed that the predominant cross-linking reactions were those that formed ether and peroxy cross-links (2,3). Mass spectroscopic studies showed that only about 5% of the cross-links were new C-C bonds (2). Substantial levels of epoxy groups were detected in the reaction mixture, rising to a maximum in about 5 days and virtually disappearing in 100 days; it is suggested that epoxy groups may react with carboxyl groups to form ester cross-links.

Rearrangement and cleavage of hydroperoxides to aldehydes and ketones, among other products, lead to low molecular weight by-products. The characteristic odor of oil and alkyd paints during drying is attributable to such volatile by-products, as well as to the odor of organic solvents. Undesirable odor has been a factor motivating replacement of oil and alkyds in paints with latex, particularly for interior applications. The reactions leading to these odors have been extensively studied in connection with flavor changes of vegetable cooking oils (4). Aldehydes have been shown to be major by-products from the catalyzed autoxidation and from curing of drying-oil-modified alkyd resins (2,5). It has also been shown that C_9 acid esters remain in the nonvolatile reaction mixture (5).

Dried films, especially of oils with three double bonds, yellow with aging. The yellow color bleaches significantly when exposed to light; hence, yellowing is most severe when films are covered, such as by a picture hanging on a wall. The reactions leading to color are complex and are not fully understood. Yellowing has been shown to result from incorporation of nitrogen compounds and is markedly increased by exposure to ammonia. It has been proposed that ammonia reacts with 1,4-diketones formed in autoxidation to yield pyrroles, which oxidize to yield highly colored products (6).

The rates at which uncatalyzed nonconjugated drying oils dry are slow. Many years ago, it was found that metal salts (driers) catalyze drying. The most

widely used driers are oil-soluble cobalt, manganese, lead, zirconium, and calcium salts of octanoic or naphthenic acids. Salts of other metals, including rare earths, are also used. Cobalt and manganese salts, so-called top driers or surface driers, primarily catalyze drying at the film surface. Lead and zirconium salts catalyze drying throughout the film and are called through driers. The surface-drying catalysis by cobalt and manganese salts results from the catalysis of hydroperoxide decomposition. The cobalt cycles between the two oxidation states. The activity of through driers has not been adequately explained.

Combinations of metal salts are almost always used. Mixtures of lead with cobalt and/or manganese are particularly effective, but as a result of toxicity control regulations, lead driers can no longer be used in consumer paints sold in interstate commerce in the United States. Combinations of cobalt and/or manganese with zirconium, frequently with calcium, are commonly used. Calcium does not undergo redox reactions; it has been suggested that it may promote drying by preferentially adsorbing on pigment surfaces, minimizing adsorption of active driers. The amounts of driers needed are system specific. Their use should be kept to the minimum possible level, since they not only catalyze drying but also catalyze the reactions that cause post-drying embrittlement, discoloration, and cleavage.

Oils containing conjugated double bonds, such as tung oil, dry more rapidly than any nonconjugated drying oil. Free-radical polymerization of the conjugated diene systems can lead to chain-growth polymerization, rather than just a combination of free radicals to form cross-links. High degrees of polymerization are unlikely because of the high concentration of abstractable hydrogens acting as chain-transfer agents. However, the free radicals formed by chain transfer also yield cross-links. In general, the water and alkali resistance of films derived from conjugated oils are superior, presumably because more of the cross-links are stable carbon-carbon bonds. However, since the (*E,Z,E*)-9,11,13-octadecatrienoic acid [506-23-0] (α -eleostearic acid) in tung oil has three double bonds, discoloration on baking and aging is severe.

The most commonly used polyol in preparing alkyds is 1,2,3-propanetriol [56-81-5] (glycerol), the most commonly used dibasic acid is 1,3-isobenzofurandione [85-44-9] (phthalic anhydride) (PA), and a widely used oil is soybean oil. Let us consider a simple, idealized example of the alkyd prepared from 1 mol of PA, 2 mol of glycerol, and 4 mol of soybean fatty acids. A typical fatty acid composition data for soybean oil is as follows: saturated fatty acids [hexadecanoic acid [57-10-3] (palmitic acid) and octadecanoic acid [57-11-4] (stearic acid)], 15%; (*Z*)-9-octadecenoic acid [112-80-1] (oleic acid), 25%; linoleic acid, 51%; and linolenic acid, 9%. Any oil with an f_n higher than 2.2 is a drying oil. Although soybean oil is a semidrying oil, this alkyd would have an f_n of 2.76 per molecule and, therefore, would dry to a solid film. The alkyd would form a solvent-resistant film in about the same time as a 2,2-bis(hydroxymethyl)-1,3-pentanediol [115-77-5] (pentaerythritol), ester of soybean fatty acids, since they have the same f_n . However, the alkyd would form a tack-free film faster because the rigid aromatic rings from PA increases the T_g of the film.

If the mole ratio of PA to glycerol were 2 to 3, 5 mol of soybean fatty acid could be esterified to yield an alkyd with an f_n of 3.45. This alkyd would cross-link more rapidly than the 1:2:4 mole ratio alkyd and would also form tack-free films

even faster because the ratio of aromatic rings to long aliphatic chains would be 2:5 instead of 1:4. As the ratio of PA to glycerol is increased further, the average functionality for autoxidation increases and the T_g after solvent evaporation increases because of the increasing ratio of aromatic to long aliphatic chains. For both reasons, films dry faster.

A theoretical alkyd prepared from 1 mol each of glycerol, PA, and fatty acid would have an oil length of about 60. However, if one were to try to prepare such an alkyd, the resin would gel prior to complete reaction. Gelation would result from reaction of a sufficient number of trifunctional glycerol molecules with three difunctional PA molecules to form cross-linked polymer molecules, swollen with partially reacted components. Gelation can be avoided by using a sufficient excess of glycerol to reduce the extent of cross-linking. When the reaction is carried to near completion with excess glycerol, there are few unreacted carboxylic acid groups, but many unreacted hydroxyl groups.

There have been many attempts, none fully successful, to calculate the ratios of functional groups and the extent of reaction that can be reached without encountering gelation. The problem is complex. The reactivity of the hydroxyl groups can be different; for example, glycerol contains both primary and secondary alcohol groups. Under esterification conditions, polyol molecules can self-condense to form ethers and, in some cases, can dehydrate to form volatile aldehydes. Reactivity of the carboxylic acids also varies. The rate of formation of the first ester from a cyclic anhydride is more rapid than formation of the second ester. Aliphatic acids esterify more rapidly than aromatic acids. Polyunsaturated fatty acids and their esters can dimerize or oligomerize to form cross-links. The dimers form by a mechanism similar to that encountered in the drying of the oils. Of the many papers in the field, that by Blackinton recognizes the complexities best (7). In addition to the above complexities, particular emphasis is placed on the extent of formation of cyclic compounds by intramolecular esterification reactions. Equations have been developed that permit calculation of ratios of ingredients theoretically needed to prepare an alkyd of any desired oil length, number-average molecular weight, and hydroxy content (8). Just like in other equations, the important effect of dimerization of fatty acids is not included as a factor in these equations. In practice, alkyd resin formulators have found that the mole ratio of dibasic acid to polyol should be less than 1 to avoid gelation. How much less than 1 depends on many variables.

For medium oil alkyds, the ratio of dibasic acid to polyol is not generally changed much relative to alkyds with an oil length of about 60, but the fatty acid content is reduced to the extent desired. This results in a larger excess of hydroxyl groups in the final alkyd. It is commonly said that as the oil length of an oxidizing alkyd is reduced below 60, the drying time decreases to a minimum at an oil length of about 50. However, this conventional wisdom must be viewed cautiously. The ratio of aromatic rings to aliphatic chains continues to increase, increasing T_g after the solvent evaporates from the film tending to shorten the time to form a tack-free film. However, at the same molecular weight, the number of fatty acid ester groups per molecule decreases as the oil length decreases below 60, since more hydroxyl groups are left unesterified. Therefore, the time required to achieve sufficient cross-linking for solvent resistance increases.

Long oil alkyds are soluble in aliphatic hydrocarbon solvents. As the oil length decreases, mixtures of aliphatic and aromatic solvents are required, and oil lengths below about 50 require aromatic solvents, which are more expensive than aliphatics. The viscosity of solutions of long oil alkyds, especially of those with oil lengths below 65, is higher in aliphatic than in aromatic solvents; in medium oil alkyds, which require mixtures of aliphatic and aromatic solvents, viscosity decreases as the proportion of aromatic solvents increases. In former days, and to some extent still today, it was considered desirable to use a solvent mixture that gave the highest possible viscosity; then, at application viscosity, the solids were lower and the raw material cost per unit volume was less. Accordingly, alkyds were designed to have high dilutability with aliphatic solvents. This was false economy, but it was a common practice and is still being practiced to some extent. Increasingly, the emphasis is on reducing volatile organic compounds (VOC) and so the question becomes how to design alkyds with low solvent requirements rather than high dilutability potential. Furthermore, the aromatic solvents are on the hazardous air pollutants (HAP) list. High solids alkyds are discussed in a later section.

Monobasic Acid Selection. Drying alkyds can be made with fatty acids from semidrying oils, since the $\bar{f}_n$ can be well above 2.2. For alkyds made by the monoglyceride process, soybean oil is used in the largest volume. Soybean oil is economical and supplies are dependable because it is a large-scale agricultural commodity; alkyd production takes only a few percent of the world supply. For alkyds made by the fatty acid process, tall oil fatty acids (TOFA) are more economical than soybean fatty acids. Both soybean oil and TOFA contain roughly 40–60% linoleic acid and significant amounts of linolenic acid. White coatings containing linolenic acid esters gradually turn yellow. Premium cost “nonyellowing” alkyds are made with safflower or sunflower oils, which are high in linoleic acid but contain very little linolenic acid.

Applications in which fast drying and high cross-link density are important require alkyds made with drying oils. The rate of oxidative cross-linking is affected by the functionality of the drying oils used. At the same oil length and molecular weight, the time required to achieve a specific degree of cross-linking decreases as the average number of diallylic groups ($\bar{f}_n$) increases. Linseed long oil alkyds therefore cross-link more rapidly than soybean long oil alkyds. The effect is especially large in very long oil alkyds and less noticeable in alkyds with oil lengths around 60, where $\bar{f}_n$ is very high even with soybean oil and the effect of further increase in functionality by using linseed oil is small. Because of the large fraction of esters of fatty acids with three double bonds in linseed alkyds, their color and color retention are poorer than that of soybean alkyds. Tung oil based alkyds, because of the high proportion of esters with three conjugated double bonds, dry still faster. Tung oil alkyds also exhibit a high degree of yellowing. Dehydrated castor alkyds have fairly good color retention, since they contain only a small proportion of esters of fatty acids with three double bonds; they are used primarily in baking coatings.

Drying oils and drying oil fatty acids undergo dimerization at elevated temperatures. Dimerization occurs concurrently with esterification during alkyd synthesis; it generates difunctional acids, increasing the mole ratio of dibasic acids to polyol. The rate of dimerization is faster with drying oils having a higher average

number of diallylic groups per molecule and with those having conjugated double bonds. Thus, the molecular weight, and therefore viscosity of an alkyd made with the same ratio of reactants, depends on the fatty acid composition. The higher the degree of unsaturation, the higher the viscosity because of the greater extent of dimerization. Linseed alkyds have higher viscosities than soybean alkyds made with the same monomer ratios under the same conditions. The effect is particularly marked with tung oil. It is difficult to prepare straight tung alkyds because of the risk of gelation; commonly, mixed linseed-tung alkyds are used when high oxidative cross-linking functionality is desired.

A critical factor involved in the choice of fatty acid is cost. Drying oils are agricultural products and, hence, tend to be volatile in price. By far, the major use of many vegetable oils is for foods. Depending upon relative prices, one drying oil is often substituted for another in certain alkyds. By adjusting for functionality differences, substitutions can frequently be made without significant changes in properties.

Fatty acids are not the only monobasic acids used in making alkyds. Benzoic acid is also used, especially to esterify some of the excess hydroxyl groups remaining in the preparation of medium oil alkyds. The benzoic acid [65-85-0] increases the ratio of aromatic to aliphatic chains in the alkyd, thus contributing to a higher T_g of the solvent-free alkyd and more rapid formation of a tack-free film. At the same time, the reduction in the free hydroxyl content may somewhat reduce water sensitivity of the dried films. Rosin can also be used in the same fashion. Although rosin is not an aromatic acid, its polynuclear ring structure is rigid enough to increase T_g . If the critical requirement in drying is rapid development of solvent resistance, such benzoic acid and rosin modifications do not serve the purpose; they only reduce tack-free time. Frequently, benzoic acid-modified alkyds are called chain-stopped alkyds. The implication of the terminology is that the benzoic acid stops chain growth. This is not the case; the benzoic acid simply esterifies hydroxyl groups that would not have been esterified if the benzoic acid were absent. The effect on degree of polymerization is negligible.

Polyol Selection. Glycerol is the most widely used polyol because it is present in naturally occurring oils from which alkyds are commonly synthesized. The next most widely used polyol is pentaerythritol. In order to avoid gelation, the tetrafunctionality of pentaerythritol must be taken into account when replacing glycerol with pentaerythritol. If the substitution is made on a mole basis, rather than an equivalent basis, chances for gelation are minimized. As mentioned earlier, the ratio of moles of dibasic acid to polyol should be less than 1, and generally, a slightly lower mole ratio is required with pentaerythritol than with glycerol. At the same mole ratio of dibasic acid to polyol, more moles of fatty acid can be esterified with pentaerythritol. Hence, in long oil alkyds, the average functionality for cross-linking is higher, and the time to reach a given degree of solvent resistance is shorter for a pentaerythritol alkyd as compared to a glycerol alkyd. Because of this difference, one must be careful in comparing oil lengths of glycerol and pentaerythritol alkyds.

When pentaerythritol is synthesized, 2,2'-[oxybis(methylene)]-bis[2-hydroxymethyl]-1,3-propanediol [126-58-9] (dipentaerythritol) and 2,2-bis{[3-hydroxy-2,2-bis(hydroxymethyl)propoxy]methyl}1,3-propanediol [78-24-0] (tripentaerythritol) are by-products, and commercial pentaerythritol contains

some of these higher polyols. Consequently, care must be exercised in changing sources of pentaerythritol, since the amount of the higher polyols may differ. Because of the very high functionality, dipentaerythritol and tripentaerythritol ($F = 6$ and 8 , respectively) are useful in making fast drying low molecular weight alkyds.

To reduce cost, it is sometimes desirable to use mixtures of pentaerythritol and 1,2-ethanediol [107-21-1] (ethylene glycol) or 1,3-propanediol (propylene glycol). A 1:1 mole ratio of tetra- and difunctional polyols gives an average functionality of 3, corresponding to glycerol. The corresponding alkyds can be expected to be similar, but not identical. 2-Ethyl-2-(hydroxymethyl-1,3-propanediol [77-99-6] (trimethylolpropane, TMP) can also be used, but the rate of esterification is slower than with glycerol. Although all of TMP's alcohol groups are primary, they are somewhat sterically hindered by the neopentyl structure (9). Trimethylolpropane, however, gives a narrower molecular weight distribution, which provides alkyds with a somewhat lower viscosity than the comparable glycerol-based alkyd. A kinetic study demonstrated that esterification of one or two of the hydroxyl groups of TMP has little effect on the rate constant for esterification of the third hydroxyl group (9). It can be speculated that pentaerythritol behaves similarly.

Dibasic Acid Selection. Dibasic acids used to prepare alkyds are usually aromatic. Their rigid aromatic rings increase the T_g of the resin. Cycloaliphatic anhydrides, such as hexahydrophthalic anhydride, are also used. While they are not as rigid as aromatic rings, the cycloaliphatic rings also increase T_g .

By far, the most widely used dibasic acid is phthalic anhydride (PA). It has the advantage that the first esterification reaction proceeds rapidly by opening the anhydride ring. The amount of water evolved is lower, which also reduces reaction time. The relatively low melting point (the pure compound melts at 131°C) is desirable, since the crystals melt and dissolve readily in the reaction mixture. In large-scale manufacturing, molten PA is used, which reduces packaging, shipping, and handling costs.

The next most widely used dibasic acid is 1,3-benzenedicarboxylic acid [121-91-5] (isophthalic acid, IPA). Esters of IPA are more resistant to hydrolysis than are those of PA in the pH range of 4–8, the most important range for exterior durability. On the other hand, under more alkaline conditions esters of phthalic acid are more resistant to hydrolysis than isophthalic esters. The raw material cost for IPA is not particularly different from PA (even after adjusting for the extra mole of water that is lost), but the manufacturing cost is higher. The high melting point of IPA (330°C) leads to problems getting it to dissolve in the reaction mixture so that it can react. High temperatures are required for longer times than with PA; hence more dimerization of fatty acids occurs with IPA resulting in higher viscosity. The longer time at higher temperature also leads to greater extents of side reactions of the polyol components (11). Thus, when substituting IPA for PA, one must use a lower mole ratio of IPA to polyol in order to make an alkyd of similar viscosity.

2,5-Furandione [108-31-6] (maleic anhydride) is sometimes used with PA to give faster drying alkyds with little color. Aliphatic acids, such as 1,6-hexanedioic acid [124-04-9] (adipic acid), are sometimes used as partial replacements for PA to give more flexible films.

Chlorinated dibasic acids, such as 3,4,5,6,7,7-hexachloroendomethylene-1,2,3,6-tetrahydrophthalic anhydride (chlorendic acid), are used in making alkyds for fire-retardant coatings (12).

High Solids Oxidizing Alkyds. The need to minimize VOC emissions has led to efforts to increase solids content of alkyd resin coatings. Since xylene is on the HAP list, its use is being reduced. Some increase in solids can be realized by a change of solvents. Aliphatic (and to a somewhat lesser degree, aromatic) hydrocarbon solvents promote intermolecular hydrogen bonding, especially between carboxylic acids, but also between hydroxyl groups, thereby increasing viscosity. Use of at least some hydrogen-bond acceptor solvent, such as an ester or ketone, or hydrogen-bond acceptor–donor solvent such as an alcohol, gives a significant reduction in viscosity at equal solids.

The molecular weight of conventional alkyds is usually greater than 50,000. Solids can be increased by decreasing molecular weight, which is easily accomplished by decreasing the dibasic acid to polyol ratio. Alkyds with solids in the range of 60–80% are commercially available with molecular weights in the range of 12,000–20,000 (13). High solids alkyds tend to have lower functionality for cross-linking and a lower ratio of aromatic to aliphatic chains. Both changes increase the time for drying. There is also a decrease in branching with the higher hydroxyl excess.

The effect of longer oil length on functionality can be minimized by using drying oils with higher average functionality. Use of oils containing linolenic or α -eleostearic acid is limited by their tendency to discolor. One can use safflower oil, which has a higher linoleic acid content and less linolenic acid than soybean oil. Proprietary fatty acids with 78% linoleic acid are commercially available. Early hardness of the films can be improved by using some benzoic acid to esterify part of the free hydroxy groups. As noted earlier, the rigid rings of benzoic acid increase T_g to increase hardness after solvent evaporation.

Different drier combinations are recommended for use with high solids alkyds. A study of a variety of driers and drier combinations with high solids coatings has been published (14). Cobalt, neodymium, aluminum, and barium carboxylic acid salts were of particular interest. Performance was enhanced by adding bipyridyl as an accelerator. The author reports that the best drier system was 0.04% Co, 0.3% Nd with 0.07% bipyridyl (percentages based on the vehicle solids). Reference 15 reports studies of mechanisms of action of cobalt and mixed cobalt/zirconium driers.

Using optimized resins, good quality air dry and baking alkyd coatings can be formulated with VOC levels of 280–350 g/L of coating. A 250-g/L level is attainable only with some sacrifice of application and film properties; still lower limits of permissible VOC are projected.

Solids can be increased by making resins with narrower molecular weight distributions. For example, one can add a transesterification catalyst near the end of the alkyd cook; this gives more uniform molecular weight and a lower viscosity product. To study the effect of molecular weight distribution, model alkyds with very narrow molecular weight distribution were synthesized by using dicyclohexylcarbodiimide, which allows low temperature esterification (9). With the same ratio of reactants, the number-average molecular weight and polydispersity were lower than that of the conventional alkyd control. These

differences resulted from less dimerization through reactions of the double bond systems of the fatty acids and avoidance of self-etherification of polyol in the low temperature preparation. It was found that the solids could be 2–10% higher than with the conventionally prepared alkyd of the same raw material composition. The model alkyds dried more rapidly, but their film properties, especially impact resistance, were inferior to those obtained with control resins with the usual broad molecular weight distribution (16). Conventionally prepared TMP alkyds had lower molecular weights and viscosities than the glycerol alkyds. This difference may result from less self-etherification of TMP as compared to glycerol.

High solids alkyds for baking applications have been made using tripen-taerythritol. The high functionality obtained using this polyol ($F = 8$) gives alkyds that cross-link as rapidly as shorter oil length, higher viscosity glycerol alkyds (17). However, for air dry applications, the lower aromatic to aliphatic ratio lengthens the tack-free time. Presumably, progress could be made using a high functionality polyol with some combination of phthalic and benzoic acid, together with fatty acids with as high functionality fatty acids as possible. The cost of such an alkyd would be high.

Another approach to high solids alkyds is to use reactive diluents in place of part of the solvent. The idea is to have a component of lower molecular weight and much lower viscosity than the alkyd resin, which reacts with the alkyd during drying, and so it is not part of the VOC emissions. The use of reactive diluents is reviewed in Reference 18; 2,7-octadienyl maleate and fumarate are reported to be particularly effective. The use of diethers prepared from conjugated linoleic gives faster drying reactive diluents (19).

Several other types of reactive diluents have been used to formulate high solids alkyd coatings. Polyfunctional acrylate monomers (eg, trimethylolpropane trimethacrylate) have been used in force dry coatings (coatings designed to be cured in the range of 60–80°C) (20). Another example is use of dicyclopentadi-enyloxyethyl methacrylate [70191-60-5] as a reactive diluent (21). It is difunctional because of the easily abstractable allylic hydrogen on the dicyclopentadiene ring structure and the methacrylate double bond. The compound coreacts with drying oil groups in the alkyd. Mixed acrylic and drying oil fatty acid amides of hexa(aminomethoxymethyl)melamine have been recommended as reactive diluents (22,23). They contain high functionalities of $>\text{NCH}_2\text{NHCOCH}=\text{CH}_2$ and $>\text{NCH}_2\text{NHCOC}_{17}\text{H}_x$ moieties and promote fast drying. A recent patent discloses use of a reactive diluent prepared by reacting drying oil fatty acids with excess dipentaerythritol and then with 3-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane [4098-71-9] (isophorone diisocyanate) (24).

Waterborne Alkyds

As with almost all other resin classes, work has been done to make alkyd resins for coatings that can be reduced with water. One approach that has been more extensively studied in Europe than in the United States is the use of alkyd emulsions (25,26). The emulsions are stabilized with surfactants and can be prepared with little, if any, volatile solvent. Some problems limit use of alkyd emulsions

(27). Coatings prepared using alkyd emulsion loose dry time on storage because of absorption of cobalt drier on the surface of pigments and precipitation of cobalt hydroxide. Best results were obtained with a combination of cobalt neodecanoate and 2,2'-bipyridyl. It was shown that the surfactant tends to bloom to the surface of films formed from emulsions of long oil alkyds, washing a dry film tends to leave pits in the film showing a hexagonal pattern.

It is common to add a few percent of an alkyd-surfactant blend to latex paints to improve adhesion to chalky surfaces and, in some cases, to improve adhesion to metals. It is important to use alkyds that are as resistant as possible to hydrolysis. Hybrid alkyd-acrylic latices have been prepared by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization, yielding a latex with an alkyd grafted on the acrylic polymer (28,29). Nonyellowing waterborne alkyds based on rosin-fatty acid modified acrylic latices have been reported (30).

Another approach has been to make alkyds with an acid number in the range of 50, using secondary alcohols or ether alcohols as solvents. The acid groups are neutralized with ammonia or an amine. The resultant solution can be diluted with water to form a dispersion of solvent swollen aggregates in water. Molecular weight can be higher than in the case of high solids alkyd because the major factor affecting viscosity at application solids is the volume fraction of internal phase of the dispersion rather than the molecular weight of the polymer. Use of primary alcohol solvents should be avoided because they can more readily transesterify with the alkyd during resin production and storage, leading to reduction in molecular weight and $\bar{f}_n$ (31). Hydrolytic stability can be a problem with water-reducible alkyds. If the carboxylic acid groups are half esters from PA or 1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid [552-30-7] (trimellitic acid anhydride), the hydrolytic stability will be poor and probably inadequate for paints that require a shelf life of more than a few months. Because of the anchimeric effect of the neighboring carboxylic acid group, such esters are relatively easily hydrolyzed. As hydrolysis occurs, the solubilizing acid salt is detached from the resin molecules, and the aqueous dispersion loses stability. A more satisfactory way to introduce free carboxylic acid groups is by reacting a completed alkyd with maleic anhydride. Part of the maleic anhydride adds to the unsaturated fatty acid esters. The anhydride groups are then hydrolyzed with amine and water to give the desired carboxylate salt groups, which are attached to resin molecules with C—C bonds and cannot be hydrolyzed off. There is still a hydrolytic stability problem with the alkyd backbone, but hydrolysis does not result in destabilization of the dispersion. Similarly, acrylated fatty acids can be used to synthesize water-reducible alkyds with improved hydrolytic stability (32). Another approach to improving package stability is to react some of the free hydroxyl groups of an alkyd with isophorone diisocyanate and 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid [4767-03-7] (dimethylolpropionic acid, DMPA) (33) or with 1,3-bis(2,2-dimethyl-2-isocyanato)benzene (tetramethylxylene diisocyanate) and DMPA (34).

After the film is applied, the water, solvent, and amine evaporate, and the film cross-links by autoxidation. Since there are a fairly large number of residual carboxylic acid groups left in the cross-linked binder, the water resistance and particularly the alkali resistance of the films are reduced, but are still satisfactory for some applications (35). Early water resistance can be a problem if, for

example, a freshly painted surface is rained on before all the amine has evaporated from the film. Commonly, ammonia is used as the neutralizing amine because it is assumed that ammonia volatilizes faster than any other amine. This assumption is not necessarily valid; if the T_g of the alkyd film is sufficiently high before all of the amine has volatilized, loss of amine becomes controlled by diffusion rate. The rate of diffusion of amine through the carboxylic acid-functional film is affected by the base strength of the amine. A less basic amine, such as morpholine, may leave the film at a faster rate than ammonia even though its volatility is considerably lower.

Modified Alkyds

Oxidizing alkyds have been modified by reacting with a variety of other components; vinyl-modified, silicone-modified, phenolic-modified, and polyamide-modified alkyds are the most common examples.

Oxidizing alkyds can be modified by reaction with vinyl monomers. The most widely used monomers are ethenylbenzene [100-42-5] (styrene), 1-ethenyl-2-methylbenzene (vinyl toluene), and 2-methyl-2-propenoic acid methyl ester (methyl methacrylate), but essentially any vinyl monomer can be reacted in the presence of an alkyd to give a modified alkyd. Methyl methacrylate imparts better heat and weather resistance than styrene but at higher cost.

In making styrenated alkyds, an oxidizing alkyd is prepared in the usual way and cooled to about 130°C in the reactor; then styrene and a free-radical initiator such as dibenzoyl peroxide [94-36-0] (benzoyl peroxide) are added. The resulting free-radical chain process leads to a variety of reactions, including formation of low molecular weight homopolymer of styrene, grafting of polystyrene onto the alkyd, and dimerization of alkyd molecules. The reaction is generally carried out at about 130°C, which favors decomposition of benzoyl peroxide to form phenyl free radicals; phenyl radicals have a high tendency to abstract hydrogen, which favors grafting. After the reaction is complete, the resin is diluted with solvent. The ratio of alkyd to styrene can be varied over a wide range; commonly 50% alkyd and 50% styrene is used. The ratio of aromatic rings to aliphatic chains is greatly increased, and as a result, the T_g of styrenated alkyd films is higher and tack-free time is shorter. Styrenated alkyds give a dry film in 1 h or less versus 4–6 h for the counterpart nonstyrenated alkyd. However, the average functionality for oxidative cross-linking is reduced, not just by dilution with styrene, but also because the free-radical reactions involved in the styrenation consume some activated methylene groups. As a result, the time required to develop solvent resistance is longer than for the counterpart alkyd. The fast drying and low cost make styrenated alkyds very attractive for some applications, but in other cases, the longer time required for cross-linking is more critical, in which case styrenated alkyds are not appropriate.

Styrenated alkyd vehicles are often used for air dry primers. One must be careful to apply top coat almost immediately or not until after the film has had ample time to cross-link. During the intermediate time interval, application of top coat is likely to cause nonuniform swelling of the primer, leading to what is called lifting of the primer. The result of lifting is the development of wrinkled

areas in the surface of the dried film. End users who are accustomed to using alkyd primers, which do not give a hard film until a significant degree of cross-linking has occurred, are particularly likely to encounter problems of lifting if they switch to styrenated alkyd primers.

Silicone resins have exceptional exterior durability but are expensive. Silicone modification of alkyd resins improves their exterior durability. The earliest approach was simply to add a silicone resin to an alkyd resin in the reactor at the end of the alkyd cook. While some covalent bonds between silicone resin and alkyd might form, probably most of the silicone resin simply dissolves in the alkyd. Exterior durability of silicone-modified alkyd coatings is significantly better than unmodified alkyd coatings. The improvement in durability is roughly proportional to the amount of added silicone resin; 30% silicone resin is a common degree of modification. Further improvements in exterior durability are obtained by coreacting a silicone intermediate during synthesis of the alkyd. Such intermediates react readily with free hydroxyl groups of the alkyd resin. Silicone resins designed for this purpose may contain higher alkyl, as well as methyl and phenyl, groups to improve compatibility. Alkyd coatings modified with high phenylsilicone resins are reported to have greater thermoplasticity, faster air drying, and higher solubility than high methylsilicone modified alkyds. These differences result in the higher rigidity of the aromatic rings, which leads to a solid film at an earlier stage of cross-linking. Less cross-linking in the phenylsilicone-modified coatings makes them more thermoplastic and soluble. Since IPA-based alkyd resins have better exterior durability than PA alkyds, they are generally used as the alkyd component. Silicone-modified alkyds are used mainly in outdoor air dry coatings for which application is expensive (eg, in a top coat for steel petroleum storage tanks).

Phenolic-modified alkyds are made by heating the alkyd with a low molecular weight resole phenolic resin based on *p*-alkylphenols. Presumably, the methylol groups on the phenols react with some of the unsaturated groups of the alkyd to form chroman structures. The resins give harder films with improved water and chemical resistance as compared to the unmodified alkyd.

Polyamide-modified alkyds are used as thixotropic agents to increase the low shear viscosity of alkyd resin based paints. Typically, about 10% of a polyamide resin made from diamines such as 1,2-ethanediamine (ethylenediamine) with dimer acids is reacted with an alkyd resin. High solids thixotropic alkyds based on polyamides made with aromatic diamines have been developed, which give superior performance in high solids alkyd coatings (36).

Nonoxidizing Alkyds

Certain low molecular weight short-medium and short oil alkyds are compatible with such polymers as nitrocellulose and thermoplastic polyacrylates. Therefore, such alkyds can be used as plasticizers for these polymers. They have the advantage over monomeric plasticizers (eg, dibutyl or dioctyl phthalate) in that they do not volatilize appreciably when films are baked. It is generally not desirable to use oxidizing alkyds, which would cross-link and lead to embrittlement of the films, especially on exterior exposure. Therefore, nondrying oil fatty acids

(or oils) are used in the preparation of alkyds for such applications. For exterior acrylic lacquers, nonanoic acid (pelargonic acid) alkyds combine excellent resistance to photodegradation with good compatibility with the thermoplastic acrylic resins. An interesting sidelight on terminology is that these pelargonic alkyds have been called *polyesters* rather than alkyds because the word *polyester* connotes higher quality than the word *alkyd*. Castor-oil-derived alkyds are particularly appropriate for nitrocellulose lacquers for interior applications, since the hydroxyl groups on the 12-hydroxy-(*Z*)-9-octadecenoic acid [141-22-0] (ricinoleic acid) promote compatibility.

All alkyds, particularly short-medium oil and short oil alkyds, are made with a large excess of hydroxyl groups to avoid gelation. These hydroxyl groups can be cross-linked with MF resins or with polyisocyanates. In some cases, relatively small amounts of MF resin are used to supplement the cross-linking during baking of medium oil oxidizing alkyds. To achieve compatibility, butylated MF resins are used. Such coatings provide somewhat better durability and faster curing than alkyd resins alone, with little increase in cost. The important advantage of relative freedom from film defects common to alkyd coatings can be retained. However, the high levels of unsaturation remaining in the cured films reduce resistance to discoloration on overbake and exterior exposure and cause loss of gloss and embrittlement on exterior exposure. These difficulties can be reduced by using nondrying oils with minimal levels of unsaturated fatty acids. Coconut oil has been widely used; its performance can be further enhanced by hydrogenation of the small amount of unsaturated acids present in it.

Since isophthalic (IPA) esters are more stable to hydrolysis in the pH range of 4–8 than phthalate esters, the highest performance exterior alkyd-MF enamels use nonoxidizing IPA alkyds. Exterior durability of such coatings is satisfactory for automobile top coats with opaque pigmentation. The films have an appearance of greater depth than that of acrylic-MF coatings. The films are perceived to be thicker than films of acrylic-MF coatings of comparable thickness and pigmentation. However, for many applications, alkyd-MF coatings have been replaced with acrylic-MF or polyester-MF coatings to improve the overall balance of film properties.

Synthesis of Alkyd Resins

Various synthetic procedures, each with many variables, are used to produce alkyd resins; the general reference and References 37 and 38 provide useful reviews of manufacturing procedures. Alkyds can be made directly from oils or by using free fatty acids as raw materials.

Synthesis from Oils or Fatty Acids.

Monoglyceride Process. In the case of glycerol alkyds, it would be absurd to first saponify an oil to obtain fatty acids and glycerol, and then reesterify the same groups in a different combination. Rather, the oil is first reacted with sufficient glycerol to give the total desired glycerol content, including the glycerol in the oil. Since PA is not soluble in the oil, but is soluble in the glycerol, transesterification of oil with glycerol must be carried out as a separate step before the PA is added; otherwise, glyceryl phthalate gel particles would form early in the process.

This two-stage procedure is often called the monoglyceride process. The transesterification reaction is run at 230–250°C in the presence of a catalyst; many catalysts have been used. Before the strict regulation of lead in coatings, litharge (PbO) was widely used; the residual transesterification catalyst also acted as a drier. Examples of catalysts now used in the United States are tetraisopropyl titanate, lithium hydroxide, and lithium ricinoleate. The reaction is run under an inert atmosphere such as CO₂ or N₂ to minimize discoloration and dimerization of drying oils. Rather than using glycerol, the transesterification can also be carried out with higher functionality polyols such as pentaerythritol.

While the process is called the monoglyceride process, the transesterification reaction actually results in a mixture of unreacted glycerol, monoglycerides, diglycerides, and unconverted drying oil. The composition depends on the ratio of glycerol to oil and on catalyst, time, and temperature. In general, the reaction is not taken to equilibrium. At some relatively arbitrary point, the PA is added, beginning the second stage. The viscosity and properties of the alkyd can be affected by the extent of reaction before the PA addition. While many tests have been devised to evaluate the extent of transesterification, none is very general because the starting ratio of glycerol to oil varies over a considerable range, depending on the oil length of the alkyd being made. (In calculating the mole ratio of dibasic acid to polyol, the glycerol already esterified in the oil must also be counted.) A useful empirical test is to follow the solubility of molten PA in the reaction mixture. This test has the advantage that it is directly related to a major requirement that must be met. In the first stage, it is common to transesterify the oil with pentaerythritol to obtain mixed partial esters. The second stage, esterification of the monoglyceride with PA, is carried out at a temperature of 220–255°C.

Fatty Acid Process. It is often desirable to base an alkyd on a polyol (eg, pentaerythritol) other than glycerol. In this case, fatty acids must be used instead of oils, and the process can be performed in a single step with reduced time in the reactor. Any drying, semidrying, or nondrying oil can be saponified to yield fatty acids, but the cost of separating fatty acids from the reaction mixture increases the cost of the alkyd. A more economical alternative is to use TOFA, which have the advantage that they are produced as fatty acids. Tall oil fatty acid composition is fairly similar to that of soybean fatty acids. Specially refined tall oils with higher linoleic acid content are available, as are other grades that have been treated with alkaline catalysts to isomerize the double bonds partially to conjugated structures. Generally, when fatty acids are used, the polyol, fatty acids, and dibasic acid are all added at the start of the reaction, and the esterification of both aliphatic and aromatic acids is carried out simultaneously in the range of 220–255°C.

Process Variations. Esterification is a reversible reaction; therefore, an important factor affecting the rate of esterification is the rate of removal of water from the reactor. Most alkyds are produced using a reflux solvent, such as xylene, to promote the removal of water by azeotropeing. Since the reaction is run at a temperature far above the boiling point of xylene, less than 5% of xylene is used. The amount is dependent on the reactor and is set empirically such that there is enough to reflux vigorously, but not so much as to cause flooding of the condenser. Some of the xylene is distilled off along with the water; water is

separated and xylene is returned to the reactor. The presence of solvent is desirable for other reasons: vapor serves as an inert atmosphere, reducing the amount of inert gas needed, and the solvent serves to avoid accumulation of sublimed solid monomers, mainly PA, in the reflux condenser.

Reaction time is affected by reaction temperature. Higher temperatures obviously accelerate the reaction. If the reaction is carried too far, there is a major risk of gelation. There are economic advantages to short reaction times. Operating costs are reduced, and the shorter times permit more batches of alkyd to be produced in a year, increasing capacity without capital investment in more reactors. Therefore, it is desirable to operate at as high a temperature as possible without risking gelation.

A critical aspect of alkyd synthesis is deciding when the reaction is completed. Disappearance of carboxylic acid is followed by titration to determine acid number, and increase in molecular weight is followed by viscosity. Determination of acid number and viscosity both take some time. Meanwhile, in the reactor, the reaction is continuing. After it is decided that the extent of reaction is sufficient, the reaction mixture must be dropped into a larger tank containing solvent. When a 40,000-L batch of alkyd is being made, a significant time is required to get the resin out of the reactor into the reducing tank; meanwhile, the reaction is continuing. The decision to start dropping the batch must be made so that the acid number and viscosity of the batch will be right after the continuing reaction that occurs between the time of sampling, determination of acid number and viscosity, and discharging of the reactor. The time for these determinations becomes the rate-controlling step in production. If they can be done rapidly enough, the reaction can be carried out at 240°C or even higher without overshooting the target acid number and viscosity. On the other hand, if the control tests are done slowly, it may be necessary to run the reaction at only 220°C, which may require 2 h or more of additional reaction time. Automatic titration instruments permit rapid determination of acid number and so the usual limit on time required is viscosity determination. While attempts have been made to use viscosity of the resin at reaction temperature to monitor change in molecular weight, the dependence of viscosity on molecular weight at that high temperature is not sensitive enough to be very useful. The viscosity must be determined on a solution at some lower standard temperature. Since viscosity depends strongly on solution concentration and temperature, these variables must be carefully controlled.

In alkyd production, viscosity is commonly determined using Gardner bubble tubes. The cook is continued until the viscosity is high enough so that by the time the resin batch is dropped into the solvent and the batch cooled, its viscosity will be what is called for in the specification. This means starting to discharge the reactor when the test sample is at some lower viscosity. It is not possible to generalize how large this difference should be; it depends on the specific alkyd composition, the temperature at which the reaction is being run, the time required to do the determination, the time required to empty the reactor, and so on. Viscosities can be determined more rapidly using a cone and plate viscometer than with bubble tubes; the very small sample required for a cone and plate viscometer can be cooled and equilibrated at the measurement temperature more quickly.

Many variables affect the acid number and viscosity of alkyds. One is the ratio of reactants: The closer the ratio of moles of dibasic acid to polyol approaches 1, the higher the molecular weight of the backbone of the resin, but also the greater the likelihood of gelation. A useful rule of thumb for a starting point is to use a mole ratio of 0.95. The final ratio is determined by adjustments such that the combination of acid number and solution viscosity come out at the desired levels. The greater the ratio of hydroxyl groups to carboxylic acid groups, the faster the acid groups are reduced to a low level. The degree of completion of the reaction is an important factor controlling the viscosity, as well as the acid number. It is usually desirable to have a low acid number, typically in the range of 5–10.

The composition of the fatty acids is a major factor affecting the viscosity, and compositions of an oil or grade of TOFA can be expected to vary somewhat from lot to lot. Dimerization and oligomerization of the unsaturated fatty acids occur in the same temperature range at which the esterification is carried out. Fatty acids with conjugated double bonds dimerize more rapidly than those with nonconjugated bonds, and dimerization rates increase with the level of unsaturation. At the same ratio of phthalic to polyol to fatty acids, alkyds of the same acid number and solution concentration will increase in viscosity in the order soybean < linseed < tung.

Some volatilization of polyol, PA, and fatty acids out of the reactor will occur depending on the design of the reactor, the rate of reflux of the azeotroping solvent, the rate of inert gas flow, and the reaction temperature, among other variables; the amount and ratio of these losses affect the viscosity at the standard acid number. The exact ratio of reactants must be established in the reactor that is actually used for synthesis. Since gelation can occur if the ratio of dibasic acid to polyol is too high, it is better not to put all the PA into the reactor in the beginning. If the viscosity is too low when the acid number is getting down near the standard, more PA can easily be added. The amount of PA held back can be reduced as experience is gained cooking a particular alkyd in a particular reactor.

Side reactions can affect the viscosity–acid number relationship. Glycerol and other polyols form ethers to some degree during the reaction. Glycerol can also form acrolein by successive dehydrations. When these reactions occur, the mole ratio of dibasic acid to polyol increases and the number of hydroxyl groups decreases; therefore, at the same acid number, the molecular weight will be higher. Excessively high viscosity and even gelation can result. Ether formation is catalyzed by strong protonic acids; therefore, it is desirable to avoid them as catalysts for the esterification. Monobutyltin oxide has been used as an esterification catalyst; presumably, it does not significantly catalyze ether formation. As noted earlier, pentaerythritol and TMP seem less vulnerable than glycerol to undesirable side reactions such as ether formation, and glycerol is the only polyol that can decompose to form acrolein. A hydroxyl group on one end of a growing polyester chain can react with a carboxylic acid group on another end of the same molecule, leading to ring formation. Transesterification of chain linkages can have the same result. Since cyclization reactions reduce chain length, their net effect is to reduce viscosity.

Many alkyd resins have broad, uneven molecular weight distributions. It has been shown that even modest changes in reaction conditions can cause large differences in molecular weight distribution, which can have significant effects on final film properties (39). In many alkyds, very small gel particles (microgels) are formed. It has been shown that these microgels play an important role in giving greater strength properties to final films (39). Process changes that may make the alkyd more uniform may be undesirable. For example, allowing glycerolysis to approach equilibrium before addition of PA and using transesterification catalysts in the final stages of esterification both favor narrower molecular weight distributions and lower viscosities, but films made from the more uniform alkyds may exhibit inferior mechanical properties.

Urethane Derivatives

Uralkyds are also called urethane alkyds or urethane oils. They are alkyd resins in which a diisocyanate, usually 2,4(6)-toluene diisocyanate [584-84-9] (TDI), has fully or partly replaced the PA usually used in the preparation of alkyds. One transesterifies a drying oil with a polyol such as glycerol or pentaerythritol to make a monoglyceride (see section Synthesis from Oils or Fatty Acids) and reacts it with some PA (if desired) and then with somewhat less diisocyanate than the equivalent amount of $\text{N}=\text{C}=\text{O}$ based on the free OH content. To assure that no $\text{N}=\text{C}=\text{O}$ groups remain unreacted, methyl alcohol is added at the end of the process. Just like alkyds, uralkyds dry faster than the drying oil from which they were made, since they have a higher average functionality (more activated diallylic groups per average molecule). The rigidity of the TDI aromatic rings also speeds up the drying by increasing the T_g of the resin.

Two principal advantages of uralkyd over alkyd coatings are superior abrasion resistance and resistance to hydrolysis. Disadvantages are inferior color retention (when aromatic isocyanates used) of the films, higher viscosity of resin solutions at the same percent solids, and higher cost. Uralkyds made with aliphatic diisocyanates have better color retention, but are more expensive and have lower T_g . The largest use of uralkyds is in architectural coatings. Many so-called varnishes sold to the consumer today are based on uralkyds; they are not really varnishes in the original sense of the word. They are used as transparent coatings for furniture, woodwork, and floors: applications in which good abrasion resistance is important. Since they are generally made with aromatic isocyanates, they tend to turn yellow and then light brown with age; yellowing is acceptable in clear varnishes, but would be a substantial drawback in light-colored pigmented paints.

Water-reducible polyunsaturated acid substituted aqueous polyurethane dispersions are also being used (40). They can be made by reacting a diisocyanate with a polyol, monoglyceride of a drying oil, and dimethylolpropionic acid. The carboxylic acid groups are neutralized with a tertiary amine and dispersed in water. If aliphatic isocyanates are used, good color retention can be obtained. They are much more resistant to hydrolysis than conventional alkyd resins. Films also have excellent abrasion resistance. Cost can be reduced by blending in 10–20% of acrylic latex.

Epoxy Esters

Bisphenol A (BPA) epoxy resins can be converted to what are commonly called epoxy esters by reacting with fatty acids. Drying or semidrying oil fatty acids are used so that the products cross-link by autoxidation. The epoxy groups undergo a ring-opening reaction with carboxylic acids to generate an ester and a hydroxyl group. These hydroxyl groups, as well as the hydroxyl groups originally present on the epoxy resin, can esterify with fatty acids. They are generally made by starting with a low molecular weight epoxy resin (ie, the standard liquid resin, $n = 0.13$) and extending with 4,4'-(1-methylethylidene)bisphenol [80-05-7] (BPA) by the advancement process to the desired molecular weight. Off-specification epoxy resin is often used to reduce cost. The fatty acids are added to the molten, hot resin, and the esterification reaction is continued until the acid number is low, usually less than 7 mg of KOH per gram of resin. In the esterification reaction with fatty acids, the average number of sites for reaction is the n value, corresponding to the number of hydroxyl groups on the resin, plus twice the number of epoxy groups. The esterification is carried out at high temperatures (220–240°C). The rate of esterification slows as the concentration of hydroxyl groups diminishes, and side reactions occur, especially dimerization of the drying oil fatty acids (or their esters). It is not practical to esterify more than about 90% of the potential hydroxyl groups, including those from ring opening the epoxy groups. The lower useful limit of the extent of esterification is about 50%. This is required to ensure sufficient fatty acid groups for oxidative cross-linking.

Tall oil fatty acids are commonly used because of their low cost. Linseed fatty acids give faster cross-linking coatings because of higher average functionality. However, their viscosity is higher because of the greater extent of dimerization during esterification, and their cost is higher. For still faster cross-linking, part of the linseed fatty acids can be replaced with tung fatty acids, but the viscosity and cost are still higher. The color of epoxy esters from linseed and linseed–tung fatty acids is darker than the tall oil esters. Dehydrated castor oil fatty acids give faster curing epoxy esters for baked coatings. The rate of formation of a dry film from epoxy esters depends on two factors: the average number of diallylic groups $\bar{f}_n$ and the ratio of aromatic rings to long aliphatic chains. The $\bar{f}_n$ can be maximized by using higher molecular weight BPA epoxy resin and by using enough fatty acid to react with a large fraction of the epoxy and hydroxyl groups. The ratio of aromatic rings to fatty acids can be maximized by using high molecular weight epoxy resin and esterifying a smaller fraction of epoxy and hydroxyl groups.

Epoxy esters are used in coatings in which adhesion to metal is important. While the reasons are not completely understood, it is common for epoxy coatings, including epoxy esters, to have good adhesion to metals and to retain adhesion after exposure of the coated metal to high humidity, a critical factor in corrosion protection. A distinct advantage of epoxy esters over alkyd resins is their greater resistance to hydrolysis and saponification. The backbone of alkyds is held together with esters from PA and the polyol, whereas in epoxy esters, the backbone is held together with C–C and ether bonds. Of course, the fatty acids are bonded to the backbone with ester groups in both cases, but the fraction of polymer bonds in a dry film subject to hydrolysis is substantially lower in the case of epoxy esters. On the other hand, exterior durability of epoxy ester coatings is poor, as

is the case with all films made with BPA epoxy resins. As a result of these advantages and disadvantages, the major uses for epoxy resins are in primers for metal and in can coatings, such as for crowns (bottle caps), in which the important requirements are adhesion and hydrolytic stability. In baking primers, it is sometimes desirable to supplement the cross-linking through oxidation by including a small amount of MF resin in the formulation to cross-link with part of the free hydroxyl groups on the epoxy ester.

Epoxy ester resins with good exterior durability (better than alkyds) can be prepared by reacting epoxy-functional acrylic copolymers (made with glycidyl methacrylate) with fatty acids. The product is an acrylic resin with multiple fatty acid ester side chains. By appropriate selection of acrylate ester comonomers and molecular weight, the T_g of the resin can be designed so that a tack-free film is obtained by solvent evaporation; then the coating cross-links by autoxidation. For an application like repainting an automobile at ambient temperatures, the cross-linking can proceed relatively slowly and need not be catalyzed by metal salt driers. The rate of cross-linking is slower without driers, but exterior durability is better.

Epoxy esters can also be made water-reducible. The most widely used water-reducible epoxy esters have been made by reacting maleic anhydride with epoxy esters prepared from dehydrated castor oil fatty acids. Subsequent addition of a tertiary amine, such as 2-(dimethylamino)ethanol [108-01-0], in water results in ring opening of the anhydride to give amine salts. Like other water-reducible resins, these resins are not soluble in water but form a dispersion of resin aggregates swollen with water and solvent in an aqueous continuous phase. The hydrolytic stability of these epoxy esters is better than corresponding alkyds and sufficient for use in electrodeposition primers until anionic primers were replaced by cationic primers. Water-reducible epoxy esters are still used in spray applied baking primers and primer-surfacers. They are also used in dip coating primers in which nonflammability is an advantage. Their performance equals that of solvent-soluble epoxy ester primers.

Uses

In 1997, the U. S. consumption of alkyds was approximately 310,000 t and projected use in 5 years is estimated to be 280,000–290,000 t (41). Coatings are the largest market with use in 1997 of approximately 250,000 t (42). European and Japanese consumption of alkyd coating resins in 1996 has been reported to be 360,000 and 110,000 t, respectively (42). Use of alkyds has been declining at about 2% a year and is projected to decline further as they are replaced with resins with higher performance and lower volatile emissions. Higher solids alkyds have been replacing conventional solids alkyds. In 1997, about 81,000 ton with solids of 50–60% and 16,000 tons of greater than 60% were used in the United States in comparison with 150,000 t of alkyds with lower than 50% solids. Only 10,000 t of waterborne alkyds were used (41).

The principal advantages of alkyds are low cost, low toxicity, and low surface tension. The low surface tension permits wetting of most surfaces including oily steel. Also the low surface tension minimizes application defects such as

cratering. The principal limitations are generally poorer exterior durability and corrosion protection than alternative coating resins. While high solids and waterborne alkyd resins are manufactured, their properties are generally somewhat inferior to conventional solvent-borne alkyds.

The largest use for alkyds in coatings is in architectural paints, particularly in gloss enamels for application by contractors. Contractors tend to prefer alkyd enamels over latex enamels because coverage can be achieved with a single coat. Also, alkyd paints can be applied at low temperatures whereas latex paints can only be applied at temperatures above about 5°C. The do-it-yourself market is served primarily with latex paints because of ease of cleanup and lesser odor. While initial gloss of alkyd enamels is higher than of latex enamels, the latex enamels exhibit far superior gloss retention in exterior applications. Alkyd primers provide better adhesion to chalky surfaces than most latex paints. The next largest use is in aerosol paints.

The largest use of alkyds in industrial applications is in general industrial coatings for such applications as machinery and metal furniture. Significant amounts are used with UF resins in coatings for wood furniture. Alkyd resin/chlorinated rubber based coatings are used in traffic paints, but use is decreasing because of high VOC content. An approach to overcoming this problem is the use of solvent-free alkyds in hot melt traffic paints (43). Some alkyds are still used in refinish paints for automobiles since they give high gloss coatings with a minimum of polishing. An example of recent work in formulating refinish coatings is preparing an alkyd by reacting tris(hydroxyethyl)isocyanurate with drying oil fatty acids and formulating with trimethylolpropane trimethacrylate as a reactive diluent (44).

About 39,000 t of uralkyds were used in the United States in 1997 (41). The largest use for uralkyds is as the vehicle for so-called urethane varnishes for the do-it-yourself market. The abrasion resistance of such coatings is greatly superior to that obtained with conventional varnishes or alkyd resins. Epoxy esters give coatings with markedly superior corrosion protection as compared with alkyd resins while retaining the advantage of low surface tension. However, as with any BPA epoxy system, exterior durability is poor. They are used primarily in primers for steel and in flexible coatings such as for metal crowns. Maleated epoxy esters give primers with equivalent properties of solvent-borne epoxy ester coatings and are widely used in formulating waterborne primers for steel.

Noncoatings applications include foundry core binders and printing inks, especially lithographic inks.

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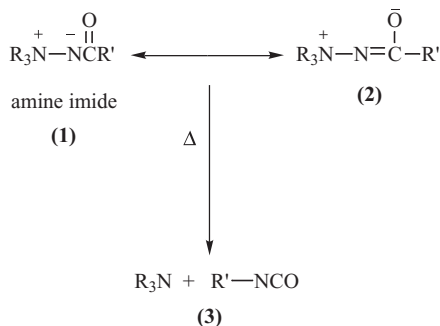
ZENO W. WICKS JR.

AMINIMIDE POLYMERS

Introduction

Monomers containing the trialkylamine acylimide moiety $\text{—}\overset{\text{O}}{\overset{+}{\parallel}}\text{CNR}_3$ give polymer chemists the capability to prepare a large variety of unique, reactive polymers. Materials of this type have a large number of potential applications. The synthesis, chemical, and physical properties of several different types of ylids, commonly called aminimides, have been the subject of several reviews (1–7). Aminimide monomers and polymers have also received attention in reviews (3,5,8).

The varied and complex nomenclature of ylids with the trialkylamine acylimide moiety has been described (3). The aminimide nomenclature is generally used, because the ylid functional group (**1**) is isoelectronic with an amine oxide (**2**) (3). The generalized aminimide structures (**1**) and (**2**) provide some insight into their chemical versatility. Absorption bands in the ir at 1555–1600 cm^{-1} support the resonance structures shown.

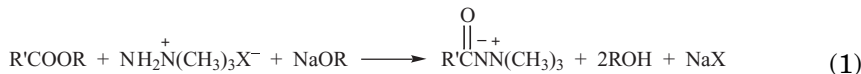


As isocyanate precursors, amine acylimides give chemists a clever method to prepare a wide variety of monomeric and polymeric, aliphatic and aromatic, isocyanates (**3**) by proper selection of the R' moiety on the aminimide. The aminimide also functions as an amine precursor, giving an easily handled source of tertiary amine.

Preparation of Monomers

Many different types of monofunctional, difunctional, etc, aminimides have been prepared at Ashland Chemical Co. and other locations (see Tables 1 and 2). The monomers in Table 1 are mainly useful in radical initiated, chain-growth polymerizations; whereas the monomers in Table 2 are useful in step-growth polymerizations or polymer derivatization reactions.

Several procedures are known for preparing molecules with the amine acylimide residue (3,7,28). The two most attractive procedures, from a commercial view, are shown in equations 1 and 2. In equation 1, stoichiometric amounts of an ester, 1,1,1-trimethylhydrazinium halide, and sodium alkoxide are combined to give excellent yields of the aminimide prepared *in situ* (3,7).



The second process, equation 2, is even more attractive, since alkoxides or other strong bases are not needed. In this case, stoichiometric amounts of an ester, 1,1-dimethylhydrazine, and an epoxide are combined to give good yields of aminimide.



Both procedures make use of a strong, nucleophilic aminimine $(\text{NHNHR}_3)^{-+}$ moiety generated *in situ* (3,7).

Polymers with backbones containing aminimide residues have been prepared by the method of equation 2, using diepoxides, esters of dicarboxylic acids and 1,1-dimethylhydrazine (28). For example, the combination of Epon 828 (4,4'-isopropylidenediphenol diglycidyl ether Epoxy Resin), dimethyl adipate, and 1,1-dimethylhydrazine produced an alcohol and a water-soluble polymer with aminimide residues in the chain and pendent hydroxyl moieties.

The procedures in equations 1 and 2 work well for most unsaturated esters, including methyl methacrylate. However, both procedures fail to give good yields of aminimide when using methyl acrylate.

The acid chloride-amine reaction, using acryloyl chloride, 1,1,1-trimethylhydrazinium chloride, and strong base, works well for preparing trialkylamine acrylimide monomers (3,7). A greatly improved technique for preparing

Table 1. Aminimide Monomers for Chain-Growth Polymerizations^a

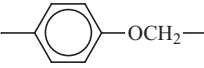
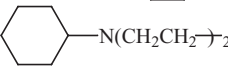
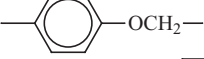
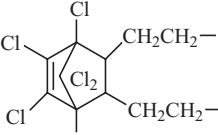
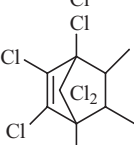
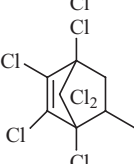
R	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{CN}-\text{N}^+(\text{CH}_3)_2\text{R}' \end{array}$		Mp, °C	Refs.
	R	R'		
CH ₃ CH=CH-	CH ₃	-CH ₃	168-170	^b
CH ₂ =C(CH ₃)-	-CH ₂ CH ₂ OH	-CH ₃	88-89	9,10
CH ₂ =C(CH ₃)-	-CH ₃	-CH ₃	149-150	9,11
<i>p</i> -CH ₂ =CHC ₆ H ₄ -	-CH ₃	-CH ₃	122-124	12,13
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₂ OH	146.5-147.5	9,14
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₂ OH	-CH ₃	122.5-123.5	9,14
CH ₂ =CH-	-CH ₃	-CH ₃	102-104	15-17
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₂ O(CH ₂) ₃ CH ₃	-CH ₂ CH(OH)CH ₂ CH ₃	59-60.5	^b
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₂ CH ₃	-CH ₂ CH(OH)CH ₂ OCH ₂ CH=CH ₂	99-101	^b
CH ₂ =C(CH ₃)-	-CH ₃	-CH ₃	140.5-141.5	15
C ₆ H ₅ CH=CH-	-CH ₂ CH(OH)CH ₃	-CH ₃	138.5-139.5	^b
C ₆ H ₅ CH=CH-	-CH ₃	-CH ₃	104.5-106	^b
<i>p</i> -CH ₂ =CHCH ₂ OC ₆ H ₄ -	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₃	124-126	^b
<i>p</i> -CH ₂ =CHCH ₂ OC ₆ H ₄ -	-CH ₂ CH(OH)C ₆ H ₅	-CH ₂ CH(OH)CH ₃	136.5-138	^b
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₃	64-66	9
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₂ O(CH ₂) ₁₁ CH ₃	63.5-65	^b
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₂ O(CH ₂) ₁₅ CH ₃	80-81.5	9
CH ₂ =C(CH ₃)-	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₂ O(CH ₂) ₇ CH ₃	liquid	9
CH ₂ =CHCH ₂ NHCH ₂ CH ₂ -	-CH ₃	-CH ₃	108.5-111	18
CH ₂ =C(CH ₃)CONHCH ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₃	116-118	19
CH ₂ =C(CH ₃)CON(C ₆ H ₁₁)CH ₂ CH ₂ -	-CH ₃	-CH ₃	144-146	19
CH ₂ =C(CH ₃)CON(C ₆ H ₅)CH ₂ CH ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₃	oil	19
CH ₂ =C(CH ₃)CONCH ₂ CH ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₂ CH(OH)CH ₃	oil	19
CH ₂ =C(CH ₃)CONCH ₂ CH ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₃	143-145	15
CH ₂ =C(CH ₃)CONHC(CH ₃) ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₃	oil	19
CH ₂ =C(CH ₃)CONHC(CH ₃) ₂ -	-CH ₂ CH(OH)CH ₃	-CH ₃	143-145	15

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CON}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	oil	19
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CON}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2-$	$-\text{CH}_3$	164-166	19
$\text{CH}_2=\text{CHCON}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2-$	$-\text{CH}_3$	175-176.5	19
$\text{CH}_2=\text{CHCONHC}(\text{CH}_3)_2-$	$-\text{CH}_3$	158-161	15
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CON}(\text{C}_6\text{H}_5)\text{CH}_2-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	130-131	19
$\text{CH}_2=\text{CH}-\text{CONHCH}_2-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	136-138	19
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCCH}_2\text{CH}_2\text{COOH}$	122-123	20
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCCH}_2\text{CH}_2\text{COOH}(\text{ortho})$	137-139	20
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCCH}_3$	82-84	20
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{OOCCH}_3)\text{CH}_2\text{OOCCH}_3$	89-91.5	19
$\text{CH}_3(\text{CH}_2)_{10}-$	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCCH}=\text{CHCOOH}$	77-79	20
CH_3-	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCCH}=\text{CHCOOH}$	oil	20
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}_2\text{OOCCH}_3$	72-73	10
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OOC}(\text{CH}_3)=\text{CH}_2$		21
$\text{CH}_2=\text{C}(\text{CH}_3)-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_4\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$		22
$(\text{CH}_2=\text{CHCH}_2)_2\text{NHCH}_2-$			
Cl^-	$-\text{CH}_3$		<i>b</i>
$+$			
$(\text{CH}_2=\text{CHCH}_2)_2\text{NHCH}_2\text{CH}_2-$			
Cl^-	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$		<i>b</i>
$+$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$		<i>b</i>
$(\text{CH}_2=\text{CHCH}_2)_2\text{NC}_6\text{H}_4(1,4)$			
$\text{HOOCCH}=\text{CH}_2-(\text{cis})$	$-\text{C}_{10}\text{H}_{21}$		23

^aNamed as 1,1-dimethyl-1-(R' alkyl)amine (R acyl)imides.

^bAshland Chemical Co. data.

Table 2. Aminimide Monomers for Step-Growth Polymerizations^a

$\text{R} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}[\text{CNN}(\text{CH}_3)_2\text{R}']_1 \text{ or } 2 \text{ (or } 3) \end{array}$			
R	R'	Mp, °C	Ref.
$\begin{array}{c} \text{CH}_2-\text{CH}- \\ \quad \\ \text{CH}_2-\text{CH}- \end{array}$	$-\text{CH}_3$		24
$\text{C}_6\text{H}_3(1,2,4)$	$-\text{CH}_3$	185–187	18
$-(\text{CH}_2)_4-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	191–192	9
$-(\text{CH}_2)_4-$	$-\text{CH}_3$	208–208.5	^b
	$-\text{CH}_3$	230–233	^b
	$-\text{CH}_3$	300 (dec)	^b
$-\text{CH}_2\text{CH}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \quad \\ \text{N} \quad \text{N} \\ \quad \\ \text{CH}_2\text{CH}_2- \end{array}$	$-\text{CH}_3$	215–217	^b
$-\text{CH}_2\text{CH}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \quad \\ \text{N} \quad \text{N} \\ \quad \\ \text{CH}_2\text{CH}_2- \end{array}$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	191–194	^b
	$-\text{CH}_3$	176–178	^b
	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	174–176	^b
$(-\text{CH}_2\text{CH}_2\text{NH}-\text{C}_6\text{H}_4)_2\text{CH}_2$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	144–146	^b
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{CH}_2\text{CH}_2)_2$	$-\text{CH}_3$	128–130	^b
	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	212 (dec)	25
	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$		25
	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	157–160	25
$-(\text{CH}_2)_7-$	$-\text{CH}_3$	136–137	24
$-(\text{CH}_2)_8-$	$-\text{CH}_3$	138–141	24
$-(\text{CH}_2)_{10}-$	$-\text{CH}_3$	139–141	^b
$\text{C}_6\text{H}_4(1,3)-$	$-\text{CH}_3$	251 (dec)	24
$\text{C}_6\text{H}_4(1,4)-$	$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	225–227 (dec)	^b

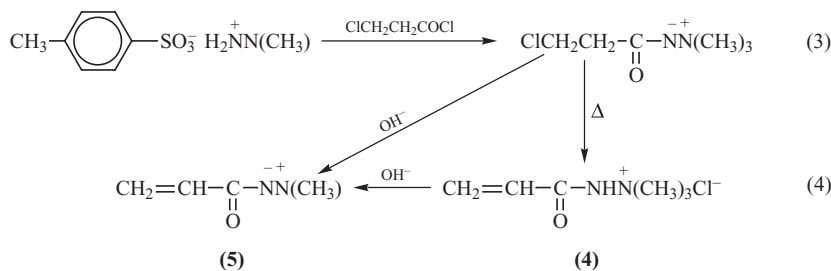
(Continued)

Table 2. (Continued)

$\begin{array}{c} \text{O} \\ \\ \text{R}[\text{CNN}(\text{CH}_3)_2\text{R}']_1 \text{ or } 2 \text{ (or } 3) \end{array}$			
R	R'	Mp, °C	Ref.
C ₆ Cl ₄ (1,4)–	–CH ₃	240–241	25
C ₆ Br ₄ (1,3)–	–CH ₂ CH(OH)CH ₃		25
$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array} \text{NCH}_2\text{CH}_2\text{–}$	–CH ₂ CH(OH)CH ₃	oil	26
$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array} \text{NCH}_2\text{CH}_2\text{–}$	–CH ₂ CH(OH)CH ₃ OH	oil	26
$\begin{array}{c} \text{CH}_3\text{CH} \\ \\ \text{CH}_2 \end{array} \text{NCH}_2\text{CH}_2\text{–}$	–CH ₂ CH(OH)CH ₃	oil	26
$\begin{array}{c} \text{CH}_3\text{CH} \\ \\ \text{CH}_2 \end{array} \text{NCH}_2\text{CH}_2\text{–}$	–CH ₂ CH(OH)CH ₂ OH	oil	26
(HOCH ₂ CH ₂) ₂ NCH ₂ CH ₂ –	–CH ₃	oil	^b
C ₆ H ₅ NHCH ₂ CH ₂ –	–CH ₂ CH(OH)CH ₃	111.5–112.5	^b
CH ₃ NHC ₆ H ₅ (1,2)–	–CH ₃	135.5–137	^b
NH ₂ C ₆ H ₅ (1,2)–	–CH ₃	141–145	^b
(HOCH ₂ CH ₂) ₂ NCH ₂ CH ₃ –	–CH ₂ CH(OH)CH ₃	oil	^b
HOCH ₂ C ₆ H ₄ (1,2)–	–CH ₃	126–127	21
HOCH ₂ CH ₂ –	–CH ₃		8
HOCH ₂ CH ₂ CH ₂ –	–CH ₃	108	^b
HOCH ₂ CH ₂ CH ₂ –	–CH ₂ CH(OH)(CH ₂) ₁₃ CH ₃	101–103	^b
HO(CH ₂) ₅ –	–CH ₂ CH(OH)(CH ₂) ₁₃ CH ₃	89.5–91.0	^b
HOCH ₂ CH ₂ O–	–CH ₂ CH(OH)(CH ₂) ₁₃ CH ₃		^b
CH ₃ (CH ₂) ₇ CH(OH)CH(OH)(CH ₂) ₇ –	–CH ₃	74	^b
CH ₃ (CH ₂) ₁₄ CON(CH ₂ CH ₂ OH)CH ₂ CH ₂ –	–CH ₂ CH(OH)CH ₃	55–58	^b
ClCH ₂ –	–CH ₃	90–105	27

^aSee Table 1 for the naming system.^bAshland Chemical Co. data.

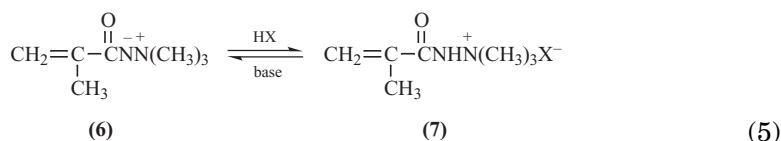
trialkylamine acrylimides (**5**) has been reported and is shown in equations 3 and 4 (15).



Properties of Monomers

Aminimides are soluble in water and a number of polar organic solvents. Aqueous solutions of aminimides are neutral (pH 6.9–7.2), remain essentially unchanged at room temperature or at 50°C for 24 h, and exhibit low conductivity (3,7). The infrared spectra of all aminimides exhibit a strong absorption band in the region 1555–1600 cm⁻¹, assignable to the –O–C=N– stretching frequency. This absorption band is highly useful for following rates of formation and reaction of aminimides (3,7).

As shown in equation 5, aminimides are acid-accepting compounds. Using this important feature, it is possible to use nonaqueous titration techniques to determine percent aminimide functionality for both monomeric and polymeric materials (12,29).



Equation 5 also illustrates another important feature, ie, monomeric hydrazinium salts are readily prepared from aminimides. Hydrazinium salt monomers, such as (7) exhibit copolymerization characteristics different than the parent monomer (6) and this feature may be exploited to prepare additional types of reactive polymers (29).

Aminimides exhibit good shelf stability. However, when heated at or above their melting points they undergo nitrogen–nitrogen bond cleavage, rearrangement, or elimination reactions. Substituents on the ylid residue determine the course of the reaction (3,7). In this article, reference is made to only the N–N cleavage and/or carbon–nitrogen migration. Analogous to the well known Curtius, Hofmann, Schmidt, and Lossen rearrangements (3,7), amine acylimides suffer rearrangement with heat to give isocyanates. Equation 6 illustrates these reactions, which proceed by a concerted mechanism



where X = (CH₃)₃N, N₂, Cl, Br, or OCOR'

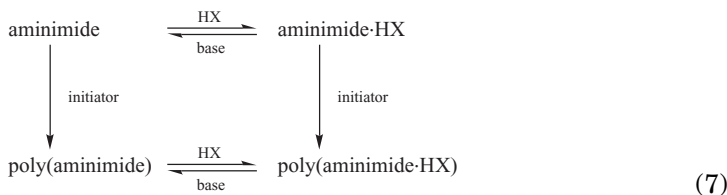
Thermal rearrangement of either monomeric (8) or polymeric (29) aminimides is carried out neat or in high boiling, nonreactive solvents at atmospheric or reduced pressure (5,7,8,16). High yields of isocyanates are obtained from heating monomers such as trimethylamine methacrylimide and trimethylamine sebacimide (8). In both cases, the isopropenyl isocyanate or 1,6-hexamethylenediisocyanate are obtained in >80% yield. Aminimides are not a good source of aromatic isocyanates or vinyl isocyanate because of the tertiary amine catalyzed trimerization reaction. However, suitably active hydrogen compounds may be used to trap the aromatic isocyanate (3), showing the isocyanate is produced in high yield.

Polymerization

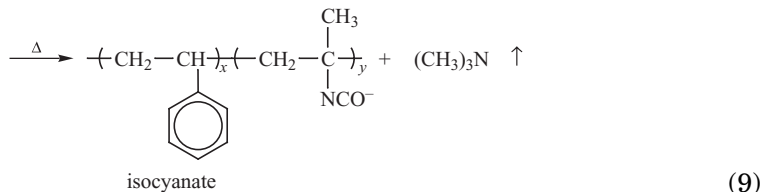
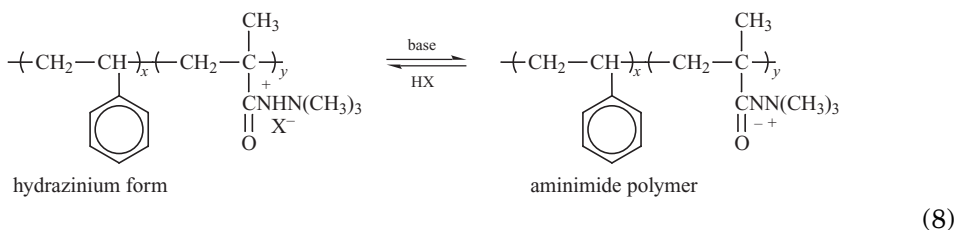
Aminimide monomers with acrylic and methacrylic residues (Tables 1 and 3) readily homo- and copolymerize, using nonoxidative, free-radical initiators (3,8,15). Peroxides, such as hydrogen and benzoyl peroxide, are not efficient initiators, since monomer-initiator reactions destroy both the monomer and the initiator at a much faster rate than radical polymerization occurs.

In strongly acidic solutions the aminimide monomer or polymer exists as a hydrazinium salt (**7**). The hydrazinium monomer (Table 3) exhibits homo- and copolymerization characteristics significantly different from those of the parent aminimide monomer. Peroxides work well as polymerization initiators for the hydrazinium monomers. In general, the hydrazinium monomer polymerizes more readily to higher molecular weight than the corresponding parent aminimide (29).

The polymerization scheme (eq. 7) for vinyl aminimides and the hydrazinium form of these monomers shows the versatility available in producing homo- and copolymers.



The reactivity ratios and Q and e -values (Table 3) give evidence that the vinyl aminimides copolymerize with many vinyl monomers. Where copolymerizations are difficult, the hydrazinium form of the aminimide parent monomer gives additional capability to prepare functional polymers. Using styrene and trimethylamine methacrylimide comonomers, equations 8 and 9 illustrate these concepts (29).



The great worth of aminimide monomers in preparing reactive and/or functional polymers is additionally illustrated by the synthesis of poly(*n*-butyl

Table 3. Reactivity Ratios, Q and e Values for Aminimide Monomers

M_1	M_2	r_1	r_2	Q	e	Ref.
1,1,1-trimethylamine methacrylimide	acrylonitrile	0.10	0.37	0.18	-0.60	11
1,1,1-trimethylamine 4-vinylbenzimidate	styrene	0.63	0.4	0.88	0.31	12
1,1-dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide	methyl methacrylate	0.04	1.60	0.24	-1.24	14
1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide	methyl methacrylate	0.00	1.99	0.12	-2.45	14
1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide	4-vinylpyridine	0.41	0.77	0.68	0.58	30
1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide	<i>N</i> -vinylpyrrolidinone	0.15	0.37	0.14	0.58	30
1,1,1-trimethylacrylhydrazinium chloride	styrene	0.46	0.58	0.69	0.34	17
1,1,1-trimethylmethacrylhydrazinium chloride	styrene	0.23	0.51	0.61	0.66	17
1,1-dimethyl-1-(2-hydroxypropyl)methacrylhydrazinium chloride	styrene	0.33	0.35	0.88	0.67	29
1,1-dimethyl-1-(2-hydroxyethyl)amine methacrylimide	methyl methacrylate	0.05	2.10	0.20	-1.04	10
1,1-dimethyl-1-(2-hydroxyethyl)amine methacrylimide	<i>N</i> -vinylpyrrolidinone	0.53	0.30	0.10	-0.23	10
1,1-dimethyl-1-(2-succinoylpropyl)amine methacrylimide	methyl methacrylate	0.49	2.46	0.25	-0.04	31
1,1-dimethyl-1-(2-phthaloxypyl)amine methacrylimide	methyl methacrylate	0.54	2.25	0.27	-0.05	31

ac-rylate-*co*-isopropenyl isocyanate) (32). Both the isocyanate copolymer and its *N,N*-ethylene ureido derivative, obtained from reaction of the isocyanate groups with ethylenimine, are useful as wool shrink-proofing agents.

The aminimides in Table 2 are useful in a wide variety of step-growth polymerizations, polymer modifications, and polymer cross-linking reactions. In most of these reactions the polyfunctional aminimide is exploited as an isocyanate precursor, with tertiary amine availability to promote reactions. The reaction of difunctional aminimides with diepoxides to give polyoxazolidones (34), and with polyester polyols to give polyurethanes (24,33), are two good examples of this chemistry. Permachem Asia Co. has taken great advantage of this chemistry to design one part, thermosetting epoxy resin compositions (35). In these systems, the aminimide functions as a latent hardener/promoter to cross-link the epoxy resin, giving adhesives and coatings with high tensile and high impact strength. The compound 1,1-dimethyl-1-(2-hydroxy-3-allyloxypropyl)amine β -lactimide is particularly useful as a latent epoxy resin hardener.

Variations of the above scheme employ epoxides, glycols and other active hydrogen materials to cross-link polymers with pendent aminimide residues. Also, the use of difunctional aminimides to cross-link polymers with pendent active hydrogens is useful for producing thermosetting materials (36).

Several of the monomers in Table 2 are useful for preparing water-soluble polyurethanes. For example, reaction of 1,1,1-trimethylamine β -di(2-hydroxyethyl)aminopropionimide with toluene-2,4-diisocyanate gives a water-soluble polymer. The polymer liberates amine and becomes water-insoluble when heated at 125°C.

Ethylenimine (aziridiny) substituted aminimide monomers (Table 2) are useful for modification of pendent carboxylic acid functional groups on polymer chains. For example, poly(styrene-*co*-butyl acrylate-*co*-acrylic acid) materials were treated with 1,1-dimethyl-1-(2-hydroxypropyl)amine β -1-aziridinypropionimide. The resultant modified copolymers were readily cross-linked at 125°C, to give coatings having high gloss and good adhesion to a variety of substrates (26).

Polymers with a plurality of hydroxyl groups, such as cellulose materials, are readily derivatized with 1,1,1-trimethylamine α -chloroacetimide (15,27). Like other aminimide polymers, these materials also eliminate amine and cross-link at 125°C, via the aminimide rearrangement and subsequent isocyanate-hydroxyl reaction.

Polymer Properties

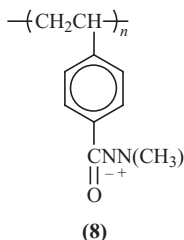
Aminimide polymer films are hard, brittle materials. When heated at or above 125°C, the films become insoluble in water, alcohol, and other common organic solvents. Infrared spectra, taken during heating, show that the aminimide carbonyl band at 1560 cm^{-1} vanishes and a new absorption band appears at 2260 cm^{-1} , indicating isocyanate formation. Heating the films isothermally at various temperatures and following the rate of disappearance of the 1560 cm^{-1} band shows that the carbon-nitrogen migration reaction is a temperature dependent, first-order reaction (37). Differential thermal (dta) and thermogravimetric

analysis (tga) studies show that trimethylamine acylimide polymers start to decompose at approximately 125°C and lose theoretical amounts of trimethylamine from 125–200°C (11). In contrast, polymers containing the 1,1-dimethyl-1-(2-hydroxypropyl)amine or 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine residues fail to lose amine when heated under the same conditions. A significant amount of the hydroxyalkylamine is retained in the polymer films, through isocyanate reactions with the hydroxyalkylamine fragment generated.

The temperature at which the nitrogen–nitrogen bond cleavage reaction occurs is somewhat lowered for polymers substituted with the 1,1-dimethyl-1-(2,3-diacetoxypropyl)amine moieties (20). No suitable catalysts have been discovered to lower the thermolysis temperature of aminimides significantly.

The trialkylamine acylimides and the hydrazinium salt form of the aminimide monomers have great influence on the solubility characteristics of polymers (3,14,29). In general, the hydrophilicity of copolymers is directly proportional to the percent of dipolar aminimide or hydrazinium salt residues on the backbone of the polymer molecule. All aminimide polymers are water-soluble. Copolymers may be water-soluble, depending on aminimide or hydrazinium salt content. Poly(styrene-*co*-trimethylamine methacrylimide) becomes water-soluble at about 30% by weight aminimide.

High molecular weight poly(trimethylamine *p*-vinylbenzimidide) (**8**) has very unique solubility properties in water (38).



Aqueous solutions with only 5% of this polymer form thermoreversible gels, similar to gelatin, and the polymer is compatible with many other polymer latices, giving thermoreversible gels. It is salt sensitive and readily salted out of solution. Aqueous solutions with only 2.5% polymer (**8**) show the property of negative thixotropy, ie, the solution thickens with even mild stress and actually gels, but relaxes and melts when the shear stress is removed. The gelation and negative thixotropy property is destroyed by protonation of the aminimide group to form the hydrazinium salt.

The dipolar ylid residue has a great effect on the adhesion of copolymers to various surfaces (9,14). Variations of the adhesion character are readily achieved by changes in the type of alkyl substituent on the aminimide functionality.

Copolymers with aminimide residues also suffer nitrogen–nitrogen bond breaking reactions and elimination of tertiary amine when heated at 125°C. Thermolysis reactions of the copolymers may be achieved either neat or in refluxing solvents (9,19,29,30). This concept has been used to prepare soluble poly(styrene-*co*-isopropenyl isocyanate) (2,17,29), poly(*n*-butyl acrylate-*co*-isopropenyl isocyanate) (19,32,41), poly(4-vinylpyridine-*co*-isopropenyl isocyanate) (30), poly(methyl methacrylate-*co*-isopropenyl isocyanate) (17), and

poly(*N*-vinylpyrrolidinone-*co*-isopropenyl isocyanate) (30,41) materials. These isocyanate-containing copolymers are readily cross-linked with active hydrogen compounds, such as glycols, diamines, polymeric active hydrogen compounds, etc (8,11,12,14,29,30,37).

Applications

With the exception of Permachem Asia Company's interest in one package epoxy resin systems (35), the once bright future proclaimed (43–45) for aminimide monomers and polymers has never developed. For the most part, Ashland Chemical backed off from marketing aminimidexes, because of the lack of 1,1-dimethylhydrazine availability, concern for the adverse toxicological properties of hydrazines, cost of monomers, and specialty market size. Even though Ashland did develop an economical route to 1,1-dimethylhydrazine (46–49), which had no dimethylnitrosoamine intermediate, the spirit to market aminimides was never rekindled. The once bright future still remains and aminimides offer many untapped opportunities to prepare new products.

Uses for aminimide monomers and polymers may take advantage of their dipolar ion structure, water-solubility, or their nature as isocyanate precursors and latent amine sources. In all areas of possible uses for aminimides, adhesives, coatings, films, elastomers, etc, these materials continue to offer opportunities to design new products, if monomers become available. Since the last reviews of possible aminimide applications (8,50) several patents have been issued that give additional insight on potential uses of aminimide monomers to prepare highly modified perfluoroalkyl acrylate coatings (51–54), photographic films (55), photopolymerizable compositions (56), thermosetting cationic electrophoretic coating systems (57), and 2-acrylamido-2-methylpropane sulfonic acid containing copolymers with surfactant-suspending and electrical conductivity properties (58).

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AMINO RESINS AND PLASTICS

Introduction

Amino resins are thermosetting polymers made by combining an aldehyde with a compound containing an amino ($-\text{NH}_2$) group. Urea–formaldehyde (U/F) accounts for over 80% of amino resins; melamine–formaldehyde accounts for most of the rest. Other aldehydes and other amino compounds are used to a very minor extent. The first commercially important amino resin appeared about 1930, or some 20 years after the introduction of phenol–formaldehyde resins and plastics (see PHENOLIC RESINS).

The principal attractions of amino resins and plastics are water solubility before curing, which allows easy application to and with many other materials, colorlessness, which allows unlimited colorability with dyes and pigments, excellent solvent resistance in the cured state, outstanding hardness and abrasion resistance, and good heat resistance. Limitations of these materials include release of formaldehyde during cure and, in some cases, such as in foamed insulation, after cure, and poor outdoor weatherability for urea moldings. Repeated cycling of wet and dry conditions causes surface cracks. Melamine moldings have relatively good outdoor weatherability.

Amino resins are manufactured throughout the industrialized world to provide a wide variety of useful products. Adhesive Compounds, representing the largest single market, are used to make plywood, chipboard, and sawdust board. Other types are used to make laminated wood beams, parquet flooring, and for furniture assembly.

Some amino resins are used as additives to modify the properties of other materials. For example, a small amount of amino resin added to textile fabric imparts the familiar wash-and-wear qualities to shirts and dresses. Automobile tires are strengthened by amino resins which improve the adhesion of rubber to tire cord. A racing sailboat may have a better chance to win because the sails of Dacron (Du Pont) polyester have been treated with an amino resin (1). Amino resins can improve the strength of paper even when it is wet. Molding compounds based on amino resins are used for parts of electrical devices, bottle and jar caps, molded plastic dinnerware, and buttons.

Amino resins are also often used for the cure of other resins, such as Alkyd Resins, and reactive acrylic polymers. These polymer systems may contain 5–50% of the amino resin and are commonly used in the flexible backings found on carpets and draperies, as well as in protective surface coatings, particularly the durable baked enamels of appliances, automobiles, etc.

The term *amino resin* is usually applied to the broad class of materials regardless of application, whereas the term *aminoplast* or sometimes *amino plastic* is more commonly applied to thermosetting molding compounds based on amino resins. Amino plastics and resins have been in use since 1920s. Compared with other segments of the plastics industry, they are mature products, and their growth rate is only about half of that of the plastics industry as a whole. They account for about 3% of the U.S. plastics and resins production.

History. The basic chemistry of amino resins was established as early as 1908 (2), but the first commercial product, a molding compound, was patented in England (3) only in 1925. It was based on a resin made from an equimolar mixture of urea and thiourea and reinforced with purified cellulose fiber and was trademarked Beetle (indicating it could “beat all” others). Patent rights were acquired by the American Cyanamid Company along with the Beetle trademark, and by 1930 a similar molding compound was being marketed in the United States. The new product was hard and not easily stained and was available in light, translucent colors; furthermore, it had no objectionable phenolic odor. The use of thiourea improved gloss and water resistance, but stained the steel molds. As amino resin technology progressed the amount of thiourea in the formulation could be reduced and finally eliminated altogether.

In the early 1920s, experimentation with urea–formaldehyde resins [9011-05-6] in Germany (4) and Austria (5,6) led to the discovery that these resins might be cast into beautiful clear transparent sheets, and it was proposed that this new synthetic material might serve as an organic glass (5,6). In fact, an experimental product called Polloplas was introduced, but lack of sufficient water resistance prevented commercialization. Melamine–formaldehyde resin [9003-08-1] does have better water resistance but the market for synthetic glass was taken over by new thermoplastic materials such as polystyrene and poly(methyl methacrylate) (see METHACRYLIC ESTER POLYMERS; STYRENE POLYMERS).

Melamine resins were introduced about 10 years after the Beetle molding compound. They were very similar to those based on urea but had superior qualities. Henkel in Germany was issued a patent for a melamine resin in 1936 (7). Melamine resins rapidly supplanted urea resins and were soon used in molding, laminating, and bonding formulations, as well as for textile and paper treatments. The remarkable stability of the symmetrical triazine ring made these products resistant to chemical change once the resin had been cured to the insoluble, cross-linked state.

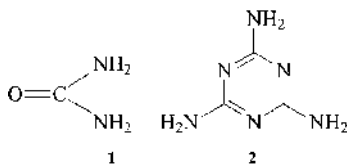
Prior to the rapid expansion of thermoplastics following World War II, amino plastics served a broad range of applications in molding, laminating, and bonding. As the newer and more versatile thermoplastic materials moved into these markets, aminos became more and more restricted to applications demanding some specific property best offered by the thermosetting amino resins. Current sales patterns are very specific. Urea molding powders find application in moldings for electrical devices and in closures for jars and bottles. Melamine molding compound is used principally for molded plastic dinnerware. Urea resins have retained their use in electrical-wiring devices because of good electrical properties, good heat resistance, and an availability of colors not obtainable with phenolics. Urea-formaldehyde resins are useful as closures because of their excellent resistance to oils, fats, and waxes often found in cosmetics, and their availability in a broad range of colors. Melamine plastic is used for molded dinnerware primarily because of outstanding hardness, water resistance, and stain resistance. Melamine-formaldehyde is the hardest commercial plastic material.

Aminoplasts and other thermosetting plastics are molded by an automatic injection-molding process similar to that used for thermoplastics, but with an important difference (8). Instead of being plasticized in a hot cylinder and then injected into a much cooler mold cavity, the thermosets are plasticized in a warm cylinder and then injected into a hot mold cavity where the chemical reaction of cure sets the resin to the solid state. The process is best applied to relatively small moldings. Melamine plastic dinnerware is still molded by standard compression-molding techniques. The great advantage of injection molding is that it reduces costs by eliminating manual labor, thereby placing the amino resins in a better position to compete with thermoplastics (see INJECTION MOLDING).

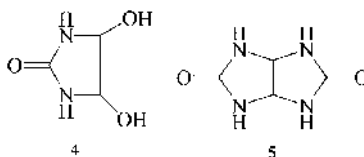
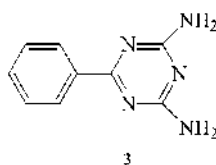
The future for amino resins and plastics seems secure because they can provide qualities that are not easily obtained in other ways. New developments will probably be in the areas of more highly specialized materials for treating textiles, paper, etc, and for use with other resins in the formulation of surface coatings, where a small amount of an amino resin can significantly increase the value of a more basic material. Additionally, since amino resins contain a large proportion of nitrogen, a widely abundant element, they may be in a better position to compete with other plastics as raw materials based on carbon compounds become more costly.

Raw Materials

Most amino resins are based on the reaction of formaldehyde [50-00-0] with urea [57-13-6] (1) or melamine [108-78-1] (2).



Although formaldehyde will combine with many other amines, amides, and aminotriazines to form useful products, only a few are used and are of minor importance compared with products based on urea and melamine. Benzoguanamine [91-76-9] (3), for example, is used in amino resins for coatings because it provides excellent resistance to laundry detergent, a definite advantage in coatings for automatic washing machines. Dihydroxyethylene urea [3720-97-6] (4) is used for making amino resins that provide wash-and-wear properties in clothing. Glycoluril [496-46-8] (5) resins provide coatings with high film flexibility.



Aniline-formaldehyde resins were once quite important because of their excellent electrical properties, but their markets have been taken over by newer thermoplastic materials. Nevertheless, some aniline resins are still used as modifiers for other resins. Acrylamide occupies a unique position in the amino resins field since it not only contains a formaldehyde reactive site, but also a polymerizable double bond. Thus it forms a bridge between the formaldehyde condensation polymers and the versatile vinyl polymers and copolymers (see ACRYLAMIDE POLYMERS).

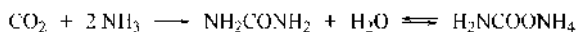
In the sense that formaldehyde can supply a methylene link between two molecules, it is difunctional. Each amino group has two replaceable hydrogens that can react with formaldehyde; hence, it also is difunctional. Since the amino compounds commonly used for making amino resins, urea, and melamine contain two and three amino groups, they are polyfunctional and react with formaldehyde to form three-dimensional, cross-linked polymer structures. Compounds with a single amino group such as aniline or toluenesulfonamide can usually react with formaldehyde to form only linear polymer chains. However, in the presence of an acid catalyst at higher temperatures, the aromatic ring of aniline may react with formaldehyde to produce a cross-linked polymer.

Urea. Urea (carbamide), $\text{CH}_4\text{N}_2\text{O}$, is the most important building block for amino resins because urea-formaldehyde is the largest selling amino resin,

and urea is the raw material for melamine, the amino compound used in the next largest selling-type of amino resin. Urea is also used to make a variety of other amino compounds, such as ethyleneurea, and other cyclic derivatives used for amino resins for treating textiles. They are discussed later.

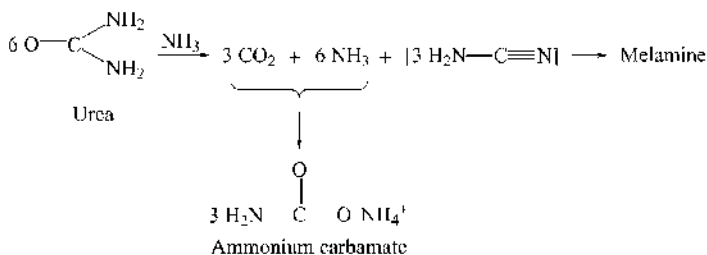
Urea is soluble in water, and the crystalline solid is somewhat hygroscopic, tending to cake when exposed to a humid atmosphere. For this reason, urea is frequently *pelletized* or *prilled* (formed into little beads) to avoid caking and making it easy to handle.

Only about 10% of the total urea production is used for amino resins, which thus appear to have a secure source of low cost raw material. Urea is made by the reaction of carbon dioxide and ammonia at high temperature and pressure to yield a mixture of urea and ammonium carbamate; the latter is recycled.



Melamine. Melamine (cyanurotriamide 2,4,6-triamino-s-triazine), $\text{C}_3\text{H}_6\text{N}_6$, is a white crystalline solid, melting at approximately 350°C with vaporization, only slightly soluble in water. The commercial product, recrystallized grade, is at least 99% pure. Melamine was synthesized early in the development of organic chemistry, but it remained of theoretical interest until it was found to be a useful constituent of amino resins. Melamine was first made commercially from dicyandiamide [461-58-5] is now made from urea, a much cheaper starting material (9-12).

Urea is dehydrated to cyanamide which trimerizes to melamine in an atmosphere of ammonia to suppress the formation of deamination products. The ammonium carbamate [1111-78-0] also formed is recycled and converted to urea. For this reason the manufacture of melamine is usually integrated with much larger facilities making ammonia and urea.



Since melamine resins are derived from urea, they are more costly and are therefore restricted to applications requiring superior performance. Essentially all of the melamine produced is used for making amino resins and plastics.

Formaldehyde. Pure formaldehyde, CH_2O , is a colorless, pungent smelling reactive gas. The commercial product is handled either as solid polymer, paraformaldehyde (13), or in aqueous or alcoholic solutions. Marketed under the trade name Formcel, solutions in methanol, *n*-butanol, and isobutyl alcohol are widely used for making alcohol-modified urea and melamine resins for surface coatings and treating textiles.

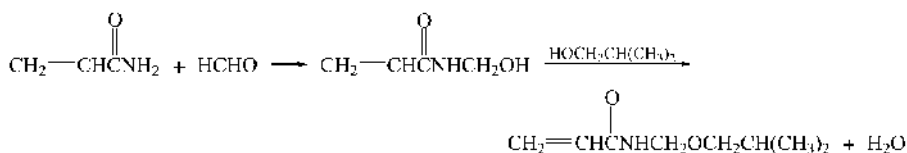
Aqueous formaldehyde, known as formalin is usually 37 wt% formaldehyde, although more concentrated solutions are available. Formalin is the general-purpose formaldehyde of commerce supplied unstabilized or methanol-stabilized. The latter may be stored at room temperature without precipitation of solid formaldehyde polymers because it contains 5–10% methyl alcohol. The uninhibited type must be maintained at a temperature of at least 32°C to prevent the separation of solid formaldehyde polymers. Large quantities are often supplied in more concentrated solutions. Formalin at 44, 50, or even 56% may be used to reduce shipping costs and improve manufacturing efficiency. Heated storage tanks must be used. For example, formalin containing 50% formaldehyde must be kept at a temperature of 55°C to avoid precipitation. Formaldehyde solutions stabilized with urea are used (14), and various other stabilizers have been proposed (15,16). With urea-stabilized formaldehyde the user need only adjust the U/F ratio by adding more urea to produce a urea resin solution ready for use.

Paraformaldehyde [30525-89-4] is a mixture of polyoxymethylene glycols, $\text{HO}(\text{CH}_2\text{O})_n\text{H}$, with n from 8 to as much as 100. It is commercially available as a powder (95%) and as flake (91%). The remainder is a mixture of water and methanol. Paraformaldehyde is an unstable polymer that easily regenerates formaldehyde in solution. Under alkaline conditions, the chains depolymerize from the ends, whereas in acid solution the chains are randomly cleaved (17). Paraformaldehyde is often used when the presence of a large amount of water should be avoided as in the preparation of alkylated amino resins for coatings. Formaldehyde may also exist in the form of the cyclic trimer trioxane [110-88-3]. This is a fairly stable compound that does not easily release formaldehyde; hence, it is not used as a source of formaldehyde for making amino resins.

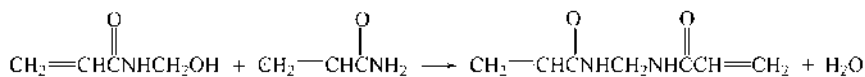
Approximately 25% of the formaldehyde produced in the United States is used in the manufacture of amino resins and plastics.

Other Materials. Benzoguanamine and acetoguanamine may be used in place of melamine to achieve greater solubility in organic solvents and greater chemical resistance. Aniline and toluenesulfonamide react with formaldehyde to form thermoplastic resins. They are not used alone, but rather as Plasticizers for other resins including melamine and urea-formaldehyde. The plasticizer may be made separately or formed *in situ* during preparation of the primary resin.

Acrylamide [79-06-1] is an interesting monomer for use with amino resins; the vinyl group is active in free-radical-catalyzed addition polymerizations, whereas the $-\text{NH}_2$ group is active in condensations with formaldehyde. Many patents describe methods of making cross-linked polymers with acrylamide by taking advantage of both vinyl polymerization and condensation with formaldehyde. For example, acrylamide reacts readily with formaldehyde to form *N*-methylolacrylamide [924-42-5], which gives the corresponding with isobutyl alcohol.



This compound is soluble in most organic solvents and may be easily copolymerized with other vinyl monomers to introduce reactive side groups on the polymer chain (18). Such reactive polymer chains may then be used to modify other polymers including other amino resins. It may be desirable to produce the cross-links first. Thus, *N*-methylolacrylamide can react with more acrylamide to produce methylenebisacrylamide, a tetrafunctional vinyl monomer.

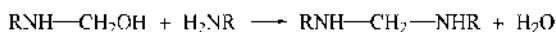


Chemistry of Resin Formation

The first step in the formation of resins and plastics from formaldehyde and amino compounds is the addition of formaldehyde to introduce the hydroxymethyl group, known as *methylolation* or *hydroxymethylation*:



The second step is a condensation reaction that involves the linking together of monomer units with the liberation of water to form a dimer, a polymer chain, or a vast network. This is usually referred to as *methylene bridge formation*, *polymerization*, *resinification*, or simply *cure*, and is illustrated in the following equation:



Success in making and using amino resins largely depends on the precise control of these two chemical reactions. Consequently, these reactions have been much studied (19–30).

The first reaction, the addition of formaldehyde to the amino compound, is catalyzed by either acids or bases. Hence, it takes place over the entire pH range. The second reaction joins the amino units with methylene links and is catalyzed only by acids. The rates of these reactions have been studied over a broad range of pH (28). The results are presented in Figure 1.

The same study also examined some of the subsequent reactions involved in the formation of more complex U/F condensation products. Rate constants for these reactions at 35°C are shown in Table 1.

The methylol compounds produced by these reactions are relatively stable under neutral or alkaline conditions, but undergo condensation, forming polymeric products under acidic conditions. Consequently, the first step in making an amino plastic is usually carried out under alkaline conditions. The amino compound and formaldehyde are combined and form a stable resin intermediate that may be used as an adhesive or combined with filler to make a molding compound. The second step is the addition of an acidic substance to catalyze the curing reaction, often with the application of heat to cure the amino resin to the solid cross-linked state. In this reaction, the methylol group is probably protonated

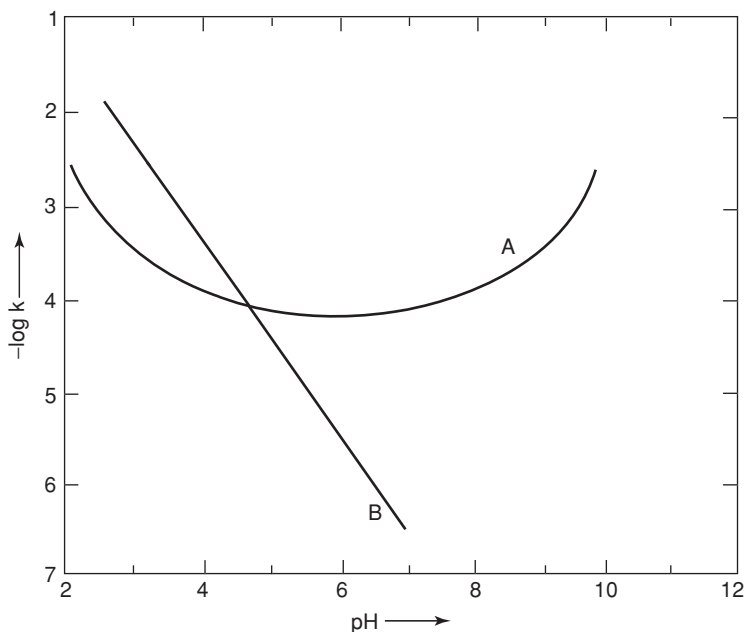


Fig. 1. Influence of pH on (A) the addition reaction of urea and formaldehyde (1:1), and (B) the condensation of methylolurea with the amino hydrogen of a neighboring urea molecule. Temperature = 35°C; 0.1 *M* aq. [Full View].

and a molecule of water lost, giving the intermediate carbonium–imonium ion. This then reacts with an amino group to form a methylene link.

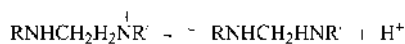
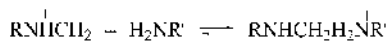
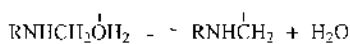
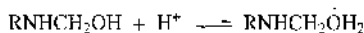


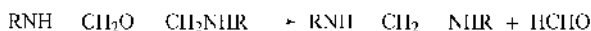
Table 1. Urea–Formaldehyde (U/F) Reaction Rate Constants

Reaction at 35°C and pH 4.0	<i>k</i> , L/(mol·s)
U + F → U/F	4.4×10^{-4}
U/F + U → U–CH ₂ –U	3.3×10^{-4}
U/F + U/F → U–CH ₂ –U/F	0.85×10^{-4}
U/F ₂ + U/F → FU–CH ₂ –U/F	0.5×10^{-4}
U/F ₂ + U/F ₂ → FU–CH ₂ –U/F ₂	$<3 \times 10^{-6}$

In addition to the two main reactions, ie, methylation and condensation, there are a number of other reactions important for the manufacture and uses of amino resins. For example, two methylol groups may combine to produce a dimethylene ether linkage and liberate a molecule of water:



The dimethylene ether so formed is less stable than the diamino-methylene bridge and may rearrange to form a methylene link and liberate a molecule of formaldehyde.



The simple methylol compounds and the low molecular weight polymers obtained from urea and melamine are soluble in water and quite suitable for the manufacture of adhesives, molding compounds, and some kinds of textile treating resins. However, amino resins for coating applications require compatibility with the film-forming Alkyd Resins or copolymer resins with which they must react. Furthermore, even where compatible, the free methylol compounds are often too reactive and unstable for use in a coating-resin formulation that may have to be stored for some time before use. Reaction of the free methylol groups with an alcohol to convert them to alkoxy methyl groups solves both problems.

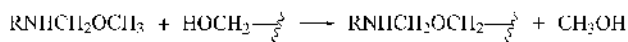
The replacement of the hydrogen of the methylol compound with an alkyl group renders the compound much more soluble in organic solvents and more stable. This reaction is also catalyzed by acids and usually carried out in the presence of considerable excess alcohol to suppress the competing self-condensation reaction. After neutralization of the acid catalyst, the excess alcohol may be stripped or left as a solvent for the amino resin.

The mechanism of the alkylation reaction is similar to curing. The methylol group becomes protonated and dissociates to form a carbonium ion intermediate which may react with alcohol to produce an alkoxymethyl group or with water to revert to the starting material. The amount of water in the reaction mixture should be kept to a minimum since the relative amounts of alcohol and water determine the final equilibrium.

Another way of achieving the desired compatibility with organic solvents is to employ an amino compound having an organic solubilizing group in the molecule, such as benzoguanamine. With one of the $-\text{NH}_2$ groups of melamine replaced with a phenyl group, benzoguanamine-formaldehyde resins [26160-89-4] have some degree of oil solubility even without additives. Nevertheless, benzoguanamine-formaldehyde resins are generally modified with alcohols to provide a still greater range of compatibility with solvent-based surface coatings. Benzoguanamine resins provide a high degree of detergent resistance, together with good ductility and excellent adhesion to metal.

Displacement of a volatile with a nonvolatile alcohol is an important reaction for curing paint films with amino cross-linkers and amino resins on textile

fabrics or paper. Following is an example of a methoxymethyl group on an amino resin reacting with a hydroxyl group of a polymer chain:



A troublesome side reaction encountered in the manufacture and use of amino resins is the conversion of formaldehyde to formic acid. Often the reaction mixture of amino compound and formaldehyde must be heated under alkaline conditions. This favors a Cannizzaro reaction in which two molecules of formaldehyde interact to yield one molecule of methanol and one of formic acid.



Unless this reaction is controlled, the solution may become sufficiently acidic to catalyze the condensation reaction causing abnormally high viscosity or premature gelation of the resin solution.

Manufacture

Precise control of the course, speed, and extent of the reaction is essential for successful manufacture. Important factors are mole ratio of reactants, catalyst (pH of reaction mixture), and reaction time and temperature. Amino resins are usually made by a batch process. The formaldehyde and other reactants are charged to a kettle, the pH adjusted, and the charge heated. Often the pH of the formaldehyde is adjusted before adding the other reactants. Aqueous formaldehyde is most convenient to handle and lowest in cost.

In general, conditions for the first part of the reaction are selected to favor the formation of methylol compounds. After addition of the reactants, the conditions may be adjusted to control the polymerization. The reaction may be stopped to give a stable syrup. This could be an adhesive or laminating resin and might be blended with filler to make a molding compound. It might also be an intermediate for the manufacture of a more complicated product, such as an alkylated amino resin, for use with other polymers in coatings.

The flow sheet (Fig. 2) illustrates the manufacture of amino resin syrups, cellulose-filled molding compounds, and spray-dried resins.

In the manufacture of amino resins every effort is made to recover and recycle the raw materials. However, there may be some loss of formaldehyde, methanol, or other solvent as tanks and reactors are vented. Some formaldehyde, solvents, and alcohols are also evolved in the curing of paint films and the curing of adhesives and resins applied to textiles and paper. The amount of material evolved in curing the resins may be so small that it may be difficult to justify the installation of complex recovery equipment. However, in the development of new resins for coatings and for treating textiles and paper, emphasis is being placed on those compositions that evolve a minimum of by-products on curing. The moist amino resin adhesive absorbs the high frequency radiation more readily than dry wood, thereby concentrating the heat in the glue line where it is needed. Hot pressing may be conducted in a hydraulic press comprising a large number of steam-heated platens, usually 5 cm thick. Pressures usually range from 1 to

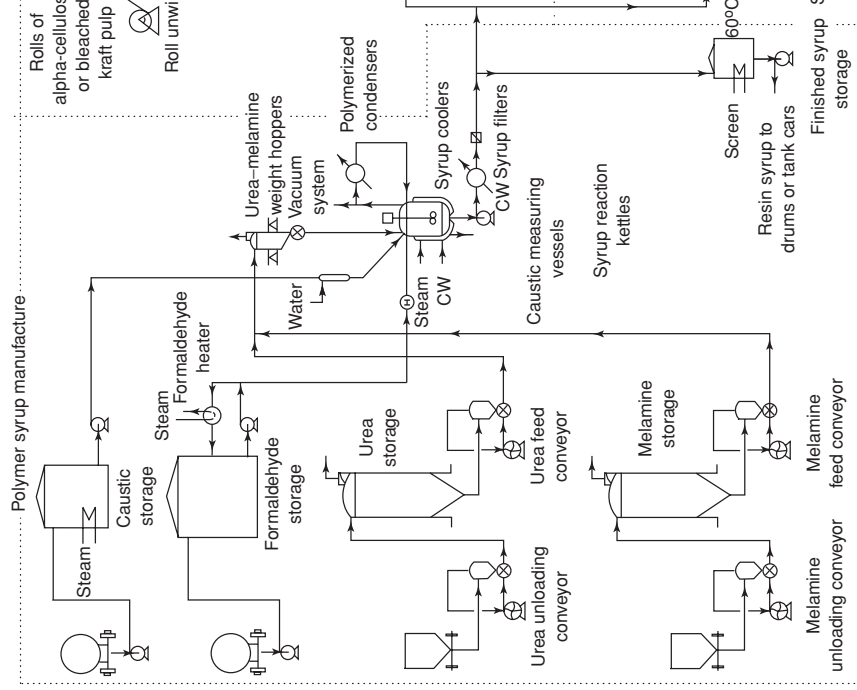


Fig. 2. Urea-formaldehyde and melamine-formaldehyde resin

2 MPa (150–300 psi). Hot-press temperatures for urea and melamine–urea are usually 115–132°C.

In plywood production with ureas, the spread veneers should be pressed as soon as possible. The time between spreading and pressing, usually called assembly time, should never exceed 1 h. With some formulations, the permissible assembly time may be no longer than 15 min. Melamine formulations and uncatalyzed melamine–urea combinations, however, can be spread and stored for as much as a week before use.

Ureas are not satisfactory for prolonged water immersion or for continuous exposure to warm and excessively humid conditions, although they are fairly resistant to normal humidity. Somewhat more durable bonds are obtained by heat setting. Ureas can be extended with wheat or rye flour, using as much as 150 parts flour to 100 parts dry resin. The extended glue still retains a fair degree of moisture resistance. Melamine resins have excellent water resistance, but cannot be cured at room temperature. Durable laminated wood beams used in building construction usually employ microwave technology for heat curing.

Continuous production of urea–formaldehyde resins has been described in many patents. In a typical example, urea and formaldehyde are combined and the solution pumped through a multistage unit. Temperature and pH are controlled at each stage to achieve the appropriate degree of polymerization. The product is then concentrated in a continuous evaporator to about 60–65% solids (31).

Laminating Resins

Phenolic and melamine resins are both used in the manufacture of decorative laminated plastic sheets for counters and tabletops. The phenolic is functional, being used in the backing or support sheets, whereas the melamine resin performs both decorative and functional roles in the print sheet and the protective overlay. Hardness, transparency, stain resistance, and freedom from discoloration are essential, in addition to a long-lasting working surface. Transparency is achieved because the refractive index of cured melamine–formaldehyde resin approaches that of the cellulose fibers and thus there is little scattering of light. Low cost and good mechanical properties are provided by the phenolic backing layers. In this instance, the combination of phenolic and amino resins achieves an objective that neither would normally be capable of performing alone. Developments in modified melamine resins have contributed to commercialization of premium priced through-color decorative laminates in which the dark color phenolic backing layers are replaced by color layers matching the full range of surface colors.

Phenolic resins are generally used in alcoholic solution, whereas melamine resins are best handled in water or water–alcohol mixtures. The paper or cloth web is passed through a dip tank containing resin solution, adjusted for pickup on squeeze rolls, and then passed through a heated drying oven. Once dried, the treated paper or cloth is fairly stable and, if stored in a cool place, it may be kept for several weeks or months before pressing into laminated plastic sheets.

A melamine laminating resin used to saturate the print and overlay papers of a typical decorative laminate might contain 2 mol of formaldehyde for 2 mol of melamine. In order to inhibit crystallization of methylol melamines, the reaction

is continued until about one-fourth of the reaction product has been converted to low molecular weight polymer. A simple determination of free formaldehyde may be used to follow the first stage of the reaction, and the buildup of polymer in the reaction mixture may be followed by cloud-point dilution or viscosity tests.

A particularly interesting and useful test is run at high dilution. One or two drops of resin are added to a test tube half full of water. A cloudy streak as the drop sinks through the water indicates that the resin has advanced to the point where the highest molecular weight fraction of polymer is no longer soluble in water at that particular temperature. At this high dilution, the proportion of water to resin is not critical; hence the only measurement needed is the temperature of the water. The temperature at or below which the drops give a white streak is known as the *hydrophobe temperature*. This test is particularly useful with melamine resins.

Laminates are pressed in steam-heated, multiple-opening presses. Each opening may contain a book of as many as 10 laminates pressed against polished steel plates. Curing conditions are 20–30 min at about 150°C under a pressure of about 6900 kPa (1000 psi).

Molding Compounds

Molding was the first big application for amino resins, although molding compounds are more complex than either laminating resins or adhesives. A simple amino resin molding compound might be made by combining melamine with 37% formalin in the ratio of 2 mol of formaldehyde/1 mol of melamine at neutral or slightly alkaline pH and a temperature of 60°C. The reaction should be continued until some polymeric product has been formed to inhibit crystallization of dimethylolmelamine upon cooling. When the proper reaction stage has been reached, the resin syrup is pumped to a dough mixer where it is combined with alpha-cellulose pulp, approximately one part of cellulose to each three parts of resin solids. The wet, spongy mass formed in the dough mixer is then spread on trays where it is combined with alpha-cellulose in a humidity-controlled oven to produce a hard, brittle popcorn-like intermediate. This material may be coarsely ground and sent to storage. To make the molding material, the cellulose–melamine resin intermediate is combined in a ball mill with a suitable catalyst, stabilizer, colorants, and mold lubricants. The materials must be ground for several hours to achieve the uniform fine dispersion needed to get the desired decorative appearance in the molded article. The molding compound may be used as a powder or it may be compacted under heat and pressure to a granular product that is easier to handle (32). A urea molding compound might be made in much the same way using a resin made with 1.3–1.5 mol of formaldehyde/1.0 mol of urea.

Amino molding compounds can be compression-, injection-, or transfer-molded. Urea molding compound has found wide use and acceptance in the electrical surface wiring device industry. Typical applications are circuit breakers, switches, wall plates, and duplex outlets. Urea is also used in closures, stove hardware, buttons, and small housings. Melamine molding compound is used primarily in dinnerware applications for both domestic and institutional use. It is also used in electrical-wiring devices, ashtrays, buttons, and housings.

The emergence of a new amino application is rare at this point in its relatively long life, but one such application has appeared and is growing rapidly. Because of the relative hardness of both urea and melamine moldings, a unique use has been developed for small, granular-sized particles of cut up molded articles. It is the employment of a pressurized stream of plastic particles to remove paint without damaging the surface beneath, and can be compared with a sandblasting operation. This procedure is gaining wide acceptance by both commercial airlines and the military for the refinishing of painted surfaces. It does not harm the substrate and eliminates the use of chemicals formerly used in stripping paint.

To speedup the molding process, the required amount of molding powder or granules is often pressed into a block and prewarmed before placing it in the mold. Rapid and uniform heating is accomplished in a high frequency preheater, essentially an industrial microwave oven. The prewarmed block is then transferred to the hot mold, pressed into shape, and cured.

Production of decorated melamine plastic dinner plates makes use of molding and laminating techniques. The pattern is printed on the same type of paper used for the protective overlay of decorative laminates, treated with melamine resin and dried, and then cut into disks of the appropriate size.

To make a decorated plate, the mold is opened shortly after the main charge of molding compound has been pressed into shape, the decorative foil is laid in the mold on top of the partially cured plate, printed side down, and the mold closed again to complete the curing process. The melamine-treated foil is thus fused to the molded plate and, as with the decorative laminate, the overlay becomes transparent so that the printed design shows through yet is protected by the film of cured resin.

The excellent electrical properties, hardness, heat resistance, and strength of melamine resins make them useful for a variety of industrial applications. Some representative properties of amino resin molding compounds, including the industrial-grade melamines, are listed in Table 2.

Coatings

Cured amino resins are far too brittle to be used alone as surface coatings for metal or wood substrates, but in combination with other film formers (alkyds, polyesters, acrylics, epoxies) a wide range of acceptable performance properties can be achieved. These combination binder coating formulations cure rapidly at slightly elevated temperatures, making them well-suited for industrial baking applications. The amino resin content in the formulation is typically in the range of 10–50% of the total binder solids.

A wide selection of amino resin compositions is commercially available. They are all alkylated to some extent in order to provide compatibility with the other film formers, and formulation stability. They vary not only in the type of amine (melamine, urea, benzoguanamine, and glycoluril) used, but also in the concentration of combined formaldehyde, and the type and concentration of alkylation alcohol (*n*-butanol, isobutyl alcohol, and methanol).

On curing, amino resins not only react with the nucleophilic sites (hydroxyl, carboxyl, amide) on the other film formers in the formulation, but also

Table 2. Typical Properties of Filled Amino Resin Molding Compounds

Property	ASTM or UL test	Urea		Melamine	
		Alpha-cellulose	Alpha-cellulose	Macerated Fabric	Glass fiber
<i>Physical</i>					
Specific gravity	D792	1.47–1.52	1.47–1.52	1.5	1.8–2.0
Water absorption, 24 h, 3.2 mm thick, %	D570	0.48	0.1–0.6	0.3–0.6	0.09–0.21
<i>Mechanical</i>					
Tensile strength, MPa ^a	D638	38–48	48–90	55–69	35–70
Elongation, %	D638	0.5–1.0	0.6–0.9	0.6–0.8	
Tensile modulus, GPa ^b	D638	9–9.7	9.3	9.7–11	16.5
Hardness, Rockwell M	D785	110–120	120	120	115
Flexural strength, MPa ^a	D790	70–124	83–104	83–104	90–165
Flexural modulus, GPa ^b	D7900	9.7–10.3	7.6	9.7	16.5
Impact strength, J/m ^c of notch	D256	14–18	13–19	32–53	32–1000
<i>Thermal</i>					
Thermal conductivity, 10 ^{−4} W/(m·K)	C177	42.3	29.3–42.3	44.3	48.1
Coefficient of thermal expansion, 10 ^{−5} cm/(cm·°C)	D696	2.2–3.6	2.0–5.7	2.5–2.8	1.5–1.7
Deflection temperature at 1.8 MPa, °C	D648	130	182	154	204
Flammability class	UL-94	VO ^d	VO ^d	VO	VO
Continuous no-load service temperature, °C		77 ^e	99 ^e	121	149–204
<i>Electrical</i>					
Dielectric strength, V/0.00254 cm	D149	330–370	270–300	250–350	170–300
Short time, 3.2 mm thick		220–250	240–270	200–300	170–240
Step by step					
Dielectric constant, 22.8°C	D150	7.7–7.9	8.4–9.4	7.6–12.6	9.7–11.1
At 60 Hz			7.8–9.2	7.1–7.8	
At 10 ³ Hz					
Dissipation factor, 22.8°C	D150	0.034–0.043	0.030–0.083	0.07–0.34	0.14–0.23
At 60 Hz			0.015–0.036	0.03–0.05	
At 10 ³ Hz			0.8–2.0 × 10 ¹²	1.0–3.0 × 10 ¹¹	0.9–2.0 × 10 ¹¹
Volume resistivity, 22.8°C, 50% rh, Ω·cm	D257	0.5–5.0 × 10 ¹¹	125–136	122–128	180–186
Arc resistance, s	D495	80–100			

^aTo convert MPa to psi, multiply by 145.
^bTo convert GPa to psi, multiply by 145,000.
^cTo convert J/m to ft-lbf/in., divide by 53.38.
^dApplies to specimens thicker than 1.6 mm.
^eBased on no color change.

self-condense to some extent. Highly alkylated amino resins have less tendency to self-condense (33,34) and are therefore effective cross-linking agents, but may require the addition of a strong acid catalyst to obtain acceptable cure even at bake temperatures of 120–177°C.

Amino resins based on urea have advantages in low temperature cure response and low cost. However, they are not as stable to uv radiation as melamine resins, and have poorer heat resistance; therefore, they have been successful primarily in interior wood finishes. Melamine resins, on the other hand, are uv stable, have excellent heat resistance, film hardness, and chemical resistance. They therefore dominate amino resin usage in OEM automotive coatings, general metals finishes, container coatings (both interior and exterior), and prefinished metal applications. Glycoluril resins have also found use in prefinished metal, primarily because of their high film flexibility properties. Unalkylated glycoluril resins are unique in that they are stable under slightly acidic conditions and have therefore found use in low temperature cure waterborne finishes. Benzoguanamine resins have historically been successful in appliance finishes because of their superior chemical resistance and specifically their detergent resistance. However, they have both poor uv resistance and economics, which have limited their use in other application areas.

When first introduced to the coatings industry, amino resin compositions were partially butylated and relatively polymeric in nature, with degrees of polymerization of 4–6. However, the dominant amino resin in today's industrial coating is based on a highly methylated, highly monomeric (degrees of polymerization of 1.4–2.6) melamine cross-linking agent. Variations of extent of methylolation and methylation exist along with a number of co-ethers, where the melamine molecule is both methylated and either *n*-butylated or isobutylated. This type of composition dominates because it best addresses the pollution (low volatile organic compounds) and performance requirements of today's industrial finishes (see COATINGS).

Methylation provides fast cure response, improved exterior exposure, high weight retention on curing, and suitability for both solvent and waterborne systems. Waterborne systems, in most instances, provide lower pollution than solvent-based formulations. High monomer content reduces the viscosity of the amino resin, again lowering pollution particularly when used in solvent-based systems, and also improves film flexibility and recoat adhesion. When some butylation is included as part of the alkylation, the viscosity of the amino resin is lowered, thereby lowering pollution (of the formulated coating), improving recoat adhesion, and improving wetting and flow characteristics. An amino resin is usually selected on the basis of specific performance properties required or performance to be emphasized.

Stability in storage is an important property for coating systems containing amino resins. If the amino resin undergoes self-condensation or reacts at room temperature with the alkyd or other film-forming polymer, the system may become too viscous or thicken to a gel which can no longer be used for coating. Alkyds usually contain sufficient free carboxyl groups to catalyze the curing reaction when the coating is baked, but this may also cause the paint to thicken in storage. Partial neutralization of the acid groups with an amine can greatly improve storage stability yet allow the film to cure when baked,

since much of the amine is vaporized with the solvent during the baking process. 2-Amino-2-methyl-1-propanol [124-68-5], triethylamine [121-44-8], and dimethylaminoethanol [108-01-1] are commonly used as stabilizers. Alcohols as solvent also improve storage stability. Catalyst addition just before the coating is to be applied permits rapid curing and avoids the problem of storage stability. A strong acid soluble in organic solvents such as *p*-toluenesulfonic acid is very effective and may be partially neutralized with an amine to avoid premature reaction.

A butylated urea-formaldehyde resin for use in the formulation of fast-curing baking enamels might be made beginning with the charge: urea (1 mol), paraformaldehyde (2.12 mol), and butanol (1.50 mol). Triethanolamine is added to make the solution alkaline (about 1% of the weight of the urea), and the mixture is refluxed until the paraformaldehyde is dissolved. Phthalic anhydride is added to give a pH of 4.0, and the water removed by azeotropic distillation until the batch temperature reaches 117°C. Cooling and dilution with solvent is done until the desired solids content is reached (35).

A highly methylated melamine-formaldehyde resin for cross-linking with little or no self-condensation might be made as follows (36). A solution of formaldehyde in methyl alcohol is charged to a reaction kettle and adjusted to a pH of 9.0–9.5 using sodium hydroxide. Melamine is then added to give a ratio of 1 mol of melamine/6.5 mol of formaldehyde, and the mixture is refluxed for 1.5 h. The reaction is then cooled to 35°C, and more methanol added to bring the ratio of methanol per mole of melamine up to 11. With the batch temperature at 35°C, enough sulfuric acid is added to reduce the pH to 1. After holding the reaction mixture at this temperature and pH for 1 h, the batch is neutralized with 50% NaOH and the excess methanol stripped to give a product containing 60% solids, which is then clarified by filtration. A highly methylated resin, such as this, may be used in water-based (37) or solvent-type coatings. It might also be used to provide crease resistance to cotton fabric.

The principal problems facing amino resins in the industrial coatings of the 1990s are formaldehyde emission and low temperature cure performance. Significant progress has been made in reducing the residual free formaldehyde in the amino resin, but formaldehyde generation on baking must still be addressed. Concerning low temperature cure performance, emphasis is being placed on catalyst selection. Amino resins cure at bake temperatures as low as 71–82°C, but at these bake temperatures they require high concentrations of acid catalyst, which negatively affect hydrolysis resistance or water sensitivity of the cured film. The development of improved catalysts is the most promising solution to low temperature cure performance enhancement.

Textile Finishes

Most amino resins used commercially for finishing textile fabrics are methylolated derivatives of urea or melamine. Although these products are usually monomeric, they may contain some polymer by-product.

Amino resins react with cellulosic fibers and change their physical properties. They do not react with synthetic fibers, such as nylon, polyester, or acrylics,

but may self-condense on the surface. This results in a change in the stiffness or resiliency of the fiber. Partially polymerized amino resins of such molecular size that prevents them from penetrating the amorphous portion of cellulose also tend to increase the stiffness or resiliency of cellulose fibers.

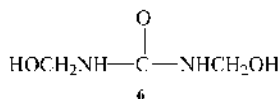
Monomeric amino resins react predominantly with the primary hydroxyls of the cellulose, thereby replacing weak hydrogen bonds with strong covalent bonds, which leads to an increase in fiber elasticity. When an untreated cotton fiber is stretched or deformed by bending, as in forming a crease or wrinkle, the relatively weak hydrogen bonds are broken and then re-form to hold the fiber in its new position. The covalent bonds that are formed when adjacent cellulose chains are cross-linked with an amino resin are five to six times stronger than the hydrogen bonds. Covalent bonds are not broken when the fiber is stretched or otherwise deformed. Consequently, the fiber tends to return to its original condition when the strain is removed. This increased elasticity is manifested in two important ways:

- (1) When a cotton fabric is cross-linked while it is held flat, the fabric tends to return to its flat condition after it has been wrinkled during use or during laundering. Garments made from this type of fabric are known as wash-and-wear, minimum care, or no-iron.
- (2) A pair of pants that is pressed to form a crease and then cross-linked tends to maintain the crease through wearing and laundering. This type of garment is called *durable-press* or *permanent press*.

This increased elasticity is always accompanied by a decrease in strength of the cellulose fiber, which occurs even though weak hydrogen bonds are replaced by stronger covalent bonds. The loss of strength is not caused by hydrolytic damage to the cellulose. If the cross-linking agent is removed by acid hydrolysis for example, the fiber will regain most, if not all, of its original strength. The loss in strength is believed to be due to intramolecular reaction of the amino resin along the cellulose chain to displace a larger number of hydrogen bonds, resulting in a net loss in strength. The intramolecular and intermolecular reactions (cross-linking) both occur at the same time.

Although there are many different amino resins used for textile finishing, all of them impart about the same degree of increase in elasticity when applied on an equal molar basis. Elasticity can be measured by determining the recovery from wrinkling. Although all these products impart about the same degree of improvement in elasticity, they also may impart many other desirable or undesirable properties to the fabric. The development of amino resins for textile finishing has been aimed toward maximizing the desirable properties and minimizing the undesirable ones. Most of the resins and reactants used in today's textile market are based on urea as a starting material. However, the chemistry differs considerably from that employed in early textile-finishing operations.

The first amino resins used commercially on textiles were the so-called urea-formaldehyde resins, dimethylolurea [140-95-4] (6), or its mixtures with monomethylolurea [1000-82-4].



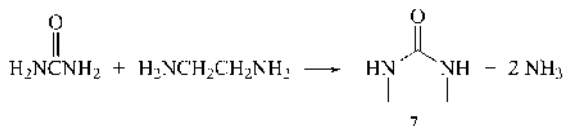
Their performance falls short of most present finishes, particularly in durability, resistance to chlorine-containing bleaches, and formaldehyde release, and they are not used much today. Both urea and formaldehyde are relatively inexpensive, and manufacture is simple; ie, 1–2 mol of formaldehyde as an aqueous solution reacts with 1 mol of urea under mildly alkaline conditions at slightly elevated temperatures.

Since the methylolurea monomers have limited water solubility (about 30%), they were usually marketed in dispersed form as soft pastes containing 55–65% active ingredient in order to decrease container and shipping costs. By increasing the temperature and using slightly acidic conditions, dimethylolureas can be made as a series of short polymers that have infinite water solubility and can be marketed at concentrations as high as 85%. However, because these result in increased fabric stiffness, they cannot be used interchangeably with the monomeric materials. Both forms polymerize readily in storage and, unless kept under refrigeration, become water insoluble within a few weeks at ambient temperatures.

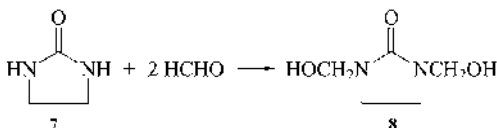
To overcome stability and water solubility problems, methylolurea resins are frequently alkylated to block the reactive hydroxyl groups. For reasons of economy the alkylating agent is usually methanol. In this process, 2 mol of aqueous formaldehyde reacts with 1 mol of urea under alkaline conditions to form dimethylolurea. Excess methanol is then added, and the reaction continued under acidic conditions to form methoxymethylurea. Both methylol groups can be methylated by maintaining low concentrations of water and using a large excess of methanol; however, methylation of only one of the methylol groups is sufficient to provide adequate shelf-life and water solubility. Upon completion of the methylation reaction, the resin is adjusted to pH 7–10, and excess methanol and water are removed by distillation under reduced pressure to provide syrups of 50–80% active ingredients.

Like methylolureas, cyclic ureas are based on reactions between urea and formaldehyde; however, the amino resin is cyclic rather than linear. Many cyclic urea resins have been used in textile-finishing processes, particularly to achieve wrinkle resistance and shrinkage control, but the ones described below are the most commercially important. They are all in use today to greater or lesser extents, depending on specific end requirements.

Ethyleneurea Resins. One of the most widely used resins during the 1950s and 1960s was based on dimethylolethyleneurea [136-84-5] [1,3-bis(hydroxymethyl)-2-imidazolidinone], commonly known as ethyleneurea resin. Ethyleneurea resin [28906-87-8] is most conveniently prepared from urea, ethylenediamine, and formaldehyde. 2-Imidazolidinone [120-93-4] (7) (ethyleneurea) is first prepared by the reaction of excess ethylenediamine [107-15-3] with urea (38) in an aqueous medium at about 116°C.

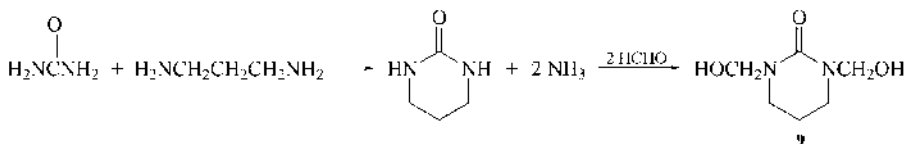


A fractionating column is required for the removal of ammonia and recycle of ethylenediamine. The molten product (mp 133°C) is then run into ice water to give a solution that is methylolated with 37% aqueous formaldehyde to form dimethylolethyleneurea (8).



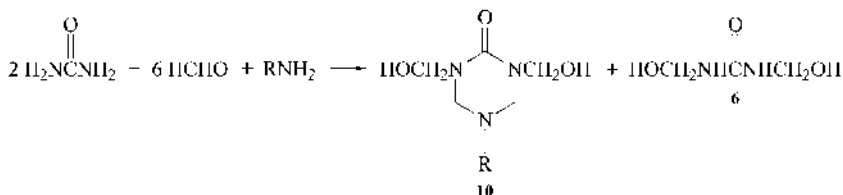
The resin, generally a 50% solution in water, has excellent shelf-life and is stable to hydrolysis and polymerization.

Propylene Urea Resins. Similar to the product from ethyleneurea (7), dimethylolpropyleneurea [3270-74-4] (9) 1,3-bis(hydroxymethyl)tetrahydro-2-(1*H*)-pyrimidinone] is the basis of propyleneurea-formaldehyde resin [65405-39-2]. Its preparation is from urea, 1,3-diaminopropane [109-76-2], and formaldehyde.



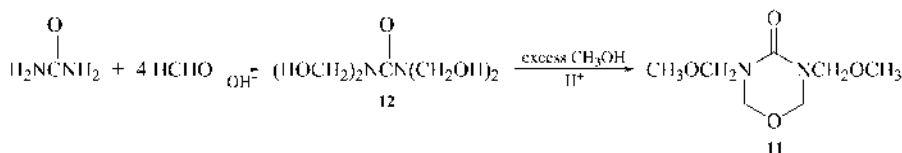
This resin was temporarily accepted, primarily because of its improved resistance to acid washes. However, the relatively high cost of the diamine precluded widespread commercial acceptance.

Triazone. Triazone is the common name for the class of compounds corresponding to the dimethylol derivatives of tetrahydro-5-alkyl-*s*-triazone (10). They can be made readily and cheaply from urea, formaldehyde, and a primary aliphatic amine. A wide variety of amines may be used to form the six-membered ring (39); however, for reasons of cost and odor, hydroxyethylamine (monoethanolamine) is used preferentially. Since the presence of straight-chain methylolureas causes no deleterious effects to the fabric finish, the triazones typically are prepared with less than the stoichiometric quantity of the amine. This results not only in a less costly resin but also in improved performance (40).

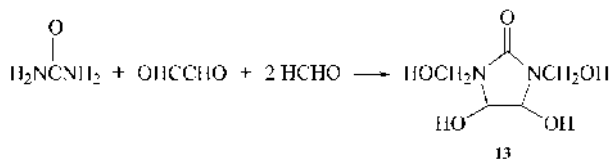


The resin is simply prepared by heating the components together. Usually the urea and formaldehyde are first charged to the kettle and heated under alkaline conditions to give a mixture of polymethylolureas, followed by the slow addition of the amine with continued heating to form the cyclic compound. The order of addition can be varied as can the molar ratios so as to yield a range of chain-ring compound ratios. The commercial resin is usually sold as a 50% solids solution in water.

Uron Resins. In the textile industry, the term uron resin *uron resin* usually refers to the mixture of a minor amount of melamine resin and so-called uron, which in turn is predominantly *N,N'*-bis(methoxymethyl)uron [7388-44-5] (11) plus 15–25% methylated urea–formaldehyde resins, a by-product. *N,N'*-bis(methoxymethyl)uron was first isolated and described in 1936 (41), but was commercialized only in 1960. It is manufactured (42) by the reaction of 4 mol of formaldehyde with 1 mol of urea at 60°C under highly alkaline conditions to form tetramethylolurea [2787-01-1] (12). After concentration under reduced pressure to remove water, excess methanol is charged and the reaction continued under acidic conditions at ambient temperatures to close the ring and methylate the hydroxymethyl groups. After filtration to remove the precipitated salts, the methanolic solution is concentrated to recover excess methanol. The product (75–85% pure) is then mixed with a methylated melamine–formaldehyde resin to reduce fabric strength losses in the presence of chlorine, and diluted with water to 50–75% solids. Uron resins do not find significant use today because of the greater amounts of formaldehyde released from fabric treated with these resins.

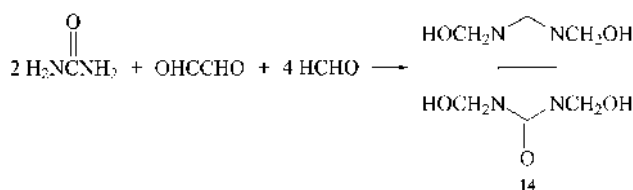


Glyoxal Resins. Since the late 1960s, glyoxal resins have dominated the textile-finish market for use as wrinkle-recovery, wash-and-wear, and durable-press agents. These resins are based on 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone, commonly called dimethyloldihydroxyethyleneurea [1854-26-8] (DMDHEU) (13). Several methods of preparation are described in the literature (43). On a commercial scale, DMDHEU can be prepared inexpensively at high purity by a one-kettle process (44): 1 mol of urea, 1 mol of glyoxal [107-22-2] as 40% solution, and 2 mol of formaldehyde in aqueous solution are charged to the reaction vessel. The pH is adjusted to 7.5–9.5 and the mixture heated at 60–70°C. The reaction is nearly stoichiometric; excess reagent is not necessary.



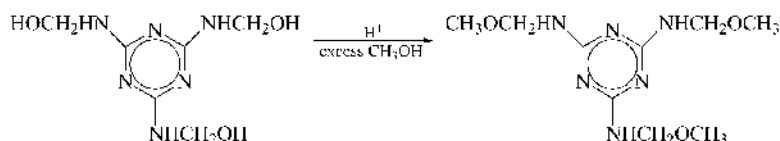
Glyoxal resins are generally sold at 45% solids solutions in water. Resin usage for crease-resistant fabrics had increased to well over 60×10^6 kg by 1974 and over half of this was DMDHEU for durable-press garments. In the early 1980s glyoxal resins modified with diethylene glycol [111-46-6] became prominent in the marketplace. These products are either simple mixtures of diethylene glycol and DMDHEU in water solution or the reaction product of diethylene glycol and DMDHEU. Rarely, ethylene glycol has been used in place of diethylene glycol. The diethylene glycol-modified DMDHEU products have the advantage of releasing significantly less formaldehyde from the finished fabric after resin curing than from fabric treated with DMDHEU. On the other hand, durable-press performance and shrinkage control are somewhat less with the glycol-modified resins.

A less important glyoxal resin is tetramethylolglycoluril [5395-50-6] (14) (tetramethylolacetylenediurea) produced by the reaction of 1 mol of glyoxal with 2 mol of urea and 4 mol of formaldehyde.



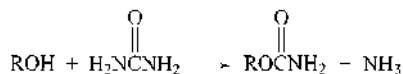
This resin was most popular in Europe, partly because of its lower requirements of glyoxal. However, because of increased availability and lower glyoxal costs plus certain application weaknesses, it has been generally replaced by DMDHEU.

Melamine-Formaldehyde Resins. The most versatile textile-finishing resins are the melamine-formaldehyde resins. They provide wash-and-wear properties to cellulosic fabrics, and enhance the wash durability of flame-retardant finishes. Butylated melamine-formaldehyde resins of the type used in surface coatings may be used in textile printing-ink formulations. A typical textile melamine resin is the dimethyl ether of trimethylolmelamine [1852-22-8], which can be prepared as follows:



Under alkaline conditions, 3 mol of formaldehyde react with 1 mol of melamine at elevated temperatures. Since water interferes with the methylation, methylation is carried out in methanol with paraformaldehyde and by simply adjusting the pH to about 4 with continued heating. After alkylation is complete the pH is adjusted to 8–10, and excess methanol is distilled under reduced pressure. The resulting syrup contains about 80% solids.

Miscellaneous Resins. Much less important than the melamine-formaldehyde and urea-formaldehyde resins are the methylol carbamates. They are urea derivatives since they are made from urea and an alcohol.



(R can vary from methyl to a monoalkyl ether of ethylene glycol). Temperatures in excess of 140°C are required to complete the reaction and pressurized equipment is used for alcohols boiling below this temperature; provision must be made for venting ammonia without loss of alcohol. The reaction is straightforward and, in the case of the monomethyl ether of ethylene glycol [109-86-4], can be carried out at atmospheric pressure using stoichiometric quantities of urea and alcohol (45). Methylolation with aqueous formaldehyde is carried out at 70–90°C under alkaline conditions. The excess formaldehyde needed for complete dimethylolation remains in the resin and prevents more extensive usage because of formaldehyde odor problems in the mill.

Other amino resins used in the textile industry for rather specific properties have included the methylol derivatives of acrylamide (46), hydantoin [461-79-3] (47), and dicyandiamide (48).

Textiles are finished with amino resins in four steps. The fabric is (1) passed through a solution containing the chemicals, (2) through squeeze rolls (padding) to remove excess solution, (3) dried, and (4) heated (cured) to bond the chemicals with the cellulose or to polymerize them on the fabric surface.

The solution (pad bath) contains one or more of the amino resins described above, a catalyst, and other additives such as a softener, a stiffening agent, or a water repellant. The catalyst may be an ammonium or metal salt, eg, magnesium chloride or zinc nitrate. Synthetic fabrics, such as nylon or polyester, are treated with amino resins to obtain a stiff finish. Cotton or rayon fabrics or blends with synthetic fibers are treated with amino resins to obtain shrinkage control and a durable-press finish.

Normally, fabrics are treated in the sequence outlined above. The temperature of the drying unit is 100–110°C and the temperature of the curing unit can vary between 120 and 200°C but usually ranges from 150 to 180°C. The higher temperatures are employed to polymerize the resins on synthetic fabrics and at the same time to heat-set the fibers. Temperatures up to 180°C are used to allow the amino resins to react with cellulosic fibers alone or blended with synthetic fibers. The fabric is held flat but with minimum tension during drying and curing, and always tends to become flat when creased or wrinkled during use or laundering. The resin-treated cellulose absorbs less water and swells less than untreated cellulose. This reduced swelling along with little or no tension induced during drying minimizes shrinkage during laundering.

The steps followed in the precure are repeated in the postcure process, except that after the drying step the goods are shipped to a garment manufacturer who makes garments, presses them into the desired shape with creases or pleats, and then cures the amino resin on the completed garment. It is important that the amino resins used in the postcure process should (1) not react with the fabric

before it has been fashioned into a garment, and (2) release a minimum amount of formaldehyde into the atmosphere, especially while the goods are in storage or during the cutting and sewing operations. These requirements are met, at present, with the diethylene glycol-modified DMDHEU resin.

Tire Cord. Melamine resins are also used to improve the adhesion of rubber to reinforcing cord in tires. Textile cord is normally coated with a latex dip solution composed of a vinylpyridine–styrene–butadiene latex rubber containing resorcinol–formaldehyde resin. The dip coat is cured prior to use. The dip coat improves the adhesion of the textile cord to rubber. Further improvement in adhesion is provided by adding resorcinol and hexa(methoxymethyl)melamine [3089-11-0] (HMMM) to the rubber compound which is in contact with the textile cord. The HMMM resin and resorcinol cross-link during rubber vulcanization and cure to form an interpenetrating polymer within the rubber matrix, which strengthens or reinforces the rubber and increases adhesion to the textile cord. Brass-coated steel cord is also widely used in tires for reinforcement. Steel belts and bead wire are common applications. Again, HMMM resins and resorcinol [108-46-3] are used in the rubber compound which is in contact with the steel cord so as to reinforce the rubber and increase the adhesion of the rubber to the steel cord. This use of melamine resins is described in the patent literature (49).

Amino Resins in the Paper Industry

Paper is a material of tremendous versatility and utility, prepared from a renewable resource. It may be made soft or stiff, dense or porous, absorbent or water repellent, textured or smooth. Some of the versatility originates with the fibers, which may vary from short and supple to long and stiff, but the contribution of chemicals should not be underestimated.

Amino resins are used by the paper industry in large volume for a variety of applications. The resins are divided into two classes according to the mode of application. Resins added to the fiber slurry before the sheet is formed are called wet-end additives and are used to improve wet and dry strength and stiffness. Resins applied to the surface of formed paper or board, almost invariably together with other additives, are used to improve the water resistance of coatings, the sag resistance in ceiling tiles, and the scuff resistance in cartons and labels.

The requirements for the two types of resins are very different. Wet-end additives are used in dilute fiber slurries in small amounts. After the sheet is formed, most of the water is drained away and some of the remaining water is pressed out of the sheet before it is dried. The amino resin must be retained (absorbed) on the surface of the cellulose fibers so that it will not be washed away. On a typical paper machine, fiber concentration in the headbox would be about 1%. If the amount of wet-strength resin used is 1% of the weight of the fiber, the concentration of resin in the headbox would be only 0.01%. If no mechanism for attaching the resin to the fiber is provided, only a trace of the resin added to the slurry would be retained in the finished sheet. Good retention is achieved

with the amino resin by making the resin cationic. Since the cellulose surface is anionic because of the carboxylic acid groups present, the cationic charge on the resin makes it substantive with the fiber leading to good retention of the resin when applied in the wet-end. Resins for application to the surface of preformed paper are not required to be substantive to cellulose and they may be formulated for adhesion, cure rate, viscosity, compatibility with other materials, etc, without concern for retention.

The integrity of a paper sheet is dependent on the hydrogen bonds which form between the fine structures of cellulose fibers during the pressing and drying operations (see CELLULOSE). The bonds between hydroxyls of neighboring fibers are very strong when the paper is dry, but are severely weakened as soon as the paper becomes wet. Bonding between the hydroxyls of cellulose and water is as energetic as bonding between two cellulose hydroxyls. As a consequence, ordinary paper loses most of its strength when it is wet or exposed to very high humidity. The sheet loses its stiffness and bursting, tensile and tearing strength.

Many materials have been used over the years in an effort to correct this weakness in paper. If water can be prevented from reaching the sites of the bonding by sizing or coating the sheet, then a measure of wet strength may be attained. Water molecules are so small and cellulose and so hydrophilic that this solution usually affords only temporary protection. Formaldehyde, glyoxal, polyethylenimine, and, more recently, derivatized starch (50) and derivatized cationic polyacrylamide resins (51) have been used to provide temporary wet strength. The first two materials must be applied to the formed paper, but the other materials are substantive to the fiber and may be used as wet-end additives. Carboxymethylcellulose–calcium chloride and locust-bean gum–borax are examples of two-component systems applied separately to paper that were used to a limited extent before the advent of the amino resins. Today three major types of wet-strength resins are used in papermaking: polyamide–polyamine resins cross-linked with epichlorohydrin (52) are used in neutral to alkaline papers; cationic polyacrylamide resins cross-linked with glyoxal are used for acid to neutral papers; and melamine–formaldehyde resins are used for acid papers.

During the 30-year period following the introduction of synthetic wet-strength additives to papermaking in 1942, most paper was made at acid pH. Low molecular weight (or even monomeric) trimethylolmelamine [1017-56-7], when dissolved in the proper amount of dilute acid and aged, polymerizes to a colloidal polymer that is retained well by almost all types of papermaking fiber, and produces high wet strength under the mild curing conditions easily attained on a paper machine (53,54). This resin, introduced by American Cyanamid in 1942, is still extensively used when rapid cure, high wet strength, and good dry strength are important in acid paper. Some processing improvements have been made, including a report (55) describing the formation of a stable melamine resin acid colloid using formic and phosphoric acids. The chemistry of this reaction is quite interesting.

Melamine–formaldehyde acts as an amine when dissolved in dilute acid, usually HCl. During polymerization, between 20 and 80 monomeric units combine to form a polymer of colloidal dimensions (6–30 nm) with the elimination of

Table 3. Formulations for Regular and HE Colloid Resins

	Regular MF ₃	HE MF ₈
Water, 20 ± 10°C, kg	412.0	330.8
HCl, 20° Bé, kg (1.16 g/mL), kg	17.7	14.1
Formaldehyde, 37%, kg		84.8
Trimethylolmelamine, kg	45.4	45.4
<i>Total</i>	<i>475.1</i>	<i>475.1</i>

water and HCl (56,57). The development of cationicity is associated with the loss of HCl, since a unit of charge on the polymer is generated for every mole of acid lost, and the pH decreases steadily during the polymerization. In a typical formulation at 12% solids at room temperature, polymerization is complete in about 3 h. The initially colorless solution develops a light blue haze and shows a strong Tyndall effect.

Such a colloidal sol is highly substantive to all papermaking fibers, kraft, sulfite, groundwood, and soda. For its successful use in paper mills, the pH must be kept low, both to prevent precipitation of the resin in an unusable form and to promote curing of the resin; and the concentration of sulfates in the white water on the paper machine must not be allowed to exceed 100 ppm, again because the resin is precipitated in an inactive form by high concentrations of sulfates. High sulfate concentrations may build up in mills using large amounts of alum for setting size or sulfuric acid for controlling pH.

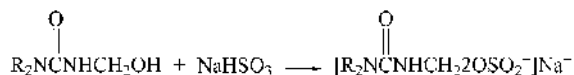
The problem of sulfate sensitivity was solved by adding formaldehyde to the aged colloid, which improved wet-strength efficiency and reduced sensitivity to sulfates (58). Later, equivalent results were obtained by adding the extra formaldehyde before the colloid was aged. The additional formaldehyde acts like an acid during the aging process and, unless compensated for by a reduction in the amount of acid charged, lowers the pH to a point where polymerization to the colloids is inhibited. The high efficiency (HE) resins have been used in mills with sulfate concentrations so high that use of regular trimethylolmelamine (MF₃) colloids would be uneconomical. Sulfate tolerance is a function of the amount of extra formaldehyde present. For best cost-performance, a family of HE colloids is necessary with composition varying from MF₄, for moderate sulfate concentrations, to MF₉, for very high sulfates.

Formulations for regular and HE colloids are shown in Table 3 (59). The materials are added, in the order listed, to a 454-L (120-gal) tank provided with good agitation and ventilation. Formaldehyde fumes are evolved even from the regular colloid. The colloids develop only after aging and freshly prepared solutions are ineffective for producing wet strength. Stability of the colloids depends on temperature and concentration. Colloids at 10–12% are stable at room temperature for at least 1 week; stability may be extended by dilution after the colloids have aged properly.

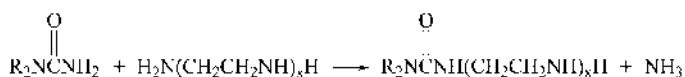
Both regular and HE colloids increase the wet strength of paper primarily by increasing adhesion between fibers; the strength of the individual fiber itself is unaffected (60). The resin appears to improve the adhesion between the

fibers, whether they are wet or dry, by forming bonds that are unaffected by water. The excess formaldehyde in the HE colloid appears to function by increasing the amount of formaldehyde bound in the colloid (59). The regular colloid, starting with about 3 mol of formaldehyde/1 mol of melamine, has about 2 mol bound in the colloid and 1 mol free. By mass action, the additional formaldehyde increases the amount of bound formaldehyde in the colloid. When an HE colloid is dialyzed or stored at very low concentrations (0.05%), it loses the extra bound formaldehyde and behaves as a regular colloid.

The first urea-formaldehyde resins used to any extent as wet-strength agents were anionic polymers made by the reaction of a urea resin with sodium bisulfite (NaHSO_3) (61). Attempts to use nonionic urea-formaldehyde polymers were unsuccessful; the neutral charge on the polymer made it unsubstantive to fiber resulting in lack of retention. The sulfomethyl group introduced by reaction with NaHSO_3 gave the polymers strong anionicity, but substantivity was largely restricted to unbleached kraft pulp. Lignin residues probably provided sites for absorption of the polymer. The use of alum as a mordant was essential, since both the resin and the fiber were anionic. The reaction of bisulfite with the urea-formaldehyde polymer may be represented as



In 1945, cationic urea resins were introduced and quickly supplanted the anionic resins, since they could be used with any type of pulp (62). Although they have now become commodities, their use in the industry has been steadily declining as the shift toward neutral and alkaline papermaking continues. They are commonly made by the reaction of urea and formaldehyde with one or more polyethylene-polyamines. The structure of these resins is very complicated and has not been determined. Ammonia is evolved during the reaction, probably according to the following:



Formaldehyde may react with the active hydrogens on both the urea and amine groups and therefore the polymer is probably highly branched. The amount of formaldehyde (2–4 mol/1 mol urea), the amount and type of polyamine (10–15%), and resin concentration are variable and hundreds of patents have been issued throughout the world. Generally, the urea, formaldehyde, polyamine, and water react at 80–100°C. The reaction may be carried out in two steps, with an initial methylation at alkaline pH, followed by condensation to the desired degree at acidic pH, or the entire reaction may be carried out under acidic conditions (63). The product is generally a syrup with 25–35% solids and is stable for up to 3 months.

The cationic urea resins are added to paper pulp preferably after all major refining operations have taken place. The pH on the paper machine must be acidic

for reasonable rates of cure of the resin. Urea resins do not cure as rapidly as melamine-formaldehyde resins and the wet strength produced is not as resistant to hydrolysis. Furthermore, the resins are not retained as well as the melamine resins. On a resin-retained basis, however, their efficiency is as good. The lower retention of the urea-formaldehyde resins is due to their polydisperse molecular weight distribution. High molecular weight species are strongly absorbed on the fibers and are large enough to bridge two fibers. Low molecular weight species are not retained as well because of fewer charge sites. Attempts to improve the performance of urea-formaldehyde resins by fractionating the syrups by salt or solvent precipitation, or selective freezing or dialysis have been technically successful but economically impractical. The process for production of resins is sufficiently simple so that some paper mills have set up their own production units. With captive production, resins with higher molecular weights and lower stability may be tolerated.

The recovery of fiber from *broke* (off-specification paper or trim produced in the paper mill) is complicated by high levels of urea-formaldehyde and melamine-formaldehyde wet-strength resin. The urea resins present a lesser problem than the melamine resins because they cure slower and are not as resistant to hydrolysis. Broke from either resin treatment may be reclaimed by hot acidic repulping. Even the melamine resin is hydrolyzed rapidly under acidic conditions at high temperature. The cellulose is far more resistant and is not harmed if the acid is neutralized as soon as repulping is complete.

The TAPPI monograph (64) is an excellent source of additional information on technical and economic aspects of wet strength. An informative overview of the chemistry and mechanisms involved in wet strength chemistry can be found in Reference 65.

Wet-strength applications account for the majority of amino resin sales to the paper industry but substantial volumes are sold for coating applications. The largest use is to improve the resistance of starch-clay coatings to dampness. In offset printing, which is becoming ever more important in the graphic arts, the printing paper is exposed to both ink and water. If the coating lifts from the paper and transfers to the plate, it causes smears and forces a shutdown for cleaning. A wide variety of materials have been added to the coatings to improve wet-rub resistance, including casein, soya protein, poly(vinyl acetate), styrene-butadiene latices, glyoxal-urea resins, and amino resins. Paper coatings are applied at as high a solids content as possible to ease the problem of drying. Retention is not a problem since the resin is applied to a preformed sheet. The important characteristics for coating resins are high solids at low viscosity, high cure rates, and high wet-rub efficiency. Urea and melamine resins or mixtures are sold as high solids syrups or dry powders. They are used with starch-pigment coatings with acidic catalysts or with starch-pigment-casein (or protein) coatings usually without catalysts. The syrups are frequently methylated for solubility and stability at high solids. All of the resins are of intrinsically low molecular weight to reduce viscosity for ease of handling (see COATINGS).

Closely allied to resins for treating paper are the resins used to treat regenerated cellulose film (cellophane) which does not have good water resistance unless it is coated with nitrocellulose or poly(vinylidene chloride). Adhesion of the waterproofing coating to the cellophane film is achieved by first treating the

cellophane with an amino resin. The cellophane film is passed through a dip tank containing about 1% of a melamine–formaldehyde acid colloid type of resin. Some glycerol may also be present in the resin solution to act as a plasticizer. Resins for this purpose are referred to as *anchoring agents*.

Other Uses

Water-soluble melamine–formaldehyde resins are used in the tanning of leather in combination with the usual tanning agents. By first treating the hides with a melamine–formaldehyde resin, the leather is made more receptive to other tanning agents and the finished product has a lighter color. The amino resin is often referred to as a *plumping agent* because it makes the finished leather firmer and fuller.

Urea–formaldehyde resins are also used in the manufacture of foams. The resin solution containing an acid catalyst and a surface-active agent is foamed with air and cured. The open-cell type of foam absorbs water readily and is soft enough so that the stems of flowers can be easily processed into it. These features make the urea resin foam ideal for supporting floral displays. Urea–formaldehyde resin may also be foamed in place. A special nozzle brings the resin, catalyst, and foaming agent together. Air pressure is used to deposit the foam where it is desired, eg, within the outside walls of older houses to provide insulation. This application might be expected to grow as energy costs increase, if undesirable odors can be controlled.

Urea–formaldehyde resins are also used as the binder for the sand cores used in the molds for casting hollow metal shapes. The amino resin is mixed with moist sand and formed into the desired shape of the core. After drying and curing, the core is assembled into the mold and the molten metal poured in. Although the cured amino resin is strong enough to hold the core together while the hot metal is solidifying, it decomposes on longer heating. Later, the loose sand may be poured out of the hollow casting and recovered.

Regulatory Concerns

Both urea– and melamine–formaldehyde resins are of low toxicity. In the uncured state, the amino resin contains some free formaldehyde that could be objectionable. However, uncured resins have a very unpleasant taste that would discourage ingestion of more than trace amounts. The molded plastic or the cured resin on textiles or paper may be considered nontoxic. Combustion or thermal decomposition of the cured resins can evolve toxic gases, such as formaldehyde, hydrogen cyanide, and oxides of nitrogen.

Melamine–formaldehyde resins may be used in paper which contacts aqueous and fatty foods according to 21 CFR 121.181.30. However, because a lower PEL has been established by OSHA, some mills are looking for alternatives. Approaches toward achieving lower formaldehyde levels in the resins have been reported (66,67); the efficacy of these systems needs to be established. Although

alternative resins are available, significant changes in the papermaking operation would be required in order for them to be used effectively.

Economic Aspects

Japan produces more amino resin than any other country; the United States is next, with the Commonwealth of Independent States, (CIS) France, the United Kingdom, and Germany following.

Many large chemical companies produce amino resins and the raw materials needed, ie, formaldehyde, urea, and melamine. Some companies may buy raw materials to produce amino resins for use in their own products, such as plywood, chipboard, paper, textiles, or paints, and may also find it profitable to market these resins to smaller companies. The technology is highly developed and sales must be supported by adequate technical service to select the correct resin and see that it is applied under the best conditions.

During the past 10 years (the 1990s) there has been considerable changes in the suppliers of amino resins as a result of acquisitions, spin-offs, and withdrawal of some of the smaller companies from the business. The following is a representative list of those currently in the business: Badische Aniline and Soda-Fabrik (BASF), Ludwigshafen, Germany; Berger International Chemicals, Newcastle upon Tyne, England; Borden Chemical Division, Columbus, Ohio; Casella Farbwerk Mainkur AG, Frankfurt-Fechenheim, Germany; Cuyahoga Plastics, Cleveland, Ohio; Cytec Industries, West Patterson, N.J.; DSM Coating Resins, Zwolle, Holland; Dainippon Ink, Ltd., Tokyo, Japan; Dynamic-Nobel, AG, Troisdorf-Koln, Germany; Fiberite Corp., Winona, Minn.; Georgia-Pacific Corp., Atlanta Ga.; Gulf Adhesives, Lansdale, Pa.; Hitachi Chemical Co., Ltd., Tokyo, Japan; Matsushita Electric Works, Ltd., Osaka, Japan; McWhorter Technologies, Carpentersville, Ill. (Division of Eastmen Chemical Co., Kingspot, Tenn.); Melamine Chemicals, Donaldson, La. (Division of Borden Chemical, Columbus, OH); Mitsui-Toatsu Chemicals Ltd., Tokyo, Japan; Mitsui-Cytec, Ltd., Tokyo, Japan; Montedison SpA, Milan, Italy; Pacific Resins, Tacoma, Wash.; Perstorp AB, Perstorp, Sweden; Perstorp Compounds, Inc., Florence, Mass.; Reichhold Chemicals, White Plains, N.Y. (Division of Dainippon Ink, Tokyo, Japan); Solutia, Inc., St. Louis, Mo.; Sumitomo Ltd., Tokyo, Japan; Vianova Resins GmbH & Co., Wiesbaden, Germany (Division of Solutia, St. Louis, Mo.).

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AMORPHOUS POLYMERS

Introduction

Amorphous materials are characterized by the absence of a regular three-dimensional arrangement of molecules; ie, there is no long-range order. However, a certain regularity of the structure exists on a local scale denoted as short-range order. For low molecular weight amorphous materials the structure is characterized with respect to the short-range order of the centers of the molecules as well as the orientational order of the molecular axes. For the case of long-chain amorphous materials it is necessary to specify an additional structural parameter, namely the conformation (1) of the chain which depends predominantly on the intramolecular interactions along the chain (see CONFORMATIONS AND CONFIGURATION).

The structure however is not static but changes continuously as a result of thermally driven orientational and translational molecular motions. The time scale of these motions may consist of a few nanoseconds up to several hundred years. The structure of the amorphous state as well as its time-dependent fluctuations can be analyzed by various scattering techniques such as x-ray, neutron, and light scattering. The static properties (structure) are probed by coherent elastic scattering methods, whereas the time-dependent fluctuations are investigated by inelastic and quasi-elastic neutron scattering, and dynamic light scattering.

Scattering Methods for the Study of Static and Dynamic Properties

X-ray experiments use radiation with a wavelength in the range $10^{-1} - 1$ nm (see X-RAY SCATTERING). The energy of x-rays is so high that all electrons are excited. The electric field of the incoming wave induces dipole oscillations in the atoms. The accelerated charges generate secondary waves that add up at large distances to the overall scattering amplitude. All secondary waves have the same frequency, but they may have different phases caused by the different path lengths. Because of the high frequency it is only possible to detect the scattering intensity, the square of the scattering amplitude, and its dependence on the scattering angle. Neutron scattering (qv) experiments allowed for measurements of polymer conformations at large scales, which were not feasible with x-rays. Neutrons interact with the nuclei of the atoms whereas x-rays interact with the electrons. The interaction with matter is different, but the problem of interfering secondary waves is the same. Instead of the electron density the scattering length density is dealt with. The essential fact in neutron scattering is the pronounced difference in the scattering amplitude between hydrogen and deuterium, which is important for the variation of the contrast between the particles and the matrix. Quasi-elastic neutron and light scattering experiments measure the correlation function of the conformational fluctuations of the macromolecules at a given length scale. Neutron scattering monitors the segmental mobility of a polymer chain in the nanometer and nanosecond region, whereas light scattering reflects translational diffusion of the whole polymer coil.

This article describes the present state of knowledge regarding the structure of amorphous polymers as obtained from scattering techniques and the corresponding dynamic properties from a structural point of view. A detailed knowledge of the structure is very important because the thermal, mechanical, viscoelastic, optical, and even electrical properties are strongly governed by the structure and its temporal fluctuations.

In order to describe the static structure of the amorphous state as well as its temporal fluctuations, correlation functions are introduced, which specify the manner in which atoms are distributed or the manner in which fluctuations in physical properties are correlated. The correlation functions are related to various macroscopic mechanical and thermodynamic properties. The pair correlation function $g(\mathbf{r})$ contains information on the thermal density fluctuations, which in turn are governed by the isothermal compressibility $\kappa_T(T)$ and the absolute temperature for an amorphous system in thermodynamic equilibrium. Thus the correlation function $g(\mathbf{r})$ relates to the static properties of the density fluctuations. The fluctuations can be separated into an isobaric and an adiabatic component, with respect to a thermodynamic as well as a dynamic point of view. The adiabatic part is due to propagating fluctuations (hypersonic sound waves) and the isobaric part consists of nonpropagating fluctuations (entropy fluctuations). By using inelastic light scattering it is possible to separate the total fluctuations into these components.

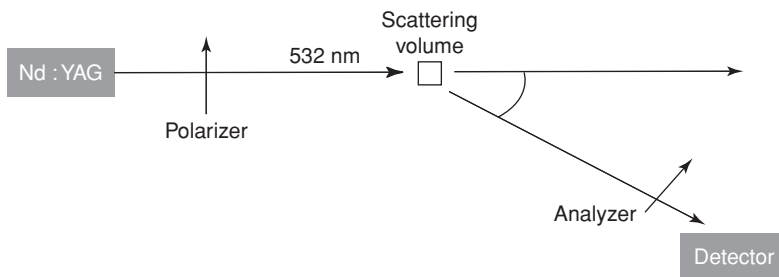
Knowledge of the density and orientational correlation functions is not sufficient to characterize the structure completely, since different structures can give rise to identical correlation functions. Therefore it is necessary to assume models. A complete description of the structure requires that the spatial arrangement of the chain elements, the chain conformation, be known. Usually, average values of the conformation (2) such as the mean square radius of gyration or the mean square end-to-end distance are determined. Direct structure measurements involve the interaction between electromagnetic radiation and the substance in question. A full description of the system will require information about both its static and dynamic properties. Structure information about the time-averaged or static state is obtained from elastic scattering experiments; ie, the scattered intensity is integrated over all frequencies. Time-dependent or dynamic structures, on the other hand, can be studied with inelastic scattering techniques; ie, the scattered intensity is analyzed with respect to the frequency. The mathematical tool which is used to relate the scattering function $S(q, \omega)$ with properties of the system is a Fourier or Laplace transformation. The system in real space is characterized by correlations between various physical properties (eg, particle densities, distances between atoms, orientations, fluctuations in the local dielectric tensor, pressure and entropy fluctuations) in terms of the corresponding correlation functions.

The theoretical analysis of the scattered spectrum was first presented by Komarov and Fisher (3) and Pecora (4) independently in 1963. In 1964 the spectrum of laser light scattered by dilute solutions of polystyrene latex spheres was observed (5) and was found to exhibit a lineshape in good agreement with theory. In a typical scattering experiment (6) a monochromatic beam of radiation is incident on the material; the wave vector is denoted as $\mathbf{k}_0$ and the frequency by ω_0 . The scattered radiation is recorded as a function of the scattering angle and

frequency shift ω , where

$$\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_0 \quad \text{with} \quad |\mathbf{q}| = \frac{4\pi n}{\lambda} \sin(\theta/2) \quad (1)$$

$\mathbf{k}_1$ is the wave vector of the scattered radiation, ω_1 the frequency, and λ the wavelength.



The distribution of the scattered radiation as a function of $\mathbf{q}$ contains information about the distribution of atoms or molecules on a molecular level, provided that the wavelength of the radiation used is of the order of magnitude of the interatomic spacings. This is the case for neutron and x-ray scattering, whereas in the case of light scattering only integral properties of the structure can be analyzed because of the large wavelength involved. It is worth mentioning that one characteristic property of elastic scattering is its coherence. Thus spatial information is contained in the phases, and the scattered intensity is determined by the interference of the scattered waves in front of the detector. Consequently, if q is a characteristic correlation length in a polymeric system, the obtained information is an ensemble average over distances of the order of q^{-1} . A polarized light scattering experiment with wavelengths 2–3 orders of magnitude longer than neutron wavelengths, observes averages over much longer correlation lengths. By correctly chosen q -range, local or global features of the polymers can be studied (7).

The method of light scattering with different techniques (8) can cover a wide dynamic range from 10^5 up to 10^{-12} s. With Fabry–Perot interferometry the Rayleigh–Brillouin (9) and depolarized spectra (10,11) can be frequency analyzed to reveal the effects of segmental (12) and orientational (13) fluctuations between 10^{-8} and 10^{-12} s. At longer time scales the scattered light can be analyzed by the photon correlation spectroscopy (pcs) technique. The polarization of the scattered light and the scattering vector $\mathbf{q}$, which determines the wavelength of the observed fluctuations, selects and characterizes the observed motion. Figure 1 shows a typical depolarized Rayleigh spectrum (14) of 1,2-polybutadiene in Aroclor at 353 K. The depolarized spectra were fit to either one or a sum of two Lorentzian functions plus a baseline, considering the overlap of neighboring orders. The integrated intensity is proportional to the effective optical anisotropy γ_{eff}^2 and is given by following the expression:

$$I_{\text{VH}} = A f(n) \rho^* \gamma_{\text{eff}}^2 \quad (2)$$

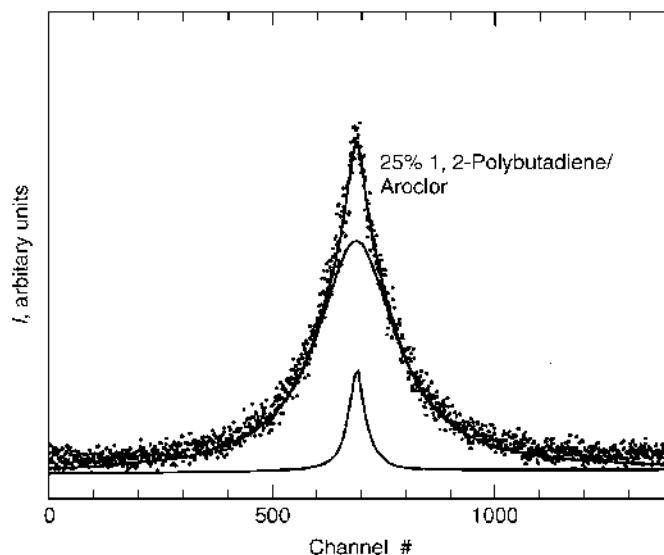


Fig. 1. Depolarized Rayleigh spectra of 1,2-polybutadiene in Aroclor at 353 K. The depolarized spectra were fit to either one or a sum of two Lorentzian functions plus a baseline, considering the overlap of neighboring orders. The integrated intensity is proportional to the effective optical anisotropy γ_{eff}^2 .

where A is a constant, $f(n)$ is the product of the local field correction and the geometrical factor $1/n^2$, with n being the refractive index and ρ^* is the number density of the solute. Figure 2 shows depolarized intensity correlation functions for a poly(styrene-*b*-1,4-isoprene) block copolymer (15) in the disordered state. The total molecular weight M_n of the copolymer is 3930 and the molecular weight of the polystyrene (PS) block is 2830. The primary contribution to the spectra comes from the local segmental motion of the PS in the copolymer and the dispersion broadens with decreasing temperature, which is evident by inspection of the curves in Figure 2.

The structure of the amorphous state is subjected to time-dependent variations, because of the existence of translational and/or orientational motions of both the individual segments and the chain as a whole (16). These motions couple to the light since they induce variations of the local dielectric constant $\epsilon(\mathbf{r}, t)$ or the local polarizability $\alpha(\mathbf{r}, t)$. Inelastic and quasi-elastic scattering measurements allow the determination of the time laws according to which these motions occur (17). The particular motion detected by the light scattering technique depends on the polarization of the scattered light and on the scattering vector $\mathbf{q}$, which gives the wavelength of the observed fluctuations. Light scattering depends on the directions of the polarizations of the scattered radiation and the incident radiation. Provided that the incident and scattered light are polarized with the electric vector at right angles to the plane containing $\mathbf{k}_1$ and $\mathbf{k}_0$, VV scattering is observed. Frequency shifts are detectable in the case of light scattering, and thus, temporal fluctuations of the structure can be determined. Individual photons may be scattered with a slight frequency shift. The

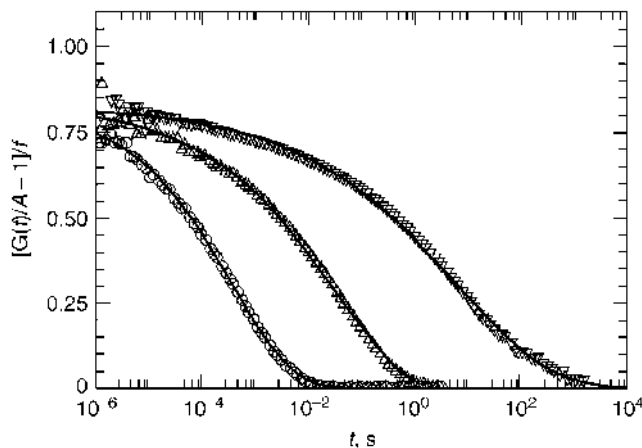


Fig. 2. Depolarized intensity correlation functions for the poly(styrene-*b*-1,4-isoprene) block copolymer. Solid curves are the KWW fits to the data and the β parameters used in the fits are given in the inset. The total molecular weight of the copolymer is $M_n = 3930$ and the molecular weight of the PS block is equal to 2830. The primary contribution to the spectra comes from the local segmental motion of the PS in the copolymer and the dispersion broadens with decreasing temperature. $\circ \beta = 0.38$ at 323 K; $\triangle \beta = 0.30$ at 303 K; $\nabla \beta = 0.25$ at 287 K.

magnitude and sign of the frequency shift depend on the velocity and the direction with respect to the incident radiation in which an individual particle is moving. This frequency shift is referred to as the *Doppler effect*. The free motion of the particles (macromolecules) in solution is a thermal diffusion with no net transport and therefore no net exchange in energy between the system and the incident light. The scattered light thus consists of a narrow Lorentzian spectrum of frequencies symmetrically broadened because of the random Brownian motion of the particles, and centered at the incident frequency of the laser. The time-correlation function and the frequency-dependent power spectrum are related by Fourier transform. This is usually referred to as quasi-elastic light scattering (qels), a technique allowing one to extract dynamical information about the system, ie, the diffusion coefficient. Because of the large wavelength of the incident light, one sees only integral structural properties, averaged over long distances. The so-called depolarized (18) (VH) light scattering (dls), where V and H indicate a vertical and horizontal direction of the polarization of the incident and scattered light relative to the scattering plane, is related to fluctuations of the anisotropy of the polarizability tensor. Thus, reorientational motions of individual optically anisotropic molecules or collective motions of such molecules may be analyzed by dls (19).

The light scattering spectrum obtained in the VV configuration contains both the anisotropic component and an isotropic one, which is related to local density fluctuations, giving rise to fluctuations of the polarizability or the dielectric constant. In most cases the anisotropic contribution is much smaller than the isotropic one; therefore, the VV scattering measures the density fluctuations (isotropic part) directly. Figure 3 shows experimental correlation functions in the

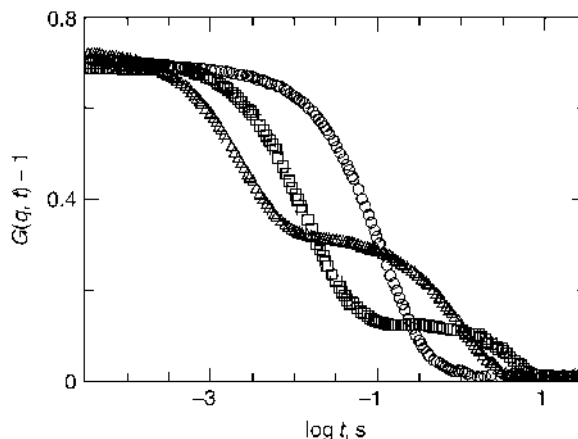


Fig. 3. Experimental intensity correlation functions in the VV configuration for a low molecular weight (PS/PI) polymer blend. Two diffusive decay rates are essentially observed in the VV configuration; however, close to the critical point the faster rate dominates. $\circ$ 315 K (VV); $\square$ 328 K (VV); $\triangle$ 348 K (VV).

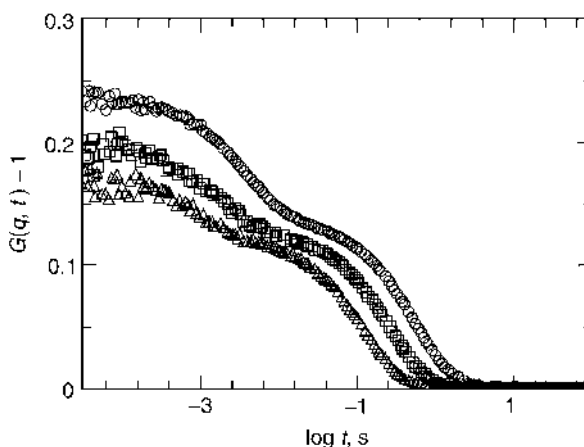


Fig. 4. Depolarized intensity correlation functions for the (PS/PI) polymer blend of Figure 3. The relaxation mode that is shown in the VH scattering geometry is due to double scattering induced by composition fluctuations. $\triangle$ 353 K (VH); $\square$ 343 K (VH); $\circ$ 333 K (VH).

VV configuration for a low M_w polystyrene/polyisoprene (PS/PI) blend, and Figure 4 shows the corresponding depolarized experimental correlation functions (20). Two diffusive decay rates are essentially observed in the VV configuration (Fig. 3); however, close to the critical point the faster rate dominates. The relaxation mode that is shown in the VH scattering geometry is due to double scattering induced by composition fluctuations.

The quantities measured in light scattering spectroscopy are either the autocorrelation function of the electric field $C(t) = \langle \mathbf{E}(t) \cdot \mathbf{E}(0) \rangle$ or its Fourier

transform, the spectrum of the scattered light $I(\omega)$, by using the Fabry–Perot interferometer.

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} C(t) dt \quad (3)$$

The correlation function $C_{\text{aniso}}(\mathbf{q}, t)$ of the total scattered field from undiluted polymers is given by

$$C_{\text{aniso}}(\mathbf{q}, t) = \left\langle \sum_{m,n}^N \sum_{i,j}^{N_s} \alpha_{yz}^{(n)}(j, t) \alpha_{yz}^{(m)}(i, 0) \exp \left\{ i\mathbf{q} \cdot [\mathbf{r}_j^{(n)}(t) - \mathbf{r}_j^{(m)}(0)] \right\} \right\rangle \quad (4)$$

where N is the number density of the polymer, and N_s is the number of scatterers per molecule. The angular brackets denote an ensemble average. According to the above equation two mechanisms are generally responsible for VH scattering: segmental orientation combined in the subscript yz and segmental center of mass motion in the exponent term. Alternatively, these two modes are not always statistically independent and frequently even reflect other motions such as overall molecular orientation and coherent internal Rouse–Zimm modes for rigid and flexible coils respectively. On the other hand the correlation function of the isotropic component of the scattered light can be written in the form

$$C_{\text{iso}}(\mathbf{q}, t) = \alpha^2 \left\langle \sum_{m,n}^N \sum_{i,j} \exp \left\{ i\mathbf{q} \cdot [\mathbf{r}_j^{(n)}(t) - \mathbf{r}_j^{(m)}(0)] \right\} \right\rangle \quad (5)$$

In contrast to the correlation function of the anisotropic component, only the segment center of mass motion affects the isotropic scattering component. However, because of intra- and interchain interactions in bulk polymers there is no rigorous calculation of the general expressions in equations 4 and 5. Only the Rayleigh–Brillouin spectrum of a viscoelastic fluid, which is determined by the high frequency part of the density fluctuations in equation 5, has an analytical form (21). A spectrum has been computed using a generalized relaxation equation. The polarized scattering is governed by thermal density fluctuations, which, from a thermodynamic point of view, can be separated into an adiabatic and an isobaric component. The adiabatic component gives rise to longitudinal hypersonic waves. The isobaric component I_R causes a nonpropagating thermal diffusive mode. The translational motion of the segments associated with the isotropic light scattering produces thermally induced longitudinal sonic waves, the nonpropagating thermal diffusive mode, and a localized motion. The first two fluctuations give rise to the shifted Brillouin doublet (22,23) I_B at frequencies $+\omega_s$ and $-\omega_s$ and to the central Rayleigh line. The line width of the unshifted central line, the Rayleigh line, is determined by the thermal conductivity. The intensity ratio, the so-called Landau–Placzek (LP) ratio, is given in the simplest case by the ratio of the specific heats C_P and C_V .

$$\frac{I_R}{2I_B} = \langle C_P/C_V \rangle - 1 \quad (6)$$

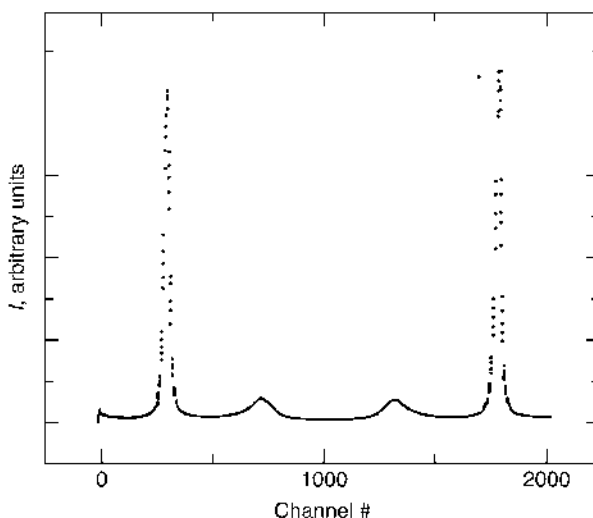


Fig. 5. Polarized Rayleigh–Brillouin spectrum of amorphous PnHMA taken with a Burleigh plane Fabry–Perot interferometer using a free spectral range of 12.4 GHz at 295 K. The two Brillouin peaks are shifted from the incident frequency by the product of the wave vector $\mathbf{q}$ and the sound velocity u . The line width of the Brillouin peaks is related to the attenuation of the sound waves. • PnHMA.

In viscous fluids, however, a coupling occurs between internal and external modes of freedom and translational motions. This structural relaxation process, characterized by a frequency ω_e , influences both the central line as well as the Brillouin doublet, depending on the frequency of this relaxation relative to the frequency of the hypersonic waves. In principal three different cases must be considered:

- (1) The so-called fast relaxation limit in which $\omega_e \gg \omega_s$. In this case the structural relaxation gives rise to a broad background scattering in the frequency scale, leaving the Rayleigh–Brillouin spectrum nearly unchanged.
- (2) The intermediate relaxation limit in which $\omega_e \cong \omega_s$. The two frequencies are of the same order of magnitude and the structural relaxation contributes heavily to the line width of the Brillouin lines. The relaxation processes can be resolved by means of the Fabry–Perot interferometry (24). Figure 5 visualizes a polarized Rayleigh–Brillouin spectrum of amorphous poly(*n*-hexyl methacrylate) taken with a Burleigh plane Fabry–Perot interferometer using a free spectral range of 12.4 GHz at 295 K. The two Brillouin peaks are shifted from the incident frequency by the product of the wave vector $\mathbf{q}$ and the sound velocity u . The line width of the Brillouin peaks is related to the attenuation of the sound waves.
- (3) The slow relaxation limit in which $\omega_e \ll \omega_s$. The structural relaxation leads to an additional central line, the so-called Mountain peak (25,26), the width of which can be determined by pcs (27). Thus, structural relaxation

processes taking place close to the glass-transition temperature can be investigated by this technique.

The dynamics of slowly varying thermal density fluctuations has been studied by means of pcs (28,29) in the frequency range between 10^{-3} and 10^7 Hz for several polymeric systems in the molten state as well as in the glassy state. The measured intensity autocorrelation function $C(\mathbf{q}, t)$ is related to the normalized time correlation function $g^{(1)}(\mathbf{q}, t)$ by

$$C(q, t) = A \left[1 + f |\alpha g^{(1)}(q, t)|^2 \right] \quad (7)$$

where f is the instrumental factor, calculated by means of a standard, α is the fraction of the total scattered intensity associated with the process under investigation with correlation times longer than 10^{-7} s, and A is the baseline. For the pcs measurements near T_g , fluctuations in density and orientation are strongly coupled and hence the relaxation times obtained are indistinguishable. Experimentally only those components with relaxation times longer than 10^{-7} s (frequencies < 0.1 MHz) will be observed by pcs. It was found that, in general, the observed correlation functions are highly nonexponential and have been fitted to the empirical Kohlraush–Williams–Watts (KWW) function

$$g^{(1)}(t) = \exp \left[- (t/\tau)^\beta \right] \quad \text{with} \quad 0 < \beta \leq 1 \quad (8)$$

and for concentration fluctuations it is written as

$$g^{(1)}(q, t) = \exp \left[- (t/\tau)^\beta \right] \quad \text{with} \quad 0 < \beta \leq 1 \quad (9)$$

Using the KWW function the mean relaxation time is given by

$$\langle \tau \rangle = \int_{-\infty}^{+\infty} g^{(1)}(t) dt = \frac{\tau}{\beta} \Gamma(\beta^{-1}) \quad (10)$$

where $\Gamma(\beta^{-1})$ is the Gamma function. $g^{(1)}(t)$ is related to the longitudinal compliance (30,31) $D(t)$ by

$$\alpha g^{(1)}(t) = [D_0 - D(t)] / D_\infty \quad (11)$$

and

$$D(t) = D_\infty + (D_0 - D_\infty) \int_{-\infty}^{+\infty} L(\ln \tau) (1 - e^{-1/\tau}) d \ln \tau \quad (12)$$

The depolarized spectrum is dominated by local fluctuations of the optical anisotropy owing to an overall orientation of stiff molecules, local motions of optically anisotropic segments or internal Rouse–Zimm modes for flexible chain

molecules. The depolarized spectrum thus reflects dynamics of collective molecular orientation when the interaction between translation and rotation can be neglected.

Density Fluctuations—Excess Scattering at Low q

From statistical fluctuation theory (32), the static structure factor is given by

$$\lim_{q \rightarrow 0} S(q) = \langle \delta N^2 \rangle = V \rho^2 k_B T \beta_T(T) \quad (13)$$

where $\delta N (= N - \langle N \rangle)$ is the fluctuation in the number of particles in the scattering volume V , ρ is the average number density, and β_T is the isothermal compressibility $[-1/V(\partial V/\partial P)_T]$. The total density fluctuation in an arbitrary volume is given by

$$\Psi_T \frac{\langle \delta N^2 \rangle}{\langle N \rangle} = e k_B T \beta_T(T) \quad (14)$$

According to the above equation, the density fluctuations should have a temperature dependence similar to that of $\beta_T(T)$, which is discontinuous at T_g . However, it has been shown earlier (33–42) that it is only the temperature coefficient of the density fluctuations which is discontinuous at T_g .

The density fluctuations defined above can be obtained experimentally in two ways: (1) from the measured compressibility data using equation 14, or (2) from small-angle x-ray scattering (saxs), using the extrapolating intensity at $q = 0$ (33–42):

$$\lim_{q \rightarrow 0} I(q) = n^2 k_B T \beta_T(T) \quad (15)$$

where n is the average electron density. Then, the particle density fluctuation is given by

$$\frac{\langle \delta N^2 \rangle}{\langle N \rangle} = \frac{I(0)}{nZ} \quad (16)$$

where Z is the number of electrons per particle.

Two examples are discussed below where the measured density fluctuations are compared with the calculated ones from the compressibility data. In Figure 6, the density fluctuations are shown for the glass-forming liquid *ortho*-terphenyl (OTP), and in Figure 7 for two polymers with slightly different backbone structures; bisphenol A polycarbonate (BPA-PC) and tetramethyl-bisphenol A polycarbonate (TMPC) (42). In both cases, at $T > T_g$, there is a good agreement between the measured and calculated density fluctuations but at $T < T_g$, the former exceed the latter by a factor of 2. Below T_g , the density fluctuation can be described as $\rho k_B T \beta_T(T_g)$, where $\beta_T(T_g)$ is the compressibility obtained from pressure–volume–temperature (PVT) measurements in a comparable time scale

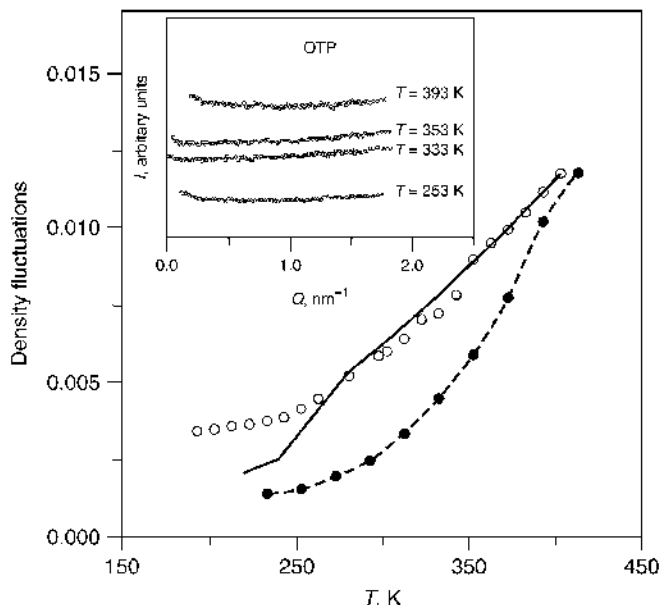


Fig. 6. Density fluctuation in OTP measured by saxes ($\circ$). The solid line gives the calculated density fluctuations from the measured isothermal compressibility. Filled symbols gives the propagating density fluctuations calculated from the Brillouin shift in a Rayleigh–Brillouin experiment. The inset shows typical saxes curves obtained with a conventional Kratky saxes camera.

with $I(0)$, without, however, displaying a leveling-off to a constant value. The much higher density fluctuations below T_g result from the non-equilibrium nature of the glass and the contribution of frozen-in fluctuations (33–42).

The free-volume fluctuation model (43) which is based on the average free volume and its fluctuations has been successful in describing such differences in density fluctuations of different polymers as well as to explain the suppression of the intensity of sub-glass processes in polymer/additive systems. According to the model, the free volume is assumed to have a Gaussian distribution characterized by two parameters: (1) the average free volume $\langle V \rangle$ and (2) the distribution of free volume, which is given by the variance $\langle \delta V^2 \rangle^{1/2}$ of the distribution $P(\delta V)$. The saxes measurements allow the direct evaluation of the density fluctuation and the average free volume can be estimated from the position of the “amorphous halo” as obtained from wide angle x-ray scattering (waxs). Figure 8 gives a schematic of the distribution $P(\delta V)$ of the density fluctuations in glassy BPA-PC and TMPC according to the free-volume fluctuation model. Peak positions and widths are determined by the average free volume and by its fluctuations, respectively. This is a nice example of a system where $\langle V \rangle$ and $\langle \delta V \rangle$ are determined to be different against the assumed “universality.” This variance reflects on the structural units; in TMPC the methyl substitution causes less efficient packing as compared to BPA-PC.

In Figure 9, the measured density fluctuations from a variety of polymers and glass-forming liquids are compared. The amount of density fluctuations at

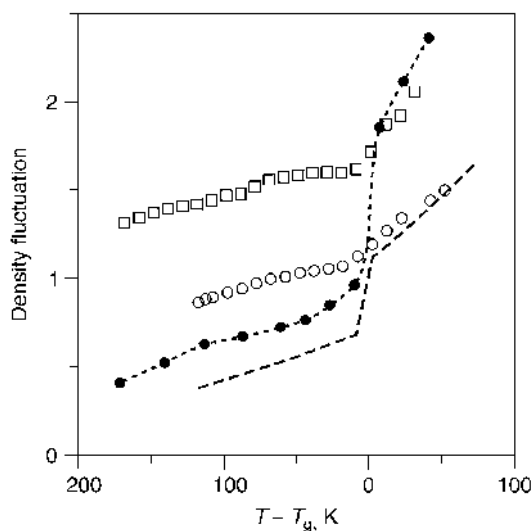


Fig. 7. Density fluctuations, measured by saxs, for BPA-PC ($\circ$) and TMPC ($\square$) as a function of $T - T_g$. The dotted line is the calculated density fluctuation of TMPC from the isothermal compressibility data of this study obtained in a PVT experiment. The dashed line represents the calculated density fluctuation of BPA-PC from the literature compressibility data.

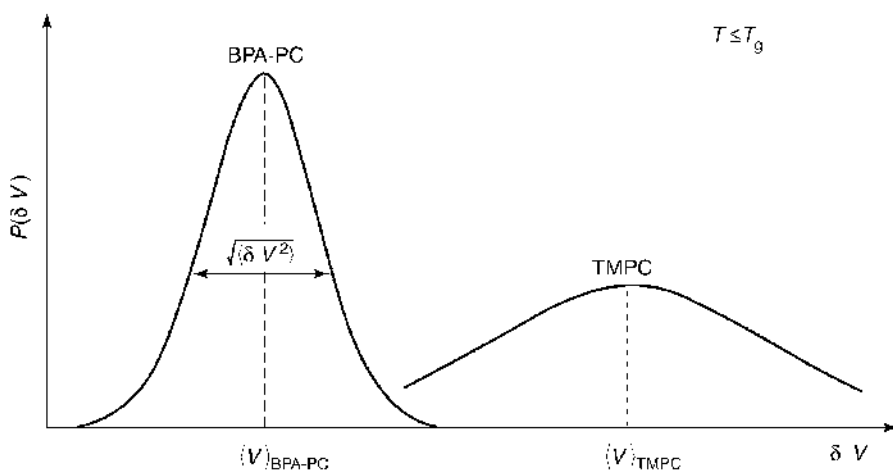


Fig. 8. Schematic of the distribution $P(\delta V)$ of the density fluctuations in glassy BPA-PC and TMPC, according to the free-volume fluctuation model.

the glass transition is typically about 1%; however, the results shown (Fig. 9) indicate considerable variation among the different polymers and glass-forming liquids investigated. Typically, glass-forming liquids possess the lowest fluctuations and in some cases (mainly within the poly(*n*-alkyl methacrylate) series, ie, for poly(methyl methacrylate) (PMMA), poly(*n*-butyl methacrylate) (PnBMA), poly(*n*-hexyl methacrylate) (PnHMA), the measured density fluctuation above

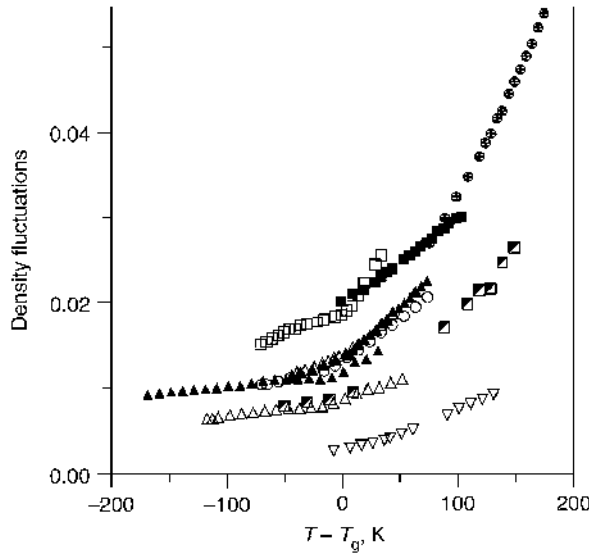


Fig. 9. Density fluctuations of some glass-forming liquids and polymers as a function of temperature difference from T_g . ∇ BKDE; $\triangle$ BPA-PC; $\blacktriangle$ TMPC; $\square$ OTP; $\circ$ poly(cyclohexyl methacrylate) (PCHMA); $\blacktriangle$ poly(*n*-butyl methacrylate); $\blacksquare$ poly(*n*-hexyl methacrylate); $\square$ poly(methyl methacrylate) (PMMA); $\bullet$ polybutadiene.

the glass transition exceeds the calculated one from the PVT measurements on identical samples. The higher contribution of density fluctuations can have different origins, such as “contamination” from concentration fluctuations (ie, additives) or contribution from short-range intersegmental density fluctuations. Additives alone, however, should be in high concentrations (44) to explain the observed behavior.

The evaluation of density fluctuations using equation 14 or 16, conceals the relative contribution of propagating and static components in the measured total density fluctuations. To overcome this difficulty one can evaluate the contribution of the propagating density fluctuations from the temperature dependence of the phonon peak obtained in the Rayleigh–Brillouin experiment (44). This is based on the notion that the propagating density fluctuations are determined from the thermal-diffuse scattering (tds) near the origin of the reciprocal space, as in the case of crystalline solids. Then in the limit $q \rightarrow 0$, this contribution is given by

$$\Psi_S = \frac{\langle \delta N^2 \rangle}{\langle N \rangle} \bigg|_{\text{phonon}} = \rho k_B T \beta_S(T) \quad (17)$$

where $\beta_S(T)$ is now the adiabatic compressibility ($\beta_S = 1/\rho^* u^2$, ρ^* is the mass density and u is the sound velocity) evaluated at the frequency ω_{phonon} . The ratio of the total to the propagating fluctuations defines an “x-ray” LP ratio (44):

$$R_{\text{LP}} = \frac{\Psi_T}{\Psi_S} - 1 = \frac{\beta_T}{\beta_S} - 1 \quad (18)$$

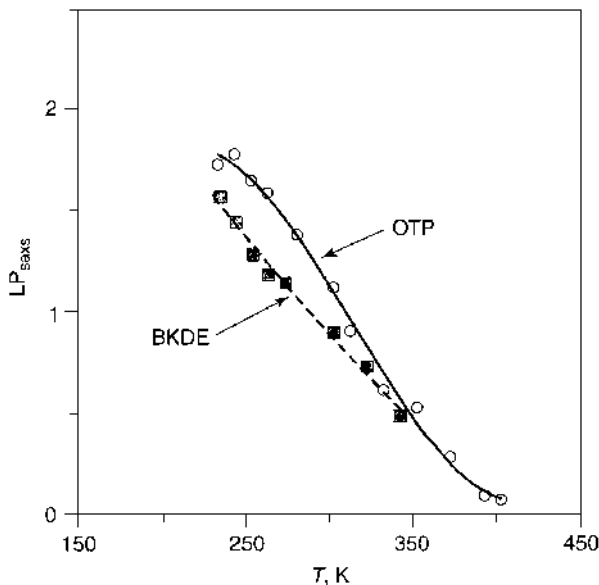


Fig. 10. LP intensity ratio obtained from the measured compressibilities of OTP (○) and BKDE (■).

which is readily obtained in a Rayleigh–Brillouin experiment from the intensities of the central (I_C) and shifted Brillouin lines (I_B) as $I_C/2I_B$. The temperature dependence of the LP ratio for two glass-forming liquids, OTP and BKDE [1,1-di(4'-methoxy-5' methyl-phenyl)cyclohexane] (45), is shown in Figure 10 and is in good agreement with the values predicted for relaxing liquids.

On the basis of the saxs results obtained within the shown q -range, one would assume that the density fluctuations of OTP and BKDE (equivalently called BMMP) behave as one would expect from equilibrium statistical mechanics. However, one can notice a slight increase of $I(q)$ at low q , which finds its counterpart at the much higher $I(q)$ at the smaller q values accessible by light scattering (ls). In order to use both sets of data (ls and saxs) in a common plot, an effective compressibility $k_B T \beta_T$ is defined, which is obtained from saxs as I/n^2 and from ls by using (45):

$$\frac{R_i(q)}{\pi^2/\lambda^4(\rho^* \partial \varepsilon / \partial \rho^*)^2} = k_B T \beta_T \quad (19)$$

where $R_i(q)$ is the isotropic Rayleigh ratio [$R_i(q) = R_{VV}(q) - (4/3)R_{VH}$]. The results, in the form of relative density fluctuations, are shown in Figure 11 for BMMP. For the description of the shape of the static scattering function one can try to use the Ornstein-Zernike function:

$$S(q) = \frac{S(0)}{1 + \xi_{OD}^2 q^2} \quad (20)$$

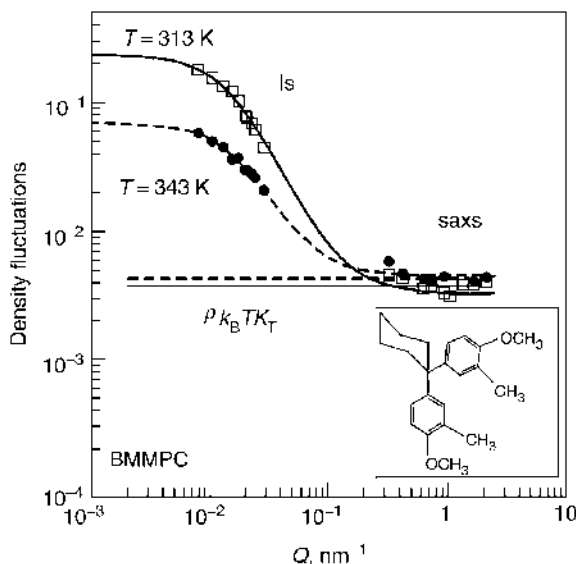


Fig. 11. Relative density fluctuations of BMMPC measured by light scattering (ls) and saxs at two temperatures: $T_g + 52$ K and $T_g + 82$ K. The curves are obtained by fitting with the Ornstein–Zernike function.

where ξ_{OD} is the static correlation length. For OTP and BMMPC, very large correlation lengths up to 180 nm at temperatures $T_g + 40$ K are obtained. On the basis of the distinct scattering feature, which violates the thermodynamic law (eq. 13), these fluctuations are called long-range density fluctuations in contrast to the normal density fluctuations detected by conventional-laboratory saxs measurements.

The essential contribution of Fischer and co-workers was not only to show the existence of long-range density fluctuations in static experiments (46–48) (which was known from earlier static light scattering measurements), but also to demonstrate the existence of a new ultraslow hydrodynamic process (ie, $\Gamma \sim q^2$) in pcs, with relaxation rates Γ about $10^{-4} - 10^{-7}$ lower than those associated with the α -process at a given temperature (45,49), and to study the associated kinetics (50). These effects are caused by long-range density fluctuations indicating a nonhomogeneous distribution of free volume and the appearance of the ultraslow mode is a result of the redistribution of free volume in space. A model has been proposed (45,49), which describes the long-range density fluctuations as a result of the coexistence of molecules with two different dynamic states, and a particular molecule and its surrounding can pass over from the “solid-like” state into the “liquid-like” state on a time scale which is given by the ultraslow mode.

Order in Amorphous Polymers and the Associated Dynamics

It is well known (51–53) that the waxes spectra of semicrystalline samples display sharp diffraction peaks whose intensity and width reflect the frequency and

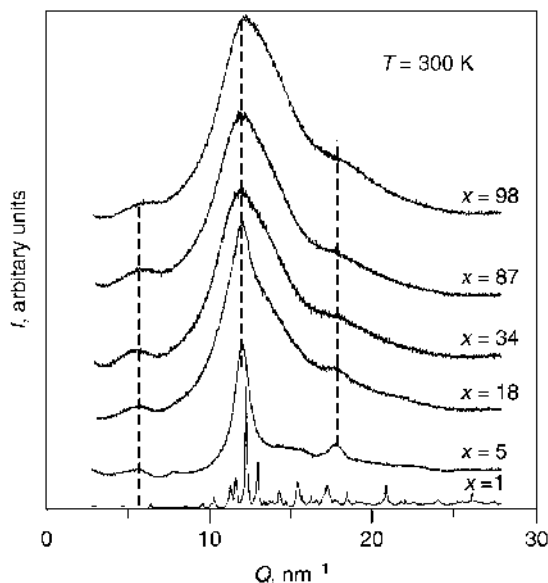


Fig. 12. Waxes spectra of different polycarbonates of bisphenol A starting from the monomer ($x = 1$), to the pentamer ($x = 5$), to the polymer. Notice the sharp diffraction maxima in the monomer (crystalline) and the broader patterns on the polymeric substances.

periodicity, respectively, of some characteristic distances obtained using Bragg's law: $d = 2\pi/q^*$. Today, there is consensus that "amorphous" polymers are not completely amorphous but they possess a reasonable degree of local order. For example, the presence of a scattering peak in x-ray diffraction patterns (called *amorphous halo*) implies the existence of fluctuations in electron density distribution within the sample. Although there is not a known one-to-one correspondence between peak position and size of the corresponding density fluctuations, the Bragg equation, $\lambda = 2d \sin \theta$, may still be applied to an amorphous halo position to provide an equivalent Bragg size for the density fluctuation. Hence, in amorphous polymers the *equivalent* Bragg spacings are discussed. It has been shown that the position of the amorphous halo varies systematically within the same family of polymers and that it is correlated with the cross-sectional area of the polymer chain in the crystal (53).

As an example of regularity in the diffraction patterns, the waxes spectra for different polycarbonates of bisphenol A (54) are shown in Figure 12. The figure shows different diffraction patterns starting from the monomer ($x = 1$, which is crystalline), the pentamer ($x = 5$), and other oligomers up to the bulk. It is interesting to note that there is a correlation of the most intense reflection in the crystalline monomer with the amorphous halo in the BPA polymers and that the first sharp diffraction peak gets broader as one moves from the pentamer to the polymer.

Another class of polymers with interesting intersegmental structure and packing properties are the poly(*n*-alkyl methacrylates) (55,56). Figure 13 gives the waxes pattern of PMMA, PnBMA, PnHMA, PnDMA, and PnLMA. With the

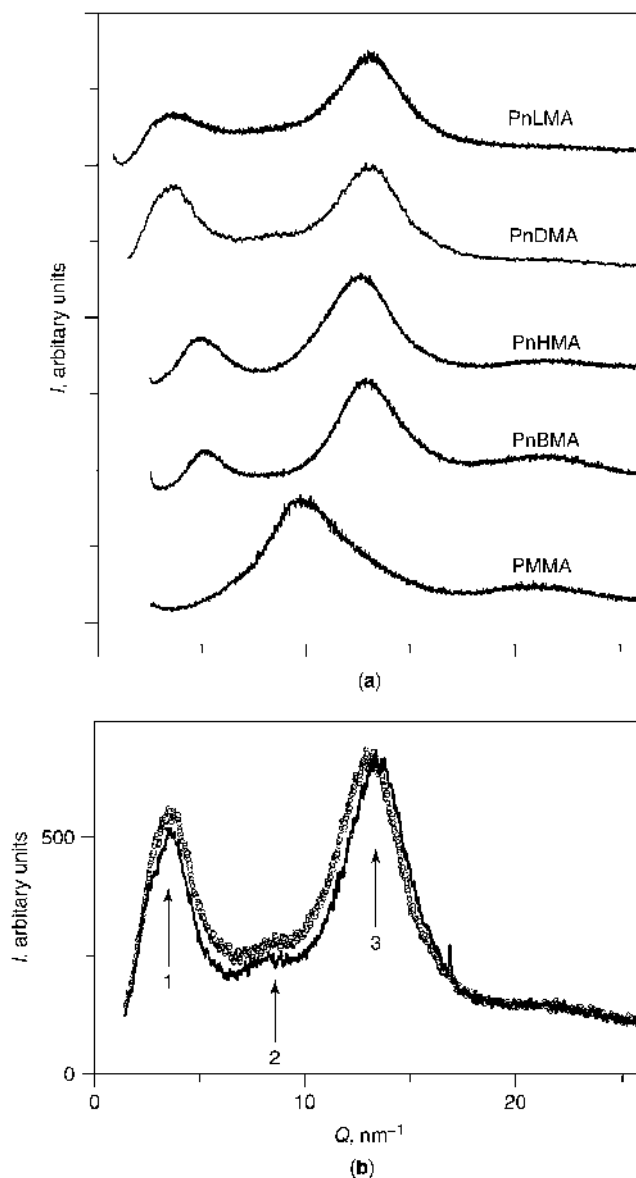


Fig. 13. (a) Waxes spectra of a series of poly(*n*-alkyl methacrylates) shown at 293 K. Notice the development of the LVDW peak which shifts to lower Q values with increasing alkyl side chain. (b) Waxes spectra for PnDMA shown at two temperatures as indicated. Arrows show the positions of the three main peaks in the spectra. $\circ$ $T = 293 \text{ K}$; — $T = 223 \text{ K}$.

exception of PMMA, the waxes spectra for poly(*n*-alkyl methacrylates) show three peaks (arrows 1, 2, and 3 in Fig. 13b). The peak at high q , with an equivalent Bragg spacing of about 0.5 nm, corresponds to the van der Waals (VDW) contacts of atoms and is known as the VDW peak. The temperature variation of this peak

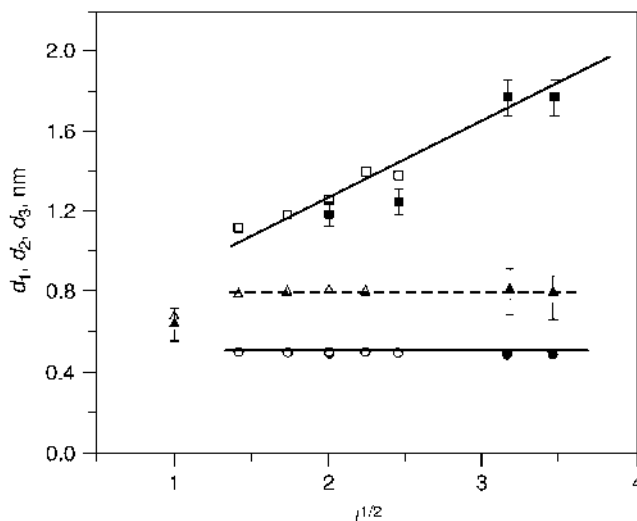


Fig. 14. Equivalent Bragg spacings as a function of the number of carbon atoms (l) on the alkyl chain. Lines are linear fits to the data. Notice the pronounced l -dependence of d_1 . • d_3 ; ▲ d_2 ; ■ d_1 .

reflects mainly the thermal expansion of the system. The peak at low q , which is usually referred as the low van der Waals (LVDW) peak, is found to have a systematic dependence in the number (l) of carbon atoms on the alkyl side chain. Figure 14 displays the dependence of the three peaks on $l^{1/2}$ for a series of poly(n -alkyl methacrylates), with l in the range $1 \leq l \leq 12$ at 293 K. The LVDW peak, with corresponding distances from 1.0 to 1.8 nm, reflects mainly the average distance between adjacent backbones, which is an increasing function of the number of carbon atoms l on the alkyl side chain. The l -dependence of d_1 can be parameterized as $d_1 = d_0 + sl^{1/2}$, with $d_0 \approx 0.7$ nm and $s \approx 0.385$ nm/CH₂. The intermediate peak (Peak #2), which is more difficult to obtain, is also plotted in Figure 14. Its position corresponds to the main peak in PMMA which, in contrast to the rest of the series, does not exhibit an LVDW peak. This feature of PMMA has been discussed in the literature earlier (51).

In the past, there has been a continuous effort to correlate specific dynamic properties, such as the boson peak, the separation of the segmental (α -) from the subglass (β -) process, and the fragility with the structure of amorphous polymers. More specifically, a correlation between the low frequency peak in the Raman spectra and the properties of the first sharp diffraction peak was shown to exist (57,58). Herein the relation of the structure factor with the dynamic property of fragility is recalled (55). The temperature dependence of the relaxation times of various members of the series of poly(n -alkyl methacrylates) is shown in Figure 15. Despite the fact that the “fragility” is usually defined for homogeneous systems, whereas here the monomer itself is intrinsically heterogeneous, one can still compare $\tau(T)$ from different samples. For this purpose one can employ the usual “fragility plot” where the relaxation times are plotted as a function of reduced temperature

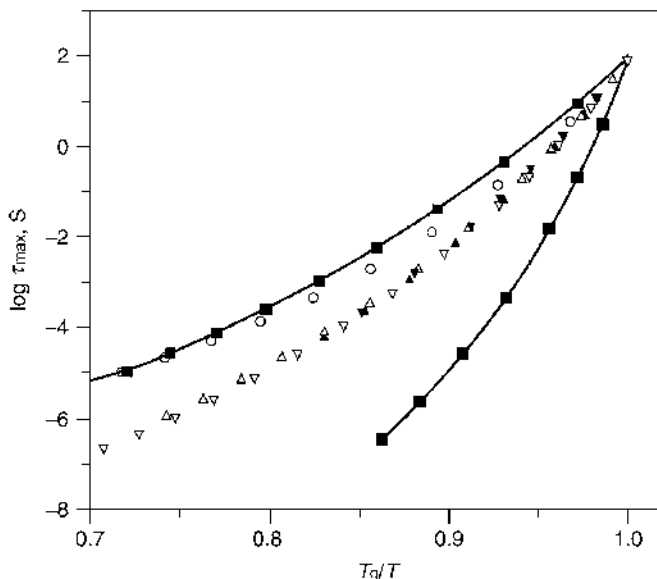


Fig. 15. T_g -scaled plot of the segmental relaxation times of PMMA (◆), PnEMA (▲), PnBMA (△), PnHMA (▼), PnNMA (▽), PnDMA (■), and PnLMA (○). The T_g is operationally defined here as the temperature at which the segmental relaxation time is 100 s. There is change in the nature of the glasses when going from PMMA to the higher member of the series, which reflects in the change from “fragile” to “strong” behavior.

(Fig. 15). Furthermore, to facilitate the comparison, the *glass-transition temperature* T_g is operationally defined as a temperature corresponding to the most probable relaxation time of 100 s. There is a pronounced variation of the curvature or the “steepness index” which is defined as

$$m = \frac{d \log \tau}{d(T_g/T)} \quad (21)$$

which is evaluated near T_g , in going from PMMA (with $m \sim 92$) to poly(*n*-decyl methacrylate) (PnDMA) ($m \sim 36$). The variation in m implies a change from “fragile” to “strong” liquids, which occurs within the same family of polymers only by increasing the length of the side chain with the addition of a CH_2 unit.

The dynamic behavior within the class of poly(*n*-alkyl methacrylates) possess the natural question as to whether this dynamic richness reflects on the structural changes, and if so, on what length scale. In other words, are the observed dynamic changes from “fragile” to “strong” reflected on the structural changes? Earlier studies already revealed a correlation between the monomer structure and the degree of intermolecular cooperativity (59). The correlation is shown in Figure 16, where both the steepness index m and the position of the LVDW peak is shown as a function of l . In doing so one is directly comparing a dynamic with a structural property. There is a nice correlation between the two quantities, which shows that the observed dynamic changes from “fragile” to

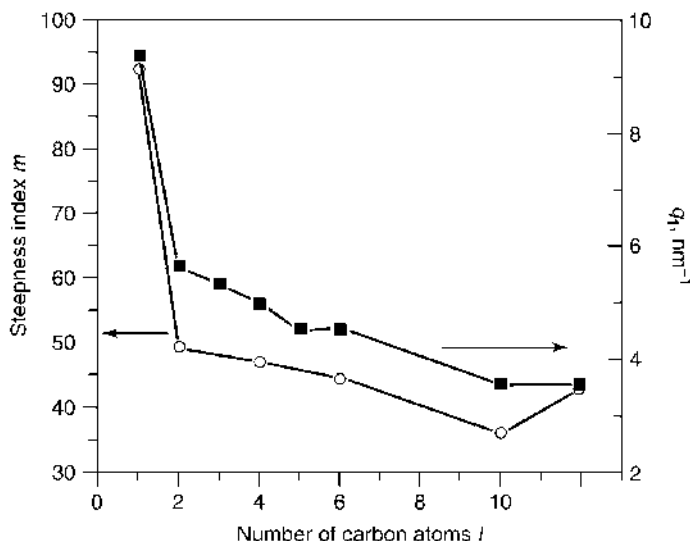


Fig. 16. Steepness index m [$=d \log \tau/d(T_g/T)$], extracted from the initial slopes in the previous figure, plotted as a function of the number of carbon atoms (l) on the side chain of poly(n -alkyl methacrylates). In the same plot the dependence of the LVDW peak in the waxes spectra Q_1 is shown. There is a one-to-one correspondence between the structural properties and the steepness index, which implies the relation of the fragility to the intersegmental correlations.

“strong” occur by reorganizations at the intersegmental distances, which are enlarged by increasing l . The above is one example where the static structure factor influence the dynamic properties within a series of polymers.

Temperature Dependence of the Amorphous State

All linear and most branched amorphous polymers are liquids. In the realm of continuum mechanics a material is a liquid if it flows. Nonrecoverable deformation resulting from applied tractions are proportional to the time of the created stresses, which are also proportional to or functions of the strain rate. They are liquid-like flow deformations. Also stresses in liquids caused by applied shear strains decay to zero with time. Most amorphous polymers are highly viscous and markedly viscoelastic. This time- and frequency-dependent mechanical behavior is dependent on molecular structure and weight, temperature, pressure, and concentration. Many of these polymers have no crystalline solid state because there are stereochemical variations along their molecular chain-like backbones. This lack of long-range regularity in the molecular structure precludes an assembly with the long-range order, which is the essence of the crystalline state. In other words irregular molecules cannot crystallize. On the other hand even some polymers with stereoregular chains, such as polycarbonate, do not crystallize readily because of exceedingly low rates of nucleation.

Upon cooling with consequent molecular crowding the mobility of molecular segments diminishes. Ultimately the local mobility becomes so low that the

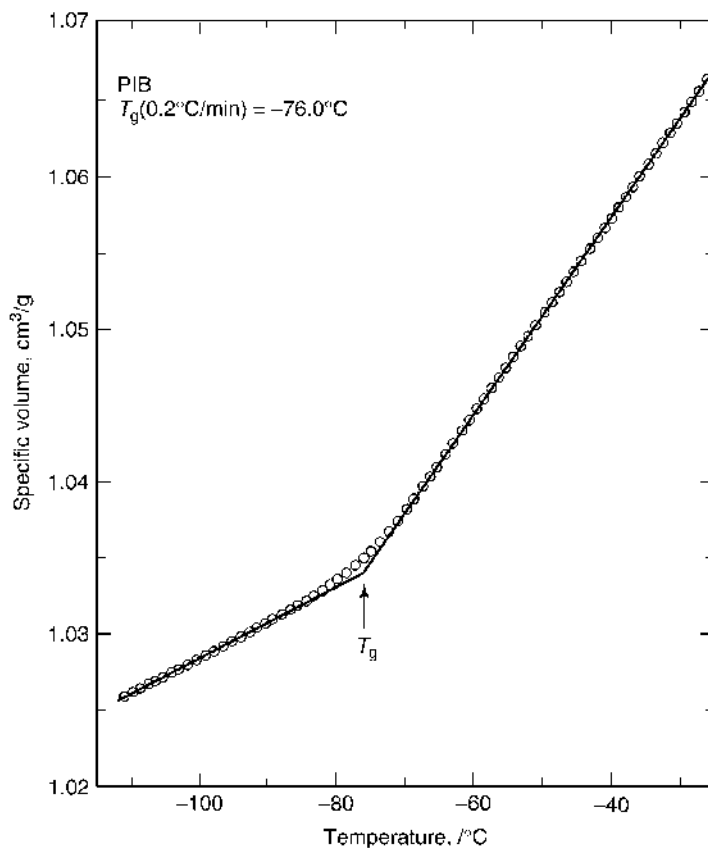


Fig. 17. Dilatometric cooling curve at 0.2°C/min for PIB obtained using the differential gas dilatometer (60).

short-range order that exists does not achieve its more compact equilibrium structure in the time allowed by the imposed cooling rate. The rate of decrease of volume with temperature upon further cooling diminishes in a usually narrow temperature range in comparison to that due to the change in magnitude of anharmonic vibrations alone. The liquid structure is thus kinetically “frozen in” and the liquid is called a glass. The intersection of the equilibrium volume–temperature line with the glass line defines the glass temperature T_g . Most often T_g is called the glass-transition temperature implying a thermodynamic change in state. Below T_g the material is said to be in the glassy state. However no change in state occurs. The amorphous material is still in the liquid state albeit with an enormous viscosity (above 10^{11} Pa·s; 10^{12} P) and extremely long relaxation and retardation times. A glass is therefore a viscoelastic liquid with a specific volume which is greater than its equilibrium value. A volume–temperature cooling curve for high molecular weight polyisobutylene (NBS PIB) is shown in Figure 17, where the decrease in the thermal contraction coefficient α in the neighborhood of T_g is clearly seen (60). The dependence of $T_g(q)$ upon the rate of cooling q

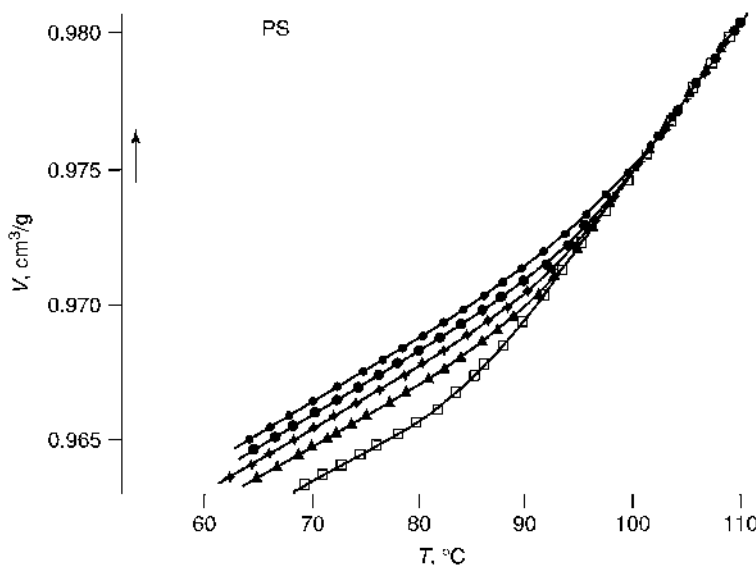


Fig. 18. Volume-temperature curves obtained at different rates of cooling q for PS encompassing the glass temperature $T_g(q)$ (61). — q , K/h: —●— 120; —○— 30; —◆— 6; —△— 1.2; —□— 0.042.

is illustrated in Figure 18, where cooling curves for polystyrene (PS) were obtained at rates ranging from 2°C/min to 1°C/day (61). When held isothermally and isobarically below T_g , the volume decreases with time toward its equilibrium value. This process is called physical aging, during which kinetic properties slow down enormously and brittleness increases. The above comments on T_g and glasses are not restricted to amorphous polymers, since all amorphous materials organic, inorganic, polymeric, and nonpolymeric will become glassy (rigid, highly viscous, and usually brittle) upon cooling if crystallization does not intervene.

Materials with molecular networks, such as cross-linked elastomers and crystalline polymers, do not flow and so are classified as viscoelastic solids. Shear stresses do not decay to zero with time, i.e., equilibrium stresses can be supported. Above T_g , such amorphous materials are still classified as solids, but most of their physical properties such as thermal expansivity, thermal conductivity, and heat capacity are liquid-like.

Viscoelastic Behavior of Amorphous Materials

The stress σ in an ideally elastic material is uniquely related to a specific strain γ , $\sigma = G\gamma$ (where G is the shear modulus), whereas the stress in a Newtonian fluid is uniquely related to the rate of strain, $\dot{\gamma} = d\gamma/dt$,

$$\sigma = \eta \dot{\gamma} \quad (22)$$

Such behavior is approximated over limited ranges. The energy input to deform an ideal elastic body is entirely recoverable. In other words, the mechanical

energy is conserved. The energy input to deform a Newtonian fluid is completely dissipated into heat. None of the deformation is recoverable. Most materials are measurably viscoelastic where the energy of deformation is partially dissipated into heat. Their mechanical response is consequently a function of time and frequency. Because of the time or frequency dependence, when mechanical measurements are made, it is necessary to hold one of the pertinent variables constant to obtain characterizing functions. The three most common measurements involve creep, stress relaxation, and dynamic (sinusoidal) deformation. Isothermal measurements are necessary, since although isochronal temperature scans may be considered easier, during such scans time-scale shifts and magnitudes of compliance or rigidity can change simultaneously. Isothermal results separate the two variables (62) (see VISCOELASTICITY).

Creep. In the creep experiment a constant stress σ_0 is created in a previously relaxed specimen at some starting time, and the resulting strain $\gamma(t)$ is followed as a function of the ensuing time. Given a sufficiently long time of creep, the velocity of creep will decelerate to zero if a viscoelastic solid is being measured or to a finite constant value if a viscoelastic liquid is being measured. Some time after an apparent constant velocity is reached, in the latter case, viscoelastic steady state is achieved. Then the stress can be made equal to zero by removing all tractions on the specimen and a portion of the deformation will be recovered; again, as a function of time. The portion that is permanent deformation reflects the contribution of viscous flow to the total deformation accumulated during creep. Since a viscoelastic solid does not flow, by definition, all of its creep deformation is recoverable. When the strains or the strain rates are sufficiently small, the creep response will be linear. In this case, when the time-dependent strain is divided by the constant stress, a unique creep compliance curve results; that is, at each time there is only one value for this ratio, which is the compliance; ie, $\gamma(t)/\sigma_0 \equiv J(t)$. Two sources of error that are most specifically deleterious to creep recovery is not reaching steady state before removing the stress (a nonunique curve results), and the presence of friction and other sources of residual stress. Ultimately, in recovery measurements, instrumental disturbances determine the longest time of valid measurement.

Stress Relaxation. The decaying stress is measured as a function of the time after a sudden "instantaneous" strain γ_0 is applied to a previously relaxed sample in the stress relaxation measurement. The stress $\sigma(t)$ eventually drops to an equilibrium finite value for a viscoelastic solid and to zero for a viscoelastic liquid. Sources of uncertainty that are particularly serious in stress relaxation are (1) the determination of applied small strains if the sample is glassy or crystalline, since the linear range of response may be exceeded even at a strain of 1% and (2) the difficulty in measuring the attendant stress over the required 4–6 orders of magnitude in the softening dispersion. Stress relaxation and creep often cover the same kind of time scale range, 0.1 s to 10 h or a day. Measurements extending for months to years have been carried out, but are not common. The stress relaxation modulus $G(t) \equiv \sigma(t)/\gamma_0$.

Dynamic Mechanical Measurements. Dynamic mechanical measurements yield either the complex modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, or the complex compliance, $J^*(\omega) = J'(\omega) - iJ''(\omega)$.

Sinusoidal stresses or strains of constant frequency are applied to a sample until a steady sinusoidal strain or stress results, with a fixed phase angle between the input and the output. Most often only about two cycles are required to establish steady conditions. The greatest errors are obtained when the system phase angle of measurement is near 0, 90, or 180°. In some forced oscillation measurements the uncertainty of the loss modulus G'' becomes great when phase angle of the system approaches 0 and 180°, and G' , the storage modulus, usually cannot be accurately determined when the material phase angle is near 90°. Dynamic moduli or compliances can be calculated without ambiguity from most sinusoidal measurements, but to avoid confusion in an already cluttered nomenclature it has become traditional to only calculate compliances from creep and moduli from stress relaxation. Dynamic measurements are the measurement of choice if information at equivalently short times is desired, since such measurements are possible at a megacycle and higher, but creep or stress relaxation measurements at times shorter than a millisecond are not possible. The circular frequency ω (in radians per second) should be associated with the reciprocal of the time t .

Questions concerning further experimental details including many on linear and nonlinear flow measurements can often be answered in References 62–68.

Significant Variables

Temperature Dependences. Each and every group of molecular mechanisms contributing to viscoelastic behavior has its own temperature-dependent rate. This is usually recognized except for behavior observed high above the T_g of amorphous polymers, where a single temperature dependence of time or frequency shifts is usually reported. The temperature dependence of the terminal zone of response, reflecting viscous flow and long-range recoverable deformation, was first reported to be different from that observed in the softening dispersion (the glassy to rubbery zone) in PS (69) and later in PVAc [poly(vinyl acetate)] (70). Numerous other examples have since been recognized (71,72). An example from atactic polypropylene (aPP) is given in Figure 19 (30,71–75).

There is evidence that the softening dispersion which extends from the glassy level ($J_g \approx 10^{-9} \text{ Pa}^{-1}$) to the rubbery level ($J_g 10^{-5} \text{ Pa}^{-1}$) of compliance has three contributions (segmental, sub-Rouse, and Rouse modes) (76–79). Reducing data to a common extended curve by shifting them along the time or frequency scale to obtain a wider range of characterization is only legitimate when all of the contributions from molecular mechanisms to deformations have the same temperature dependence. Therefore, curves of viscoelastic functions reflecting the presence of more than one mechanism cannot be validly superposed to yield accurate predictions. Such data is considered thermorheologically complex. The presence of multiple temperature dependences is also observed in permittivity and dynamic light scattering measurements. An example of the reduction of the recoverable compliance curves of PIB shown in Figure 20 is seen in Figure 21 (78). The apparent success of the reduction is shown to be illusory with data taken over a wider frequency range. This is seen in Figure 22, where loss tangent curves [$\tan \delta = J''/J' = G''/G' (1)$] presented at four temperatures from -74.2

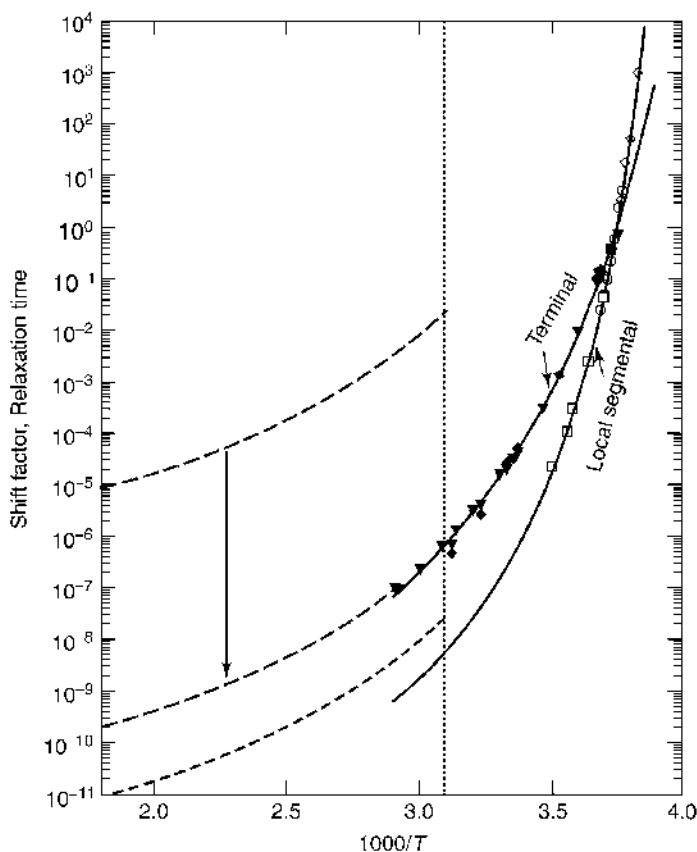


Fig. 19. Temperature dependence of the shift factors of the viscosity ($\blacktriangledown$), terminal dispersion ($\blacklozenge$), and softening dispersion ($\lozenge$) of app from Ref. 73. The temperature dependence of the local segmental relaxation time determined by dynamic light scattering ($\square$) (30) and by dynamic mechanical relaxation ($\circ$) (74). The two solid lines are separate fits to the terminal shift factor and local segmental relaxation by the Vogel–Fulcher–Tammann–Hesse equation. The uppermost dashed line is the global relaxation time τ_R , deduced from nmr relaxation data (75). The dashed curve in the middle is τ_R after a vertical shift indicated by the arrow to line up with the shift factor of viscosity (73). The lowest dashed curve is the local segmental relaxation time τ_{seg} deduced from nmr relaxation data (75).

to -35.8°C (78,80) reveal the presence of two groups of viscoelastic mechanisms which shift along the time-scale differently with temperature.

In addition to temperature time-scale shifts, which are attributed to changes in the relative or fractional free volume (62), the magnitude of the compliance or modulus can change. The kinetic theory of rubber-like elasticity suggests that the entropically based modulus contribution to the viscoelastic response should increase in direct proportion to the absolute temperature. Correspondingly the reciprocal of the steady-state recoverable compliance should be directly proportional to the absolute temperature. In Figure 23 this can be seen to be true at temperatures that are greater than $2T_g$, but between $1.2T_g$ and $2T_g$; J_s

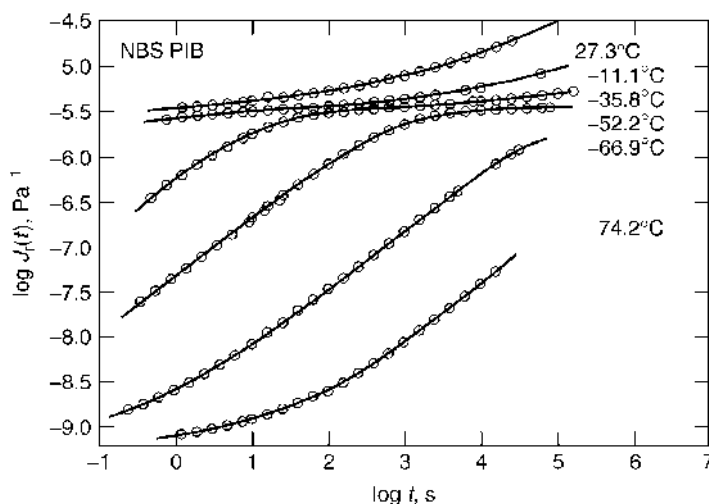


Fig. 20. Double-logarithmic plot of the recoverable compliance $J_r(t)$ of the National Bureau of Standards (NBS) PIB sample measured as a function of time at six temperatures as indicated.

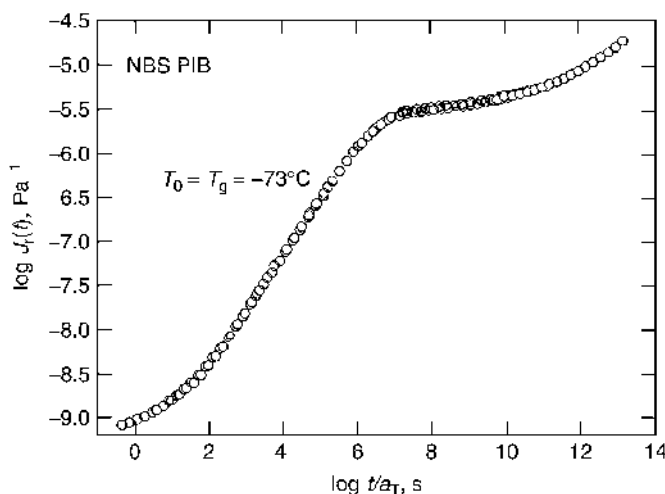


Fig. 21. Data from Figure 20 reduced to a common curve at the reference temperature T_0 of -73°C .

(identified in the figure as J_e) is essentially independent of temperature. At still lower temperatures a strong decrease of J_s is seen (81).

Molecular Weight and Distribution Dependences. The influences of molecular weight and its distribution on the viscous flow (82) viscoelastic behavior of amorphous polymers (83) have been reviewed. The flow behavior of bulk amorphous polymers and their concentrated solutions has been rationalized

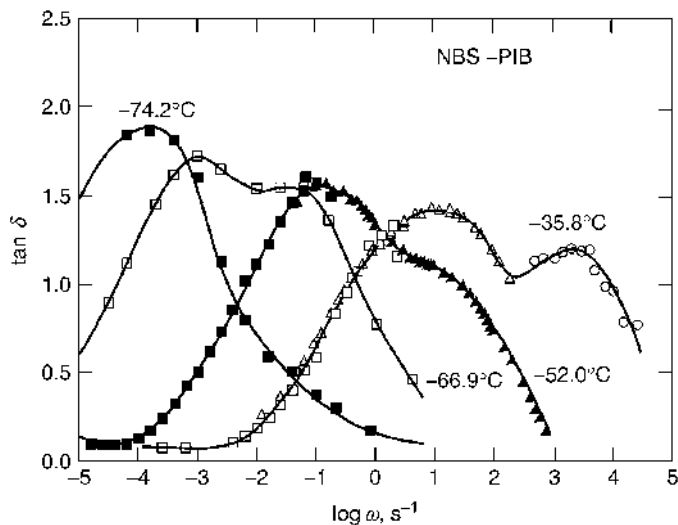


Fig. 22. $\tan \delta$ as a function of actual frequencies at several temperatures for NBS PIB. The data were obtained by using several instruments spanning the frequency range as shown in the abscissa. The high frequency data at -35.8°C ($\circ$) are from Ref. 80. The rest of the data were obtained by a combination of creep compliance and dynamic modulus measurements.

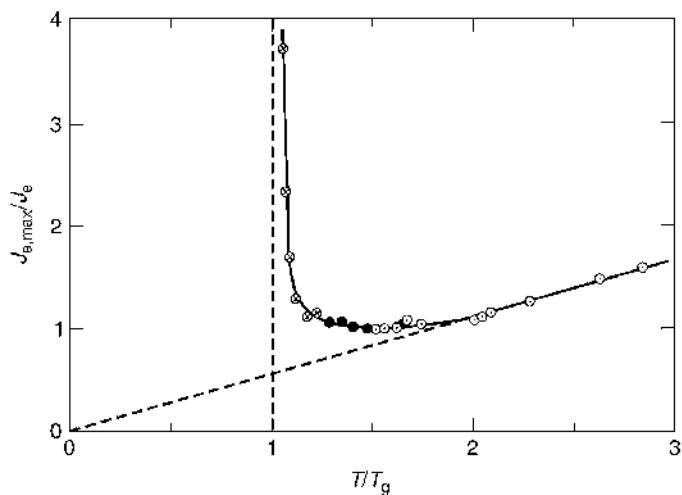


Fig. 23. Normalized reciprocal steady-state recoverable compliance $J_{e,\max}/J_e$ for three polymers, poly(dimethyl siloxane), PIB, and PS, versus the reduced temperature T/T_g ; T_g is the glass temperature and the normalized compliance $J_{e,\max}$ is the largest experimentally indicated value which appears to occur at $T/T_g \approx 1.5$. The broken line through the origin indicates the expected kinetic theory result for a rubber-like modulus. $\circ$ poly(dimethyl siloxane); $\bullet$ PIB; $\otimes$ PS.

(82). Also, the basis for analyzing the viscosity as the product of two factors has been documented:

$$\gamma = F\zeta \quad (23)$$

where F is the structure factor, which depends on the polymer chain length (molecular weight) and branching, and ζ is the friction factor per chain atom, which depends principally on temperature. The latter is influenced by the molecular weight through the variation of the glass temperature. Holding the number-average molecular weight M_n constant so that T_g does not change while varying the weight-average molecular weight M_w at constant temperature, as was done in References 83 and 84, ζ can be held constant so that the molecular weight dependence can be determined. It was found that at low molecular weights, F is proportional to the molecular weight in accord with Bueche's theory (85). Above a critical molecular weight M_c , the dependence increases to a proportionality of $M^{3.4}$ (82,83,86). This behavior appears to be universal and independent of the chemical nature of the polymer.

For polymers with broad molecular weight distributions the viscosity appears to be a function of the weight-average molecular weight M_w . This relationship fails for extreme binary blends with molecular weight ratios of 8 (87), 27 (88), and 380 (89). The blend data fall substantially below the curve determined for narrow distribution polymers.

Viscoelastic Behavior of Narrow Molecular Weight Distribution Polymers

The variations of the viscoelastic behavior of narrow molecular weight distribution amorphous polymers can most readily be seen in the broadening of the retardation spectrum $L(\lambda)$, as shown in Figure 24 (90). $L(\lambda)$, where λ is the retardation time, characterizes the contribution to the creep compliance $J(t)$, the dynamic storage compliance $J'(\omega)$, and the dynamic loss compliance $J''(\omega)$ according to the following relations (62):

$$J(t) = J_g + \int_{-\infty}^{\infty} L(1 - e^{-t/\lambda}) d \ln \lambda + \frac{t}{\eta} \quad (24)$$

$$J'(\omega) = J_g + \int_{-\infty}^{\infty} \left(\frac{L}{1 + \omega^2 \lambda^2} \right) d \ln \lambda \quad (25)$$

$$J''(\omega) = \int_{-\infty}^{\infty} \left(\frac{L\omega\lambda}{1 + \omega^2 \lambda^2} \right) d \ln \lambda + \frac{1}{\omega\eta} \quad (26)$$

The integrals involving L deal only with recoverable deformation, which for the most part reflects molecular orientation from various mechanisms. Permanent deformations are accounted for by the terms containing the viscosity coefficient

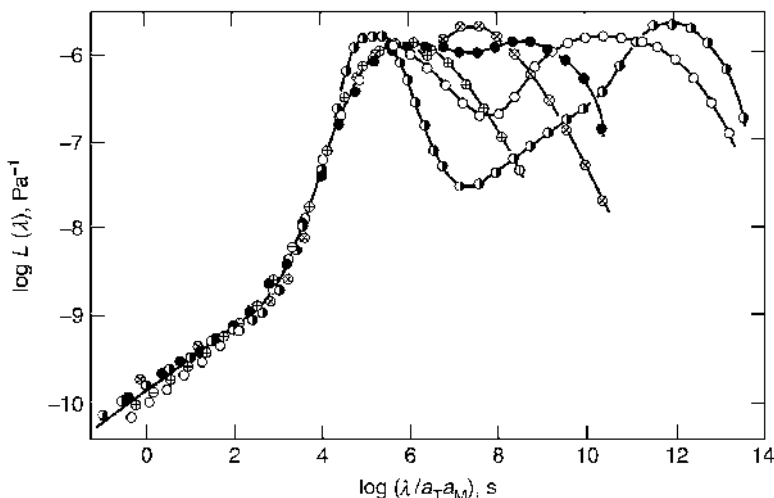


Fig. 24. Bilogarithmic plot of the retardation spectra $L(\lambda)$ of PS with narrow molecular weight distribution as functions of the reduced retardation time $\lambda_r = \lambda/a_T a_M$, where a_T is the temperature reduction factor and a_M is the molecular weight reduction factor [the latter reflects the change in $T_g(M)$]. The molecular weights and symbols for the various PSs are 4.7×10^4 , A25, $\oplus$; 9.4×10^4 , M102; $\otimes$; 1.9×10^5 , L2, $\bullet$; 6.0×10^5 , A19, $\circ$; and 3.8×10^6 , F380, $\bullet$. The reference temperature $T_0 = 100^\circ\text{C}$ and the reference molecular weight $M_0 = 1.9 \times 10^5$.

η . From equation 24 it can be seen that the long-time limiting recoverable compliance is

$$J_s = J_r(\infty) \equiv \lim_{t \rightarrow \infty} [J(t) - t/\eta] = J_g + \int_{-\infty}^{\infty} L d \ln \lambda \quad (27)$$

Thus the steady-state recoverable compliance J_s is the sum of the glassy compliance and the limiting delayed compliance,

$$J_d = \int_{-\infty}^{+\infty} L d \ln \lambda \quad (28)$$

The recoverable shear creep compliance $J_r(t) = J(t) - t/\eta$, but to obtain $J_r(t)$ over an appreciable range of time-scale in the terminal (long-time) zone of response the recoverable deformation must be measured directly, after achieving steady state in a creep measurement, and subsequently setting the stress to zero. Since the measurement of recovery is a zero-stress experiment, extensive recovery cannot be determined with instruments that employ ball-bearing to support the moving element. Air-bearing instruments are also severely limited. With a magnetically levitated moving element an optimized range of measurement is achieved. The steady-state recoverable compliance of a viscoelastic liquid in elongation may not be measurable even under the weightless condition of outer space because of

the interference of surface tension. In oscillatory measurements of dynamic compliances or moduli the interference of friction can be avoided with wire supports.

Equation 24 indicates that the strains arising from different molecular mechanisms add simply in the compliances and in principle can be separated. On the other hand, the stresses do not add and the different mechanisms cannot be easily resolved in modulus functions. In solution the solvent and the polymer contributions are also seen to be additive, as shown below. To understand the somewhat esoteric viscoelastic functions this additivity is helpful. It should also be noted that there are only two functions that do not contain contributions involving viscous flow, which obscure the recoverable responses which are largely, if not completely, due to molecular orientations. They are the storage compliance J' and the recoverable creep compliance $J_r(t)$.

Near T_g , molecular mobilities are so small that the times required to achieve steady state become enormous. To avoid this dilemma, it has been proposed that steady-state could be achieved in creep at higher temperatures in a short time and would be maintained with cooling to the neighborhood of T_g so long as the stress was held constant (31). This tactic appears to work and is extremely useful.

In Figure 24 (90) the lowest molecular weight, narrow distribution PS depicted as A25 ($M = 47,000$) has only two contributions, (1) at short times a common linear portion between $\log \lambda_r$ of -1 and 3 with a slope of $1/3$ and it is followed by (2) a symmetrical peak centered at $\log \lambda_r = 6$. The short-time region reflects the presence of Andrade creep in which the recoverable creep compliance is a linear function of $t^{1/3}$. An alternative description by a generalized Andrade creep with t^{β_α} , with β_α not necessarily equals to $1/3$ and varies from one polymer to another, is possible. Actually such a generalized Andrade creep is the short-time part of the

$$J_\alpha(t) = J_g + (J_{e\alpha} - J_g) \left\{ 1 - \exp \left[1 - (t/\tau_\alpha)^{1-n_\alpha} \right] \right\} \quad (29)$$

where $0 < (1 - n_\alpha) \leq 1$ and $(1 - n_\alpha)$ is to be identified with β_α (72,91). The steady-state compliance $J_{e\alpha}$ is the part of J_d contributed by the local segmental motion, also called the α -relaxation. As to be discussed later in sections on Dielectric Spectroscopy and Photon Correlation Spectroscopy, the time correlation function of the α -relaxation of amorphous polymers can be analyzed to have the stretched exponential form $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, similar to equation 8, and β_α varies from polymer to polymer. For example, PS and PIB have β_α equal to 0.36 and 0.55 respectively.

The retardation spectrum of $J_\alpha(t)$ from equation 29 has the τ^{β_α} dependence at a short retardation time τ (notice that λ has been used earlier to denote retardation times), and also exhibits the peak as exhibited by the nonpolymeric glass-formers (see Fig. 29 to be introduced later). $J_{e\alpha}$ has been determined only for low molecular weight polymers and is approximately $J_{e\alpha} \approx 4.0J_g$ for PS (92) and $J_{e\alpha} \approx 5.0J_g$ for poly(methylphenyl siloxane) (93).

The increase in the compliance contributed by the area under the symmetrical peak overwhelms the Andrade or the generalized Andrade contribution and increases until a rubbery level is reached at about 10^{-6} cm²/dyn (10^{-5} Pa⁻¹). This increase in compliance is attributed to the polymer chain modes, first successfully described by Rouse (94). His theory was extended by Ferry, Landel, and Williams from a dilute solution theory to one dealing with the viscoelastic

properties of undiluted polymers (95) (see VISCOELASTICITY). However, the extended Rouse model has limitations. It has been recognized (96) that by taking the short-time limit of the extended Rouse modes contribution to the modulus, one obtains $G(0) = \nu NkT = \nu \rho RT/M$, where N is the number of molecules per cm^3 and ν is the number of submolecules per chain (62). The number of monomers in a submolecule, z , is given by P/ν , where P is the number of monomers in a polymer chain. For a polymer of molecular weight 150,000 and a density of 1.5 g/cm^3 and by assuming that the smallest submolecule that can be still be Gaussian consists of five monomer units (ie, $z = 5$), it was found that $G(0) = 7.5 \times 10^6 \text{ Pa}$ [$J(0) = 1.3 \times 10^{-7} \text{ Pa}^{-1}$]. This value is about 2 orders of magnitude smaller (larger) than the experimentally determined value of the glassy modulus G_g (glassy compliance J_g) which typically falls in the neighborhood of 10^9 Pa (10^{-9} Pa^{-1}). Thus the extended Rouse model cannot account for the short-time portion of the glass-rubber dispersion of entangled polymers because here the modulus (compliance) decreases (increases) continuously from about 10^9 Pa (10^{-9} Pa^{-1}) to the plateau modulus of about 10^5 Pa (10^{-5} Pa^{-1}). These deficiencies of the extended Rouse model are not surprising because, after all, according to the model the submolecule is the shortest length of chain which can undergo relaxation and the motions of shorter segments within the submolecules are ignored. The Gaussian submolecular model of Rouse can, at best, account only for viscoelastic behavior in the longer relaxation time portion of the glass-rubber softening dispersion. Thus the extended Rouse model has to be augmented by the molecular mechanisms involving chain units smaller than the submolecule but larger than the local segmental motion, which we called the sub-Rouse modes. Clear evidences of sub-Rouse modes were found by viscoelastic measurement (78,79) and by dynamic light scattering (27,29) in PIB. The high frequency peak or shoulder of $\tan \delta$ as a function of frequency in Figure 6 is caused by the sub-Rouse modes. The softening dispersion thus has three contributions: (1) the local segmental motion responsible for $J(t)$ from $J_g \approx 10^{-9} \text{ Pa}^{-1}$ up to about $J_{s\alpha} \approx 5 \times 10^{-9} \text{ Pa}^{-1}$, (2) the sub-Rouse modes from $J_{s\alpha}$ up to somewhere near $J_{sR} \approx 10^{-7} \text{ Pa}^{-1}$, and (3) the modified Rouse modes from $J_{sR} \approx 10^{-7} \text{ Pa}^{-1}$ up to the plateau level. These estimates may vary for polymers with very different chemical structures.

Although the local segmental relaxation does not show up in Figure 22, other supplementary data indicate that all three groups of viscoelastic mechanism—local segmental, sub-Rouse, and Rouse modes—all have different temperature shift factors. For the Rouse and the sub-Rouse modes this fact was shown first by creep compliance measurements in PS in the softening dispersion (72,98) long before sub-Rouse modes were clearly resolved in PIB (Fig. 22) and the term used. It has been confirmed in PS by dynamic modulus measurements. Examples are the data on PS obtained (99) using an inverted forced oscillation pendulum and some unpublished data (72,100) on PS and TMPC (tetramethyl BPA polycarbonate) using a commercial instrument, and in PIB (101). These data are partly reproduced in a review (72). The lack of reduction of the data is clear from the dependence of the shape of the $\tan \delta$ peak with temperature of measurement and occurs over a frequency region that corresponds to compliances in the range from 10^{-5} Pa^{-1} down to about 10^{-7} Pa^{-1} . Narrowing of the softening dispersion of PMMA and PVAc with decreasing temperature was found by

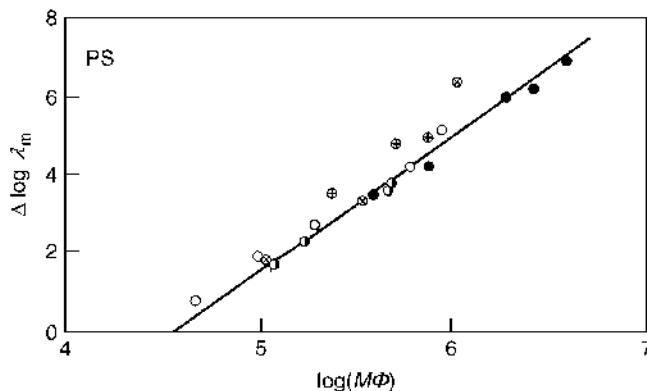


Fig. 25. Length of entanglement rubbery plateau as measured by the separation of the peaks of the retardation spectra on the logarithmic time-scale, $\Delta \log \lambda_m$, as a function of the logarithm of the product of the molecular weight M and the volume fraction of the polymer, Φ . • Blends (89); ● blends (104); ○ monodisperse (105); ⊗ TCP solution (106); ⊕ (107,108).

comparing the data obtained (102) at higher temperature (higher frequency) with that obtained (103) at lower temperature (longer times). This behavior can be considered to be unusual because viscoelastic spectra usually are seen to broaden with falling temperature. All the abnormal behaviors described in this paragraph follow as consequences of the shift factors of local segmental relaxation, the sub-Rouse modes, and the Rouse modes having decreasing sensitivity to temperature in this order, as found directly in PIB (79,97). As temperature is decreased, time-temperature superposition fails because the separations between the three groups of viscoelastic mechanisms are decreased, a phenomenon which is appropriately called *encroachment* (72,79).

As the molecular weight increases a second long-time peak develops in $L(\lambda)$, reflecting a rubber-like plateau in $J_r(t)$ which increases in length. The spectrum seen in Figure 24 for the highest molecular weight PS sample F380 (3.8×10^6) has two additional long-time features 3) a second Andrade region and 4) a terminal symmetrical peak, centered at $\log \lambda_r \cong 12$. The length of the plateau seen in $\log J_r(t)$ is measured by the time separation of the two peaks in $L(\lambda_r)$, $\Delta \log \lambda_m$. The length of the plateau can be seen to increase with the 3.4 power of the molecular weight, just as the viscosity. In fact the length of the plateau goes to zero at the viscosity critical molecular weight ($M_c \approx 35,000$) as seen in Figure 25, where λ denotes the retardation time (89). Since the rubber-like plateau is attributed to the presence of a transient entanglement network of the polymer chains, it is clear that the entanglements manifest themselves at the same molecular weight in viscous and recoverable deformations with the same degrees of enhancement with increasing molecular weight. Although Figure 24 was derived from the reduced curve obtained by time-temperature superposition of isothermal recoverable creep compliance data, actually the two shift factors of terminal dispersion and the local segmental relaxation do not have the same temperature dependence in a common temperature range above T_g (Fig. 19). None of the three mechanisms in the softening dispersion have the same temperature

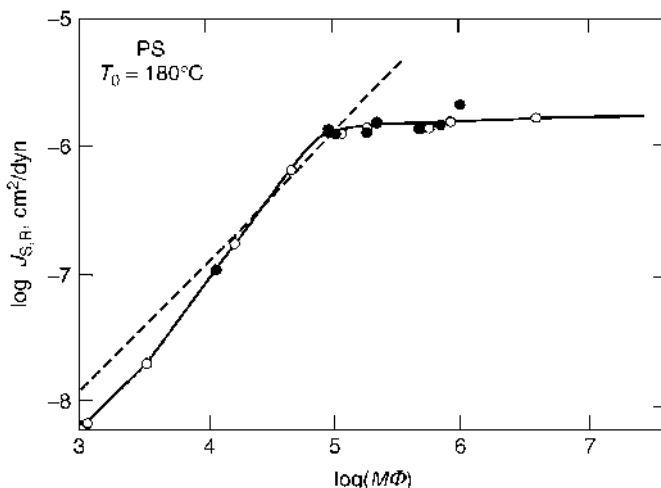


Fig. 26. Reduced steady-state compliances $J_{s,r}$ for PSs with narrow molecular weight distributions plotted logarithmically as a function of the product of the molecular weight M and the volume fraction of polymer, Φ . The dashed line represents the prediction of the modified Rouse theory. The solvent in the solutions is TCP. $\bullet J_{s,r}(\text{solution}) = J_s \Phi^2 T/T_0$; $\circ J_{s,r}(\text{bulk}) = J_s$.

dependence for their shift factors. Therefore, the shift factor a_T used to obtain master curve for polymers by time-temperature superposition, as given in Figures 21 and 24, is actually a combination of the individual shift factors of the several different viscoelastic mechanisms. At low temperatures, a_T is principally determined by the shift factor of the local segmental mode. With increasing temperature, in turn a_T is principally determined by the shift factors of the sub-Rouse modes, the Rouse modes, modes in the plateau, and the terminal modes. Hence, it is wrong to assume that a_T describes the temperature dependence of *any* or *all* of the viscoelastic mechanisms.

Applying the kinetic theory of rubber-like elasticity (62,109) to the entanglement network one can determine the molecular weight between entanglements M_e from the plateau compliance J_N or plateau modulus G_N (62);

$$J_N = G_N^{-1} = M_e / \rho RT \quad (30)$$

where ρ is the density, T is the absolute temperature (K), and R is the gas constant. At high molecular weights $M \gg M_e$ the steady-state recoverable compliance J_s has been reported to be 2–10 times larger than J_N (83). Reported values for J_s have to be accepted with caution because the dependence of J_s is far more sensitive to the molecular weight distribution than to the molecular weight. The results for $J_s(M)$ reported in Reference 105 are shown in Figure 26, where at low molecular weights J_s is amazingly close to the first power dependence predicted by the modified Rouse theory (94,95) with no adjustable parameters. At higher molecular weights, $M > 3M_e$, and J_s becomes independent of molecular weight. This surprising behavior was first reported by Tobolsky and co-workers (110). Results from nine studies on PS show that the published values vary by up to a factor of 5 (111).

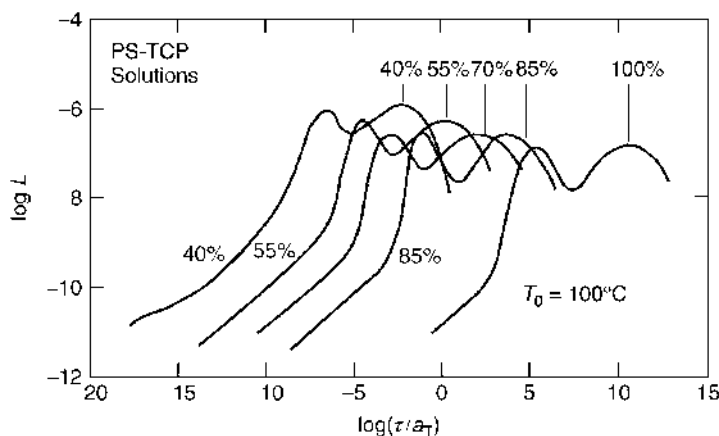


Fig. 27. Logarithmic plot of retardation spectra against reduced time for the more concentrated solutions (40% and above) of PS PC-6A (in TCP) and of the undiluted polymer. In all cases the reference temperature T_0 is 100°C.

It has been shown (112) that molecular weight blends with low concentrations of high molecular components can exhibit J_s values that are nearly 20 times greater than those shown by any of the monodisperse components. Trace amounts of high molecular tails in low molecular weight polymers can enhance the J_s by more than a 1000-fold (105). The recoverable compliance of a polymer with close to a random molecular weight distribution can be more than 10 times higher than that of a narrow distribution sample with the same number-average molecular weight M_n (113).

Long-chain branching, in particular narrow distribution, star-branched polymers (chains joined at a common center) also enhances the steady-state recoverable compliance J_s . It has been shown (114) that four- and six-arm star PS do not show the molecular weight independence at high molecular weight as seen with linear polymers. J_s continues to increase with the first power of the molecular weight; ie, the Rouse prediction continues unabated at the highest molecular weights measured.

Concentration Dependence. The effect of diluent on the viscoelastic behavior of a polymer is profound and complicated. The first and most dramatic effect is the usual strong decrease in the glass temperature T_g , which happens because the T_g of the solvent is usually much lower than that of the polymer, since T_g is tied to the local mobility of the molecules; ie, the local mobility determines when liquid structure rearrangements cannot keep up with the imposed *rate of cooling*. Thereafter the specific volume of the liquid is greater than its equilibrium value. The rearrangements needed to obtain the required local molecular packing are kinetically arrested. Contraction continues with cooling at a diminished rate only because of the reduction in the magnitude of the anharmonic molecular vibrations. Therefore, with increasing diluent concentration, at a given temperature, one obtains solutions that are further above their T_g . Hence molecular mobility is greater because of the larger relative free volume, and the viscoelastic functions $J(t)$, $G(t)$, and $G^*(\omega)$ are found at increasingly shorter times or higher

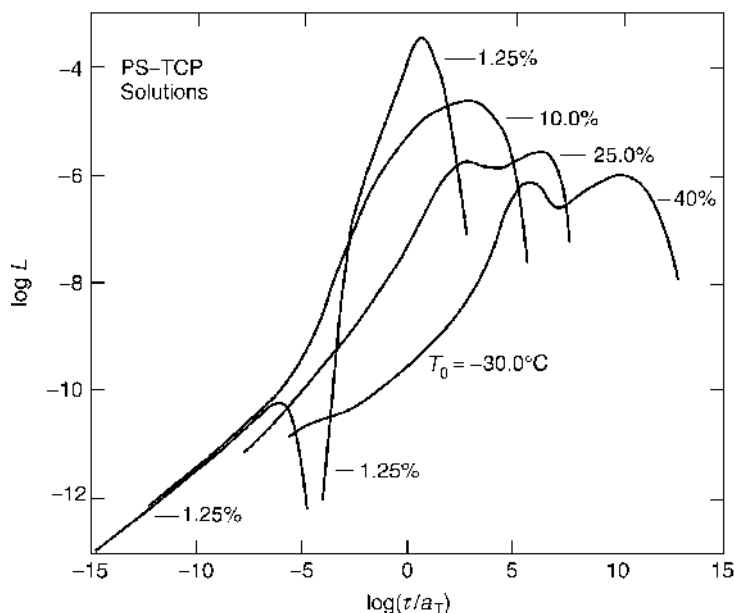


Fig. 28. Logarithmic plot of retardation spectra against reduced time for the less concentrated solutions (40% and less) of PS PC-6A (in TCP) and of the undiluted polymer. In all cases the reference temperature T_0 is -30°C .

frequencies. This shift toward shorter times with increasing diluent concentration can be seen in Figures 27 and 28 (107,108). The retardation spectra for a narrow molecular weight distribution PS ($M = 860,000$) and seven solutions in tricresyl phosphate (TCP) are presented. The spectrum for the bulk polymer is compared with those of the four most concentrated solutions (40, 55, 70, and 85 wt% of PS) at 100°C in Figure 27. The severe shifts to shorter reduced times t/a_T are due to the decrease of T_g . The four lowest concentrations 1, 25, 10, 25, and 40 wt% of PS are compared at -30°C in Figure 28, which shows the shift to shorter times, but the other two effects are most clearly seen at the lower concentrations, although they are present at all concentrations. The separation of the two major peaks diminishes with decreasing polymer concentration, reflecting the shortening rubber-like plateau. With dilution the overlap of the polymer chain coils diminishes and therefore the number of intermolecular entanglements per molecule decreases. With dilution the concentration of viscoelastic elements decreases and each element supports a greater observed compliance. Finally, it should be appreciated that the solvent manifests its independent contribution to the deformation, especially at the lowest polymer concentrations. The spectrum for the 1.25% solution is split into two peaks. Measurements on the pure solvent identified the peak at short times to be due to the solvent. Hence the second sharp peak is the polymer peak. The fact that the polymer and solvent molecule motions influence one another, but contribute additively but separately to the deformation, is the reason for the manifestation of two observed T_g 's in some of the solutions (107,108).

The Glass Temperature, A Material Characterizing Parameter

For the glass temperature to be a material characterizing parameter it must be determined by cooling from equilibrium (see GLASS TRANSITION). Heating measurements yield an approximation to the fictive temperature of the starting glassy materials, which is a function of its thermal history below T_g . The glass-transition temperature is therefore a specimen characterizing parameter and a unique function of the rate of cooling. It has been shown (115) that local segmental motions contribute both to the glassy Andrade creep region and to liquid structural relaxation. It is therefore reasonable to expect that for a given rate of cooling the local mobility which determines the T_g departure from an equilibrium liquid structure has to be the same for all amorphous materials. It has consequently been established that at T_g the retardation function, at short times, in the region of the time scale attributed to local segmental motions is the same functionally and in position for many amorphous materials including nonpolymeric, organic glass-formers, inorganic glasses, and polymers. Figure 29 shows the common viscoelastic behavior between $\log \tau$ of -6 to $+1$, where τ is the reduced retardation time. To obtain close superposition, T_g 's measured at a cooling rate of $0.2^\circ\text{C}/\text{min}$ were adjusted by up to 2°C , which is thought to reflect the usual magnitude of uncertainty (60). It is at longer times that the structural differences of the materials manifest themselves. In the region of Andrade creep dominance $L(\tau)$ was calculated by Thor Smith to be (116)

$$L(\tau) = 0.246\beta_A\tau^{1/3} \quad (31)$$

where β_A is the Andrade coefficient (117) in

$$J_r(t) = J_A + \beta_A t^{1/3} \quad (32)$$

In the short-time regime the constant J_A in equation 32 is equal to the glassy compliance J_g . From Figure 29, at $\tau = 1$ s, $L(\tau)$ is 2.24×10^{-12} cm²/dyn (or is 2.24×10^{-11} Pa⁻¹). Therefore, the temperature at which $\beta_A = 9.10 \times 10^{-12}$ cm²/(dyn·s^{1/3}) is T_g ($Q = 0.2^\circ\text{C}/\text{min}$, where Q is the rate of cooling).

Although the short-time compliance data of diverse amorphous materials can be represented by Andrade creep (eq. 32), the reason for such a "universal" behavior is unclear. The alternative description of the local segmental contribution by equation 29 with $(1-n_\alpha) \equiv \beta_\alpha$ not necessarily equal to $1/3$ and its value dependent on the material itself offers a different possibility. The generalized Andrade creep

$$J_r(t) = J_g + Bt^{1-n_\alpha} \quad (33)$$

which is the short-time limit of equation 29, will replace equation 32 and be used to fit the data at short times and determine J_g in the process.

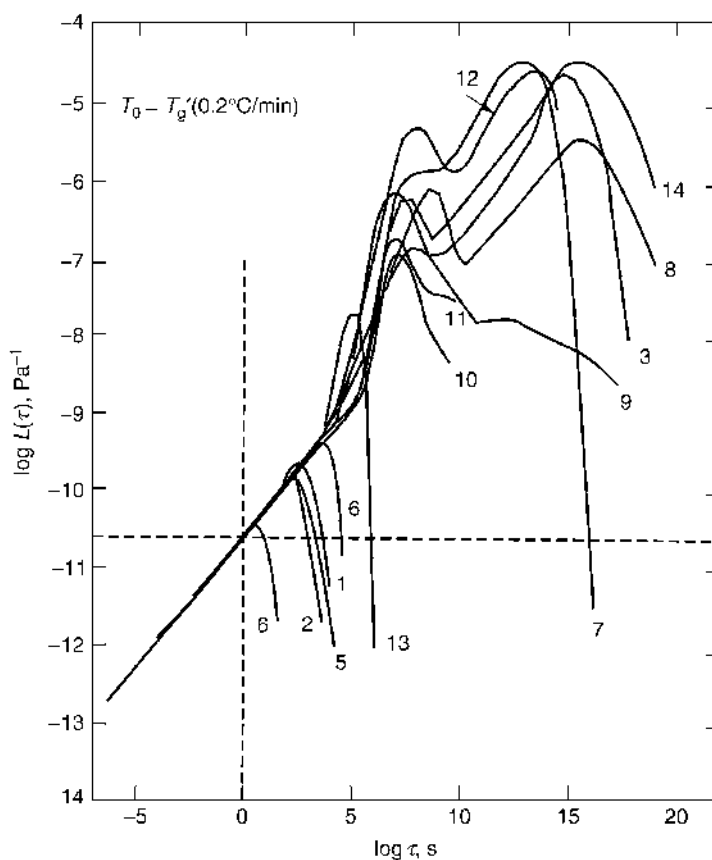


Fig. 29. Superposition of the retardation spectra at short times for 1) 6PE; 2) Aroclor 1248; 3) polypropylene; 4) TCP; 5) OTP; 6) $\text{Ti}_2\text{SeAs}_2\text{Te}_3$; 7) PS Dylene; 8) PIB; 9) Viton 10A; 10) EPON 1004/DDS; 11) EPON 1007/DDS; 12) PB/Aroclor 1248 Soln; 13) Se 14) PVAc.

Dependence of Viscoelastic and Dynamic Properties on Chemical Structure

It was recognized already in the early days of viscoelastic measurements that the time or frequency dependence of the softening zone can vary considerably with the chemical structure of the polymer. As early as in 1956 it was found that the softening dispersions of PIB and PS contrast sharply (118,119). The glassy compliance (modulus) and the plateau compliance (modulus) are similar for PIB and PS, but the width of the glass-rubber softening dispersion of PIB is several decades broader in time or frequency than that of PS. In a 1991 review (120) it was remarked that the origin of this difference is still not clear. From the discussion in previous sessions and results summarized in a review (71,72), the other differences in viscoelastic properties of PIB and PS include the lesser differences between the temperature dependences of the three viscoelastic mechanisms in the softening dispersion of the former (71,72,79). The terminal dispersion as well

as the $M^{3.4}$ molecular weight dependence of the viscosity of monodisperse entangled linear polymers does not depend on chemical structure of the repeat units. Nevertheless, the difference between the temperature dependences of the terminal dispersion (or the viscosity) and the local segmental motion is significantly less in PIB than in PS.

Dielectric relaxation and photon correlation spectroscopic measurements (to be discussed later) have found that the stretched exponential time correlation function of the α -relaxation of amorphous polymers, $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, has β_α that varies from polymer to polymer. For example, PS and PIB have β_α equal to 0.36 and 0.55 respectively. It was recognized that this difference in the stretched exponent β_α of PIB and PS is the origin of their contrasting viscoelastic properties (72,79,121,122).

Low Molecular Weight Amorphous Polymers. The most spectacular observations of breakdown in time-temperature superposition occur in low molecular weight polymers. The effect was first seen in PS by creep and recovery measurement (105). The recoverable compliance $J_r(t)$ for a 3400 Da molecular weight PS undergoes a dramatic change in shape of the recoverable compliance curve as the temperature is lowered toward T_g . At the same time the steady-state recoverable compliance J_s decreases 30-fold down to a value which is only about five times J_g . This was confirmed by complex shear modulus measurements of Gray, Harrison and Lamb (123). The viscoelastic anomalies found in low molecular weight PSs are general phenomena because they are also found in other polymers. These include polypropylene glycol (124), poly(methylphenyl siloxane) (125), and selenium, a natural polymer (126,127). An example is shown by $J_r(t)$ data of a near monodisperse poly(methylphenyl siloxane) with molecular weight of 5000 Da plotted against the logarithm of the reduced time t/a_T . The origin of the effect has been traced (122) to the stronger temperature dependence of the shift factors of the local segmental modes, the sub-Rouse modes, and the Rouse modes in this order, ie, encroachment of the local segmental mode toward the two longer time mechanisms (122). Confirmation of this explanation was provided by dielectric relaxation in polypropylene glycol and in PI (126,128).

Dynamic Properties of Amorphous Polymers Probed by Other Techniques

Besides viscoelastic measurements described above, there are a variety of techniques that can probe the dynamic and viscoelastic properties of amorphous polymers. Their advantages and disadvantages as compared with shear viscoelastic measurements in elucidating the dynamic properties become clear in the following sections.

Dielectric Spectroscopy. Dielectric experiments obtain the permittivity $\varepsilon'(\omega)$ and loss $\varepsilon''(\omega)$ of materials that has a permanent dipole moments over a wide range of frequency (129,130). The complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is given by the one-sided Fourier transform of the normalized dipole moment autocorrelation function $\phi(t) = \langle M(0) \cdot M(t) \rangle / \langle M^2(0) \rangle$ as

$$[\varepsilon^*(\omega) - \varepsilon_\infty] / (\varepsilon_0 - \varepsilon_\infty) = \int_0^\infty \exp(-i\omega t') \left[-d\phi(t')/dt' \right] dt' \quad (34)$$

where ε_0 and ε_∞ are the low and high frequency limit of $\varepsilon'(\omega)$, respectively.

By a combination of commercial instruments, the wide frequency range $10^{-4} < f = \omega/2\pi < 10^{10}$ Hz is accessible to probe the molecular motions. The technique usually probes only the local segmental relaxation (often called the primary or α -relaxation in dielectric relaxation) and the secondary (β , γ , ...) relaxations exclusively. For a few polymers such as polypropylene glycol and PI that have a component of the dipole moment parallel to the polymer chain backbone, additional relaxation processes due to some normal modes that correspond to the mechanical terminal zone, are dielectrically active (126,128,131–133). The α -loss peak has an asymmetrically skewed shape with a width which can be much larger than a Debye peak given by $\varepsilon'' \propto \omega\tau/(\omega^2\tau^2 + 1)$. The degree of departure from the Debye peak varies from polymer to polymer. The two parameter Cole–Davidson (134) and the three parameter Havriliak–Negami (HN) (135) empirical functions have often been used to fit the experimental data because these two are empirical functions of the frequency and are very convenient for fitting experimental data. An equally popular empirical function of frequency is obtained from equation 34 with $\phi(t)$ given by the KWW function (136,137)

$$\phi(t) = \exp \left[- (t/\tau)^{1-n_\alpha} \right] \quad (35)$$

with $0 < (1 - n_\alpha) \equiv \beta_\alpha < 1$. The KWW function has two parameters as compared with three parameters in the HN equation. As a consequence, the HN function always provides a better fit to the data than does the KWW function. Nevertheless the KWW function has been found to give an adequate fit (with ubiquitous deviation at high frequencies) to the dielectric data and is often used in current literature. It is also popular with theoreticians for the construction of models to explain the non-Debye behavior of the α -relaxation process. The popularity is probably due to the fact that it has only two parameters, the KWW exponent $1 - n_\alpha$ that controls both the width and the degree of skewness and τ corresponds approximately to the most probable correlation time. Irrespective of the choice of the empirical function used to fit the dielectric dispersion, the frequency of the dielectric loss maximum determines the most probable frequency of the local segmental motion. In contrast to viscoelastic measurements, the Rouse modes and the modes in the terminal zone are usually not observed. Thus the α -relaxation is the dominant contribution to $\varepsilon^*(\omega)$ and its dispersion or $1 - n_\alpha$ can be easily determined. The dielectric dispersions of small molecular glass-formers including salol, toluene, bromopentane, propylene carbonate, glycerol, propylene glycol are temperature-dependent (138), with $1 - n_\alpha$ increasing with increasing temperature and in some cases approaches unity (ie, Debye relaxation) at high temperatures. There are also some evidences that the dielectric dispersion of the α -relaxation of amorphous polymers also narrows with increasing temperature; however, apparently $1 - n_\alpha$ is not close to unity even at high temperatures where the α -relaxation time is of the order of 10^{-10} s. An example is PVAc (139,140). This difference between small molecular glass-former and amorphous polymers is due to the presence of bonded interaction between repeat units in the polymer chains (141,142). In fact, the local segmental mode of a polymer chain already has dispersion broader than the Debye relaxation as shown by dielectric relaxation measurement of dilute solution of PVAc in a solvent (143).

Photon Correlation Spectroscopy. Photon correlation spectroscopy (pcs) is one among several light scattering techniques reviewed in the beginning of this article. The technique is sensitive to density fluctuations as well as concentration fluctuations (125,144,145) and obtains directly the autocorrelation functions in the time domain. It has been suggested that pcs data correspond to the longitudinal compliance (146). The local segmental mode is the main contributor to density fluctuation and is featured exclusively in the data taken by pcs, although in addition the sub-Rouse modes have also been seen in PIB (27,31). Most pcs studies on bulk polymers as well as nonpolymeric glass-forming liquids have shown that the KWW functions are adequate representations of the experimental time-correlation functions for the density fluctuations. Thus the KWW function that fits the pcs data gives directly the dispersion of the α -relaxation. The KWW exponent $1 - n_\alpha$ characterizing the dispersion varies from polymer to polymer. For example, PS has the smaller value of 0.36 (23,29), PIB has the larger value of 0.55 (27,31), and poly(methylphenyl siloxane) has the intermediate value of 0.45 (125). Since pcs, dielectric relaxation, and shear mechanical relaxation or compliance measure different dynamic variables and different correlation functions, it is not surprising that dispersion parameter $1 - n_\alpha$ and the effective relaxation or retardation time τ_α determined by the three techniques can be different (147–150).

Besides pcs, other light scattering techniques including Brillouin scattering and Fabry–Perot interferometry described in previous sections have been applied to probe the dynamics of polymers at higher frequencies than the more conventional techniques. Interpretations of the results from these techniques are still subjects of controversy and are not discussed here.

Ultrasonic Attenuation. The frequency range of this technique is of the order of 1 MHz. The attenuation α of the longitudinal waves is related to the longitudinal loss modulus M'' by $M'' = 2\alpha\rho u^3/\omega$, and the longitudinal storage modulus M' by $M' = \rho u^2$, where ρ is the density and u is the ultrasonic velocity. For an example of the use of this techniques, see References 151 and 152.

Nuclear Magnetic Resonance Techniques. Several experimental techniques stemming from the basic principles of nuclear magnetic resonance (qv) were developed in the last decade, which probe relaxation as local as the primary local segmental motion and the secondary relaxation and as extensive as diffusion of the entire chain. Some of these techniques and representative data have been reviewed (153) and are not discussed further here. However, in Figure 30 the local segmental relaxation correlation time τ_c of high molecular weight PS is shown as a function of temperature obtained by two-dimensional exchange nmr (154,155) up to long times exceeding 100 s, and compared with the shift factor $a_{T,S}$ from time–temperature superposition of recoverable creep compliance $J_r(t)$ curves of another high molecular weight PS (PS-A25) in the glass–rubber softening region described earlier (105). Only the fits to the data of τ_c and $a_{T,S}$ by the William–Landel–Ferry (WLF) equation (156) are given. The nmr τ_c has the same temperature dependence as $a_{T,S}$ in the temperature range below 384 K, where $a_{T,S}$ is determined principally by measurements of $J_r(t) < 10^{-7} \text{ Pa}^{-1}$ and reflects the shift factors of the local segmental motion, $a_{T,\alpha}$, and the sub-Rouse modes, $a_{T,SR}$. Above 384, τ_c starts to exhibit stronger temperature dependence than $a_{T,S}$. Between approximately 384 and 407 K, $a_{T,S}$ is determined by curves with $J_r(t)$ larger than 10^{-7} Pa^{-1} and consist of Rouse modes and possibly some

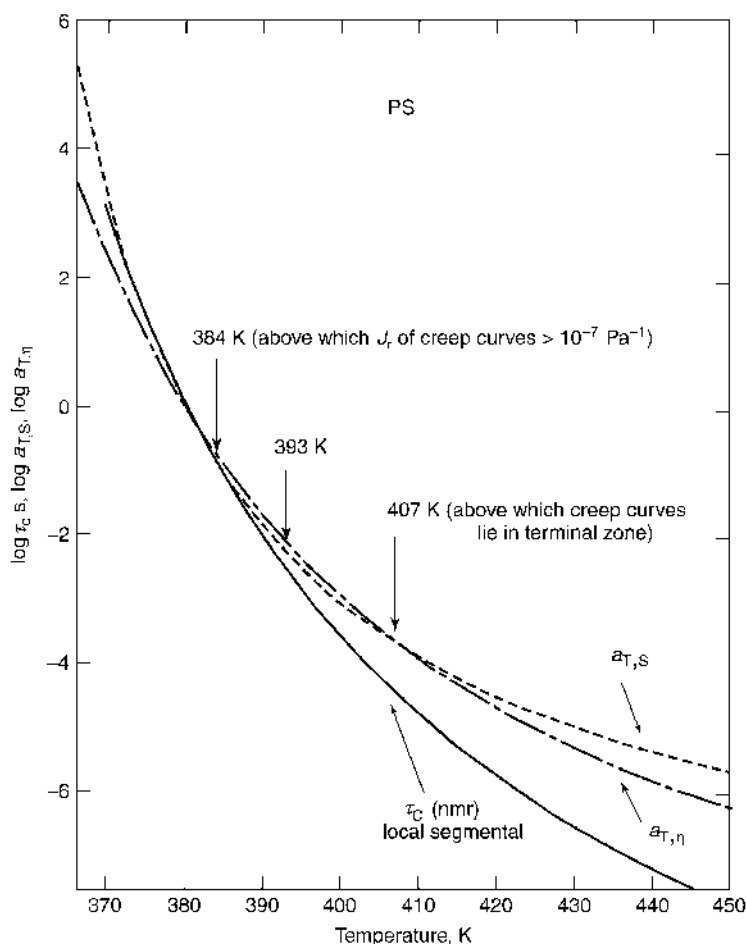


Fig. 30. The local segmental relaxation correlation time τ_c of high molecular weight PS as a function of temperature obtained by two-dimensional exchange nmr (154,155) up to long times exceeding 100 s, and compared with the shift factor $a_{T,S}$ from time-temperature superposition of recoverable creep compliance $J_r(t)$ curves of another high molecular weight PS (PS-A25) in the glass-rubber softening region (105). Only the fits to the data of τ_c (—) and $a_{T,S}$ (----) by the WLF equation are given. The viscosity shift factor $a_{T,\eta}$ is also shown (-·-·-). The nmr τ_c clearly has stronger temperature dependence than the viscosity in the *entire* temperature range. There is also good agreement between the temperature dependence of τ_c and $a_{T,S}$ at temperatures below 384 K where $a_{T,S}$ becomes sequentially the shift factor of first the sub-Rouse modes and second the local segmental modes as temperature is decreased toward T_g .

shorter time modes in the plateau. Thus the nmr data gives another proof that the local segmental relaxation time has stronger temperature dependence than the Rouse modes (71,72). Above approximately 407 K, the creep compliance data is contributed entirely by the terminal viscoelastic mechanism, which has exactly the same temperature dependence as the viscosity shift factor $a_{T,\eta}$ shown also in Figure 30. It is unsurprising that the extrapolation of $a_{T,S}$ to this high temperature regime shows a different (weaker) temperature dependence than the actual shift factor for the viscosity. More important is that the nmr data τ_c of the local

segmental relaxation time τ_α clearly has stronger temperature dependence than the viscosity in the *entire* temperature range shown in Figure 30.

Quasi-elastic Neutron Scattering. Coherent and incoherent inelastic neutron scattering are unique experimental techniques to characterize molecular motions on a time scale between 10^{-14} and 10^{-8} s. The continued development of high resolution inelastic scattering techniques in the past two decades (157–159) enables measurement of the dynamic structure factor $S(Q, \omega)$ and the intermediate scattering function $S(Q, t)$ in the typical Q (momentum transfer) range of $0.01 \text{ nm}^{-1} < Q < 0.5 \text{ nm}^{-1}$, suitable for the study of the local segmental motion in polymers. $S(Q, t)$ is related to the density–density correlation function. The advantage of quasi-elastic neutron scattering (QENS) is the information on the Q -dependence. Also partial replacement of hydrogen atoms by deuterons in the repeat units of the polymer let the experimenter select the location of the motion to be studied by the technique. The disadvantage is the presence of scattering by anharmonic vibrations and faster processes, which make the extraction of the part of the data related to local segmental relaxation difficult. Consequently, at present interpretation of QENS data is unclear and controversial, and is not discussed here.

Enthalpy and Heat Capacity Relaxation. The conventional techniques based on differential scanning calorimetry by which enthalpy relaxation is measured at different cooling and heating rates is discussed elsewhere in the encyclopedia by others. Extensive review of the subject can be found in Reference 160. Measurements of heat capacity and entropy of polymers as a function of temperature are well documented and the data can be found in Reference 161. Frequency-dependent heat capacity spectroscopy has been developed (162,163) and application to study the local segmental dynamics of polymers has been made (163).

Positronium Annihilation Lifetime Spectroscopy. Positron annihilation lifetime spectroscopy (pals) is primarily viewed as technique to parameterize the unoccupied volume, or so-called free volume, of amorphous polymers. *In vacuo*, the ortho-positronium (o-Ps) has a well-defined lifetime τ_3 of 142 ns. This lifetime is cut short when o-Ps is embedded in condensed matter via the “pick-off” mechanism whereby o-Ps prematurely annihilates with one of the surrounding bound electrons. The quantum mechanical probability of o-Ps “pick-off” annihilation depends on the electron density of the medium, or the size of the heterogeneity. Typically the heterogeneity is assumed to be a spherical “cavity” (164,165) so that τ_3 can be easily related to an average radius R ($R_0 = R + \Delta R$) of the nanopore:

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right] \quad (36)$$

Novel studies on zeolites (165–167) confirm the validity of this approach and find ΔR , the o-Ps penetration depth into the electron cloud surrounding the cavity, to be nearly constant ($\Delta R \approx 0.161 \text{ nm}$). For amorphous polymers, it is understood that spherical nanopores are a first-order approximation at best. Nevertheless, pals is widely used for the structural characterization of the unoccupied volume in glassy materials. There are many works on pals studies of amorphous polymers. Only some of the more recent works are cited here (168–170).

Pressure Dependence of Polymer Dynamics. Pressure is one of the essential thermodynamic variables that control the structure and the associated dynamics of polymers and glass-forming systems. The pressure dependence of the viscoelastic relaxation times is of paramount importance because hydrostatic pressure is encountered in polymer processing. Dielectric spectroscopy was among the first dynamic techniques to take advantage of pressure through the recognition of the fact that the dynamic state of a glass-forming system can only be completely defined if T and P are specified. This observation motivated studies of the effect of pressure on the dielectric α - and β -processes in a number of systems in the early 1960s (171–174). The main concern in these pioneering studies was to unravel the effect of pressure on separating mixed processes.

However, since then and until only recently, the lack of a versatile experimental setup has put a halt in these studies and made pressure, for a number of years, the “forgotten” variable. During the past 20 years, polymer chemistry has produced an unparalleled number of polymeric compounds with unmatched physical properties ranging from polymer blends with a well-defined thermodynamic state to block copolymers with well-controlled nanostructures. Moreover, the interest in traditional fields such as polymer crystallization has been rejuvenated through the possibility of new experimental probes and novel synthesis. Pressure, however, was not applied up until recently in systems where the thermodynamic state of the system is of importance.

Herein an example of current interest is provided, where the thermodynamic state of the system play a dominant role in polymer dynamics. The example consists of studying the effect of pressure on the local and global chain dynamics (175,176).

The effect of pressure on the local segmental dynamics and on sub- T_g relaxations has been studied in detail (172–174). It was found that pressure exerts a stronger influence on the segmental as compared to the local sub- T_g relaxations and is the right variable if a separation of the two modes is needed. On the other hand, the effect of pressure on the global chain dynamics that control the flow regime and thus of interest in polymer processing only recently has started to be explored.

Herein the results of recent studies (175,176) are reviewed, treating the effect of pressure on the segmental and chain dynamics as a function of polymer molecular weight. The polymer is PI, which has been extensively studied before as a function of temperature for different molecular weights. Being a Type-A polymer (according to Stockmayers classification) it has components of the dipole moment both parallel and perpendicular to the chain, giving rise, respectively, to end-to-end vector and local segmental dynamics. The aim is to investigate the effect of P on M_e . This question is not only of fundamental importance but has industrial implications as well (ie, in polymer processing). For this purpose five *cis*-PIs have been used: PI-1200, PI-2500, PI-3500, PI-10600, and PI-26000, with the numbers indicating number-average molecular weights and with polydispersity of less than 1.1. The entanglement molecular weight of PI is 5400; thus the first three samples are not entangled.

The molecular weight dependence of the segmental and longest normal modes are shown in Figure 31 in the different samples as a function of pressure, at 320 K. Notice that the segmental modes (through the higher apparent

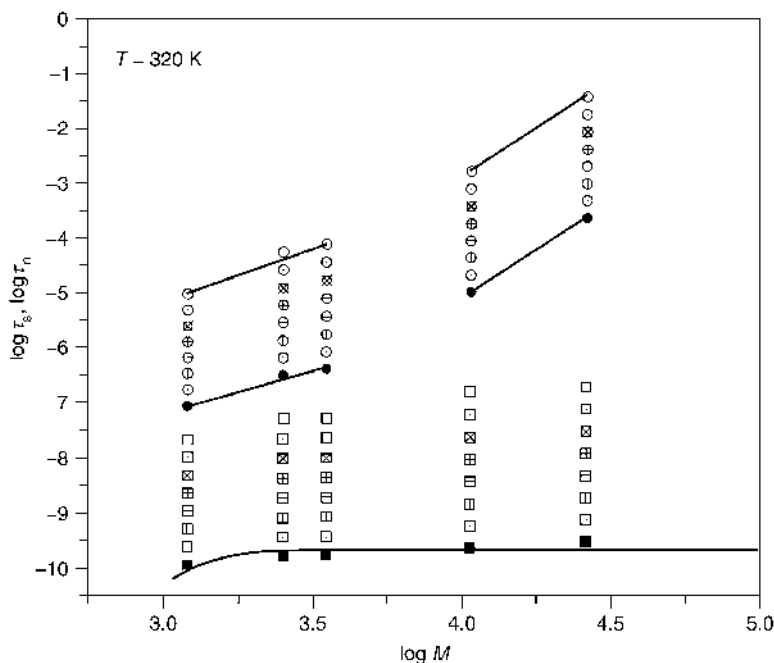


Fig. 31. Molecular weight dependence of the segmental ($\square$) and longest normal mode ($\circ$) for the five PIs investigated, plotted for different pressures at 320 K. The shortest time corresponds to the data at 1 bar and the rest are interpolated data shown at intervals of 0.5 kbar. The line through the segmental times at atmospheric pressure is a guide for the eye.

activation volume) exhibit a stronger P -dependence than the corresponding normal modes. At any given P , the longest normal mode times exhibit a weak molecular weight dependence for $M < M_e$ ($\tau \sim M^2$) and a stronger dependence for $M > M_e$ ($\tau \sim M^{3.4}$). Notice the additional molecular weight dependence for the smaller molecular weights due to chain-end effects. Nevertheless, increasing pressure does not change significantly the picture from atmospheric pressure and this signifies that there is a minor, if any, dependence of M_e on P .

The main results can be summarized as follows. The spectral shape of the normal modes and of the segmental mode is invariant under variation of T and P . However, both time-temperature superposition and time-pressure superposition of the entire spectrum fails because of the higher sensitivity of the segmental mode to T and P variations, respectively. The former has been discussed in earlier sections (71,72,79,126,128). The latter results from the higher activation volume for the segmental mode. The activation volume of the segmental mode for the different molecular weights exhibits a strong T -dependence and scales as $T - T_g$. Lastly, M_e does not show a significant P -dependence.

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ANIONIC POLYMERIZATION

Introduction

This article describes the general aspects of anionic polymerization of vinyl, carbonyl, and heterocyclic monomers. Polymerizations involving multicomponent catalyst systems (coordinated anionic polymerization) are not discussed. Anionic polymerization is a chain reaction polymerization in which the active species is formally an anion, ie, an atom or group with a negative charge and an unshared pair of electrons. Anions can be considered to be the conjugate bases of the corresponding acids, as shown in the following equation. The stability and reactivity of anionic species can be deduced from pK_a values for the equilibria depicted in this equation for the corresponding conjugate acid. The more acidic conjugate acids (lower pK_a values) are associated with a correspondingly more stable anionic species.



In general, these anions are associated with a counterion, typically an alkali metal cation. The exact nature of the anion can be quite varied depending on the structure of the anion, counterion, solvent, and temperature. The range of possible species is depicted in terms of a Winstein spectrum of structures as shown in equation 2 for a carbanionic chain end (R^-). In addition to the aggregated (1) and unassociated (2) species, it is necessary to consider the intervention of free ions (5) and the contact (3) and solvent-separated (4) ion pairs; Mt^+ represents a metallic counterion such as an alkali metal cation (1). In hydrocarbon media, species (1–3) would be expected to predominate. Polar solvents tend to shift the Winstein spectrum to the right, ie, toward more reactive, less associated, more ionic species. With respect to the nature of the bonding in organoalkali metal compounds, it is generally agreed that the carbon–alkali metal bond is ionic for sodium, potassium, rubidium, and cesium. For carbon–lithium bonds, however, there is disagreement regarding the relative amount of covalent versus ionic bonding (1–3). One unique aspect of anionic polymerization is that the reactive propagating species are not transient intermediates. Carbanions and organometallic species can be prepared and investigated independently of the polymerization process. These species can also be characterized during the polymerization.

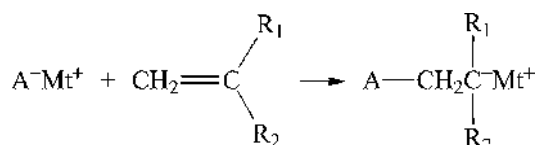


Living Anionic Polymerization

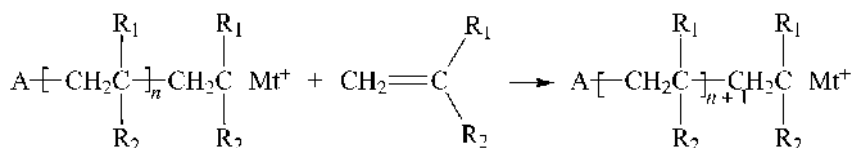
A *living polymerization* is a chain polymerization that proceeds in the absence of the kinetic steps of termination and chain transfer (4,5). For living anionic polymerization of vinyl monomers, the propagating species is a carbanion associated with the corresponding counterion, as shown in the scheme below. Living

polymerizations provide versatile methodologies for the preparation of macromolecules with well-defined structures and low degrees of compositional heterogeneity. Using these methodologies it is possible to synthesize macromolecular compounds with control of a wide range of compositional and structural parameters including molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, branching, and chain-end functionality. Anionic polymerization is the archetype of a living polymerization and it embodies the following defining characteristics of living polymerizations (6).

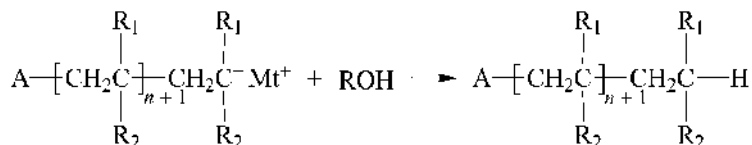
(1) *Initiation*



(2) *Propagation*



(3) *Deliberate termination* (no spontaneous termination)



Molecular Weight. The number-average molecular weight (M_n) in living anionic polymerization is a simple function of the stoichiometry and the degree of conversion of the reaction since one polymer is formed for each initiator molecule. The expected number-average molecular weight can be calculated, as shown in equation 3, as a function of conversion.

$$M_n = \text{grams of monomer consumed / moles of initiator} \quad (3)$$

From a practical point of view, polymers can be prepared with predictable molecular weights ranging from $\approx 10^3$ to $> 10^6$ g/mol using living anionic polymerizations. The ability to predict and control molecular weight depends critically on the absence of significant amounts of terminating species that react with the initiator, decrease the effective number of molecules of initiator, and thus increase the observed molecular weight relative to the calculated molecular weight.

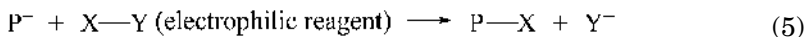
Molecular Weight Distribution. In principle, it is possible to prepare a polymer with a narrow molecular weight distribution (Poisson distribution) by using living polymerization when the rate of initiation is competitive with or faster than the rate of propagation (5,7). This condition ensures that all of the chains grow for essentially the same period of time. The relationship between the polydispersity and the degree of polymerization for a living polymerization is shown in equation 4:

$$X_w/X_n = 1 + [X_n/(X_n + 1)^2] \approx 1 + (1/X_n) \quad (4)$$

The second approximation is valid for high molecular weights. The Poisson distribution represents the ideal limit for termination-free polymerizations. Thus, it is predicted that the molecular weight distribution will become narrower with increasing molecular weight for a living polymerization system. Broader molecular weight distributions are obtained using less active initiators, with mixtures of initiators or with continuous addition of initiator as involved in a continuous flow, stirred tank reactor. Thus, living polymerizations can form polymers with broader molecular weight distributions. It has been proposed that a narrow molecular weight distribution (monodisperse) polymer should exhibit $M_w/M_n \leq 1.1$ (8).

Block Copolymers. One of the important aspects of living polymerizations is that since all chains retain their active centers when the monomer has been consumed, addition of a second monomer will form a diblock copolymer (9–11). Sequential addition of monomer charges can generate diblocks such as A–B, triblocks such as A–B–A, A–B–C, and even more complex multiblock structures. In principle, each block can be prepared with controlled molecular weight and narrow molecular weight distribution.

Chain-End Functionalized Polymers. In principle, the propagating carbanionic center that remains at the end of the polymerization can react with a variety of electrophilic species to incorporate functional groups (–X) at the chain end, as shown in equation 5 (12–14):

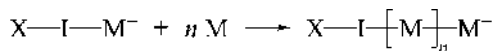
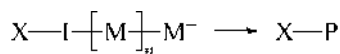


Methods have been reported and tabulated for the synthesis of a diverse array of functional end groups.

An alternative methodology for the synthesis of functionalized polymers using living anionic polymerization is the use of functionalized initiators (15,16). If a functional group (or a suitably protected functional group) is incorporated into the initiator, then that functional group will be at the initiating end of every polymer molecule, as shown below:

(1) *Initiation*



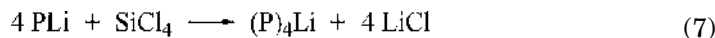
(2) *Propagation*(3) *Termination*

where X is the functional group in the initiating species X—I[−] and X—P is the α-functionalized polymer. In principle, this method can quantitatively produce functionalized polymers with controlled molecular weights and narrow molecular weight distributions.

Star-Branched Polymers. An extension of the concept of controlled termination reactions is the ability to prepare star-branched polymers by post-polymerization reactions with multifunctional linking reagents as shown in equation 6, where L is a linking agent of functionality *n* (17–20):



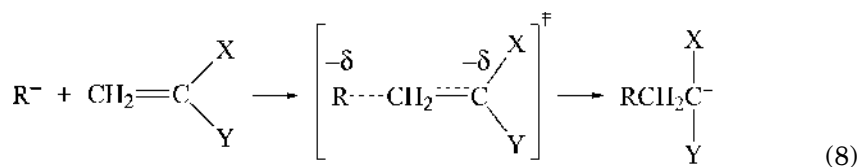
For example, termination of a living anionic polymerization with a tetrafunctional electrophile such as silicon tetrachloride will produce a four-armed star polymer as shown in equation 7. Given that PLi is a well-defined living polymer, a branched polymer with a predictable, well-defined structure will be formed from the linking reaction.



A variety of linking agents with variable functionalities have been described and tabulated in the literature (11,18,19).

General Considerations

Monomers. Two broad types of monomers can be polymerized anionically: vinyl, diene, and carbonyl-type monomers with difunctionality provided by one or more double bonds; and cyclic (eg, heterocyclic) monomers with difunctionality provided by a ring that can open by reaction with nucleophiles. For vinyl monomers, there must be substituents on the double bond that can stabilize the negative charge that develops in the transition state for monomer addition, as shown in equation 8:



These substituents must also be stable to the anionic chain ends; thus, relatively acidic, proton-donating groups (eg, amino, hydroxyl, carboxyl, acetylene functional groups) or strongly electrophilic functional groups that can react with bases and nucleophiles must not be present or must be protected by conversion to a suitable derivative. In general, substituents that stabilize the negative charge by anionic charge delocalization render vinyl monomers polymerizable by an anionic mechanism. Such substituents include aromatic rings, double bonds, as well as carbonyl, ester, cyano, sulfoxide, sulfone, and nitro groups. The general types of monomers that can be polymerized anionically without the incursion of termination and chain-transfer reactions include styrenes, dienes, methacrylates, vinylpyridines, aldehydes, epoxides, episulfides, cyclic siloxanes, lactones, and lactams. Monomers with polar substituents such as carbonyl, cyano, and nitro groups often undergo side reactions with initiators and propagating anions; therefore, controlled anionic polymerization to provide high molecular weight polymers is generally not possible. Many types of polar monomers can be polymerized anionically, but do not produce living, stable, carbanionic chain ends. These types of polar monomers include acrylonitriles, cyanoacrylates, propylene oxide, vinyl ketones, acrolein, vinyl sulfones, vinyl sulfoxides, vinyl silanes, halogenated monomers, ketenes, nitroalkenes, and isocyanates.

The simplest vinyl monomer, ethylene, although it has no stabilizing moiety, can be polymerized by an anionic mechanism using butyllithium complexed with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as a complexing ligand. The conversion of a double bond to two single bonds provides the energetic driving force for this reaction. Because of the insolubility of the crystalline, high density polyethylene formed by anionic polymerization, the polymer precipitates from solution during the polymerization.

Solvents. The choice of suitable solvents for anionic polymerization is determined in part by the reactivity (basicity and nucleophilicity) of initiators and propagating anionic chain ends. For styrene and diene monomers, the solvents of choice are alkanes and cycloalkanes, aromatic hydrocarbons, and ethers; the use of alkenes has also been described, although chain transfer can occur. Aromatic hydrocarbon solvents provide enhanced rates of initiation and propagation relative to the alkanes; however, chain transfer reactions can occur with alkylated aromatic solvents, eg, toluene.

Polar solvents such as ethers and amines react with organometallic initiators, as well as propagating polystyryl and polydienyl carbanions, to decrease the concentration of active centers (21–23). The rate of reaction with ethers decreases in the order $\text{Li} > \text{Na} > \text{K}$. For example, dilute solutions of poly(styryl)lithium in tetrahydrofuran (THF) at room temperature decompose at the rate of a few percent each minute. Alkylolithium initiators also react relatively rapidly with ethers; the order of reactivity of organolithium compounds with ethers is tertiary $\text{RLi} >$ secondary $\text{RLi} >$ primary $\text{RLi} >$ phenyllithium $>$ methyllithium $>$ benzylolithium (21). An approximate order of reactivity of ethers toward alkylolithium compounds is dimethoxyethane, $\text{THF} >$ tetrahydropyran $>$ diethyl ether $>$ diisopropyl ether. Tertiary amines can also react with alkylolithium compounds. The importance of these reactions can be minimized by working at lower temperatures (eg, $<0^\circ\text{C}$); it is also advisable to use only the minimum amounts of ethers and other Lewis bases required as additives.

For less reactive anionic chain ends such as those involved in the propagation of heterocyclic monomers, a wider range of solvents can be utilized. For example, dipolar aprotic solvents such as dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and hexamethylphosphoramide (HMPA) can be used for polymerizations of epoxides.

Initiation

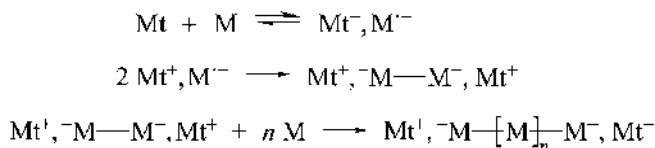
A useful guide to choose an appropriate initiator for anionic polymerization of a given monomer is that the initiator should have a reactivity (stability) similar to that of the propagating anionic species (23,24). If the initiator is too reactive, then side reactions are promoted. If the initiator is relatively unreactive, the initiation reaction may be slow or inefficient.

The stabilities of anionic initiators can be deduced from the pK_a values of the corresponding conjugate acids as shown in equation 1 (25). Monomer reactivity in anionic polymerization can be categorized in terms of the stability of the anions formed by nucleophilic addition or ring opening as deduced from the pK_a values for the conjugate acids of these anions. Thus, those monomers that form the least stable anions, ie, have the largest values of pK_a for the corresponding conjugate acids, are the least reactive monomers in anionic polymerization; in turn, these less reactive monomers require the use of the most reactive, organometallic initiators as shown in Table 1. Initiators can be classified in terms of their mechanisms of initiation: (1) initiation by electron transfer (alkali and alkaline-earth metals and radical anions) and (2) nucleophilic addition. The following sections discuss each of these initiator types.

Initiation by Electron Transfer.

Alkali Metals. The direct use of alkali metals and alkaline-earth metals as initiators for anionic polymerization of diene monomers as first reported in 1910 is primarily of historical interest because these are uncontrolled, heterogeneous processes (4). One of the most significant developments in anionic vinyl polymerization was the discovery reported in 1956 by Stavely and co-workers (26) at Firestone Tire and Rubber Co. that polymerization of neat isoprene with lithium dispersion produced high *cis*-1,4-polyisoprene, similar in structure and properties to *Hevea* natural rubber. This discovery led to the development of commercial anionic solution polymerization processes using alkyllithium initiators.

The mechanism of the anionic polymerization of styrenes and 1,3-dienes initiated by alkali metals has been described in detail (27). Initiation is a heterogeneous process occurring on the surface of the metal (Mt) by reversible transfer of an electron to adsorbed monomer (M), as shown in the following scheme:



The initially formed radical anions ($\text{M}^{\bullet -}$) rapidly dimerize to form dianions. Monomer addition to these dianions forms adsorbed oligomers that desorb and

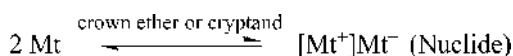
Table 1. Relationships between Monomer Reactivity, Carbanion Stability, and Suitable Initiators^{a, b}

Monomer type	pK _a		Initiators ^c
	DMSO	H ₂ O	
Ethylene	56		RLi
Dienes	44		NH ₂ ⁻ , RLi, RMt
Styrenes	43		Naphthalene radical anions ^d , cumyl K, Mt
Acrylonitrile	32		RMgX
Alkyl methacrylates	30–31	27–28	Fluorenyl ⁻ , Ar ₂ RC ⁻ , ketyl radical anions ^e
Vinyl ketones	26	19	
Oxiranes	29–32	16–18	RO ⁻
Thiiranes	17	12–13	
Nitroalkenes	17	10–14	
Siloxanes		10–14	RO ⁻ , OH ⁻
Lactones	12	4–5	RCO ₂ ⁻
Cyanoacrylates	11		HCO ₃ ⁻ , H ₂ O
Vinylidene cyanide	11	11	

^aRef. 24.^bpK_a of the conjugate acid of the anionic propagating intermediate.^cMt refers generally to alkali metals (Li, Na, K, Rb, Cs).^dFor example, naphthalene radical anion^{•-} Li⁺/Na⁺/K⁺.^eAr₂CO^{•-}.

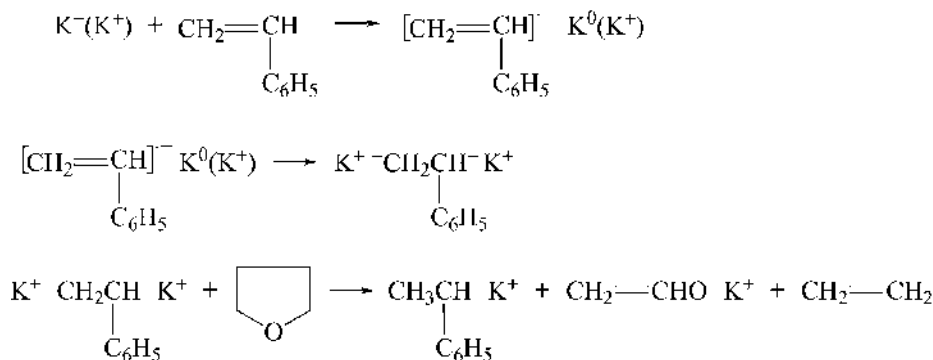
continue chain growth in solution. Unlike homogeneous anionic initiation processes with organometallic compounds, this heterogeneous initiation reaction continues to generate new active chain ends during the course of the subsequent propagation reactions. Consequently, there is little control of molecular weight, and relatively broad molecular weight distributions have been reported for the soluble polymer obtained from these bulk polymerizations ($M_w/M_n = 3\text{--}10$) (28); formation of a high degree of branching and gel content (45%) have also been reported for these processes (26,28).

Alkali metals can dissolve in solvating media such as ethers and amines to form blue solutions of solvated electrons. In the presence of strongly complexing ligands such as crown ethers or cryptands, electriles (complexed alkali cation and electron) or nuclides (complexed alkali cation and alkali metal anion) can be formed as shown below (29):



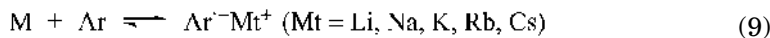
Nuclides have been shown to react with monomers such as styrene and methyl methacrylate to form intermediate dianions that are rapidly protonated by the

solvent THF to form the monoanion initiating species, as shown below (30,31):

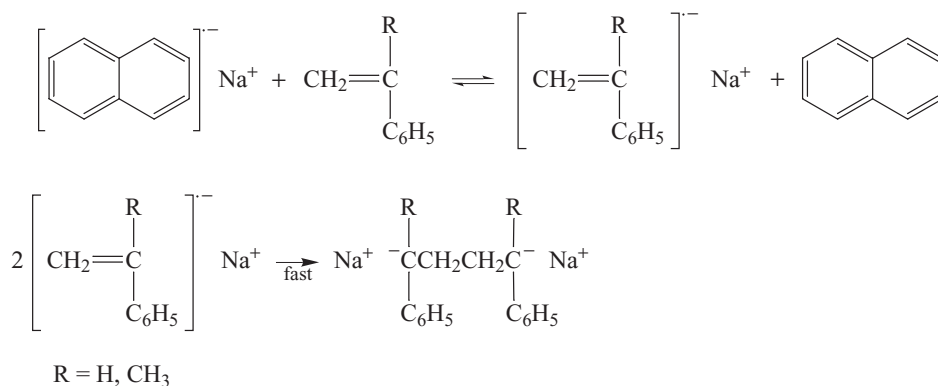


For the nuclide-initiated polymerization of methyl methacrylate, although there was good agreement between calculated and observed molecular weights, the molecular weight distributions were broad ($M_w/M_n = 1.2\text{--}1.6$) (31).

Radical Anions. Many aromatic hydrocarbons react reversibly with alkali metals in polar aprotic solvents to form stable, homogeneous solutions of the corresponding radical anions, as shown in equation 9 (4,27).



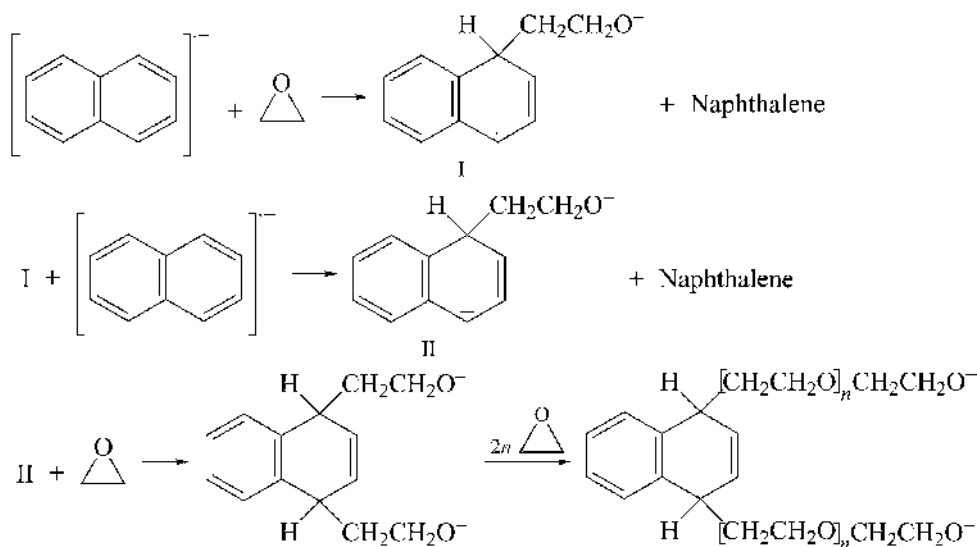
Radical anions can only be formed efficiently in polar aprotic solvents such as THF and glymes. Aromatic radical anions such as sodium naphthalene react with monomers such as styrene by reversible electron transfer to form the corresponding monomer radical anions, as shown in the following scheme ($\text{R} = \text{H}$):



Although the equilibrium between the radical anion of the monomer and the aromatic radical anion lies far to the left because of the low electron affinity of the monomer, this is an efficient initiation process because the resulting monomer radical anions rapidly undergo tail-to-tail dimerization reactions with rate constants that approach diffusion control.

The reactions of monomers with aromatic radical anions or directly with alkali metals can be used to prepare oligomeric dianionic initiators from monomers such as α -methylstyrene that have accessible ceiling temperatures ($T_c = 61^\circ\text{C}$) (32), as shown in the above scheme ($R = \text{CH}_3$). Dimers or tetramers can be formed depending on the alkali metal system, temperature, and concentration.

Monomers that can be polymerized with aromatic radical anions include styrenes, dienes, epoxides, and cyclosiloxanes. For epoxides and cyclosiloxanes, the mechanism of initiation involves nucleophilic addition of the radical anion to these monomers, as shown below, in contrast to the electron transfer mechanism occurring for hydrocarbon monomers (see previous scheme).



Initiation by Nucleophilic Addition.

Alkylolithium Compounds. Although anionic polymerization of vinyl monomers can be effected with a variety of organometallic compounds, alkyl-lithium compounds are the most useful class of initiators (1,21,24,33). A variety of simple alkylolithium compounds are readily available commercially in hydrocarbon solvents such as hexane and cyclohexane. They can be prepared by reaction of the corresponding alkyl chlorides with lithium metal.

Alkylolithium compounds are generally associated into dimers, tetramers, or hexamers in hydrocarbon solution (2,21). The degree of association is related to the steric requirements of the alkyl group; ie, the degree of association decreases as the steric requirements of the alkyl group increase.

The relative reactivities of alkylolithiums as polymerization initiators are intimately linked to their degree of association, as shown below, with the average degree of association in hydrocarbon solution, where known, indicated in brackets after the alkylolithium (2,23,33):

(1) *Styrene polymerization*: Menthylolithium [2] > *s*-C₄H₉Li [4] > *i*-C₃H₇Li [4–6] > *i*-C₄H₉Li > *n*-C₄H₉Li [6] > *t*-C₄H₉Li [4]

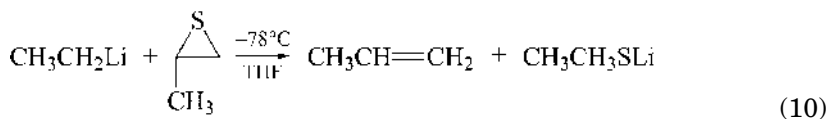
(2) *Diene polymerization*: Menthylolithium [2] > *s*-C₄H₉Li [4] > *i*-C₃H₇Li [4–6] > *t*-C₄H₉Li [4] > *i*-C₄H₉Li > *n*-C₄H₉Li [6]

In general, the less associated alkylolithiums are more reactive as initiators than the more highly associated species.

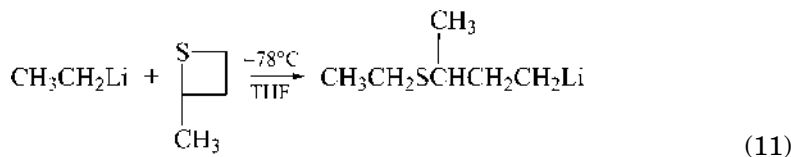
Alkylolithium initiators are primarily used as initiators for polymerizations of styrenes and dienes (see Table 1). They effect quantitative, living polymerization of styrenes and dienes in hydrocarbon solution. In general, these alkylolithium initiators are too reactive for alkyl methacrylates and vinylpyridines (see Table 1). *n*-Butyllithium is used commercially to initiate anionic homopolymerization and copolymerization of butadiene, isoprene, and styrene with linear and branched structures. Because of its high degree of association (hexameric), *n*-butyllithium-initiated polymerizations are often effected at elevated temperatures (>50°C) to increase the rate of initiation relative to propagation and thus to obtain polymers with narrower molecular weight distributions (34).

sec-Butyllithium is used commercially to prepare styrene–diene block copolymers because it can initiate styrene polymerization rapidly as compared to propagation so that even polystyrene blocks with relatively low molecular weights (10,000–15,000 g/mol) can be prepared with stoichiometric control and narrow molecular weight distributions.

Alkylolithiums react quite differently with cyclic sulfides compared to the normal nucleophilic ring-opening reaction with epoxides (35,36). Ethyllithium reacts with 2-methylthiacyclopropane to generate propylene and lithium ethanethiolate. The resulting lithium ethanethiolate is capable of initiating polymerization of 2-methylthiacyclopropane.



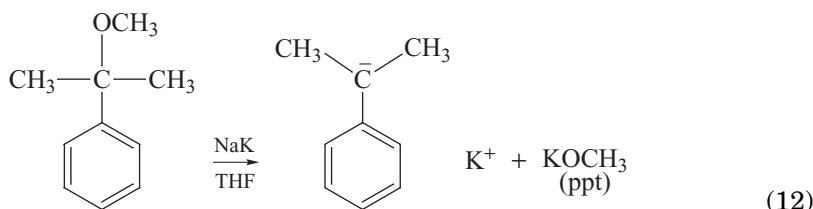
In contrast, ethyllithium reacts with 2-methylthiacyclobutane to form an alkyl-lithium product that is capable of initiating polymerization of styrene.



Organoalkali Initiators. In general, the simple organoalkali metal derivatives other than lithium are not soluble in hydrocarbon media. However, higher homologues of branched hydrocarbons are soluble in hydrocarbon media. The reaction of 2-ethylhexyl chloride and sodium metal in heptane produces soluble

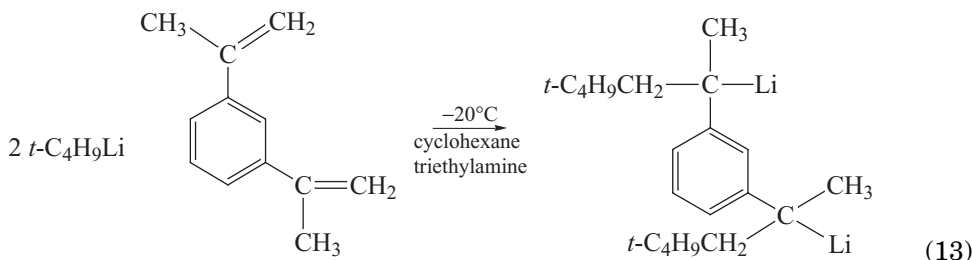
2-ethylhexylsodium (37). This initiator copolymerizes mixtures of styrene and butadiene to form styrene—butadiene copolymers with high (55–60%) vinyl microstructure (38,39).

Cumyl potassium ($pK_a \approx 43$ based on toluene) is a useful initiator for anionic polymerization of a variety of monomers, including styrenes, dienes, methacrylates, and epoxides. This carbanion is readily prepared from cumyl methyl ether, as shown in equation 12, and is generally used at low temperatures in polar solvents such as THF.



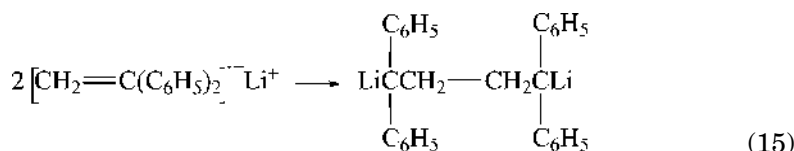
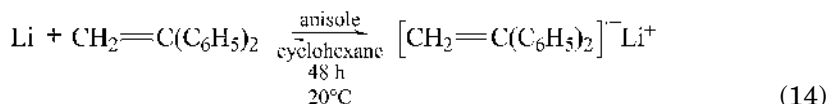
Difunctional Initiators. Aromatic radical anions, such as lithium naphthalene or sodium naphthalene, are efficient difunctional initiators (see scheme under Radical Anions). However, the need to use polar solvents for their formation limits their utility for diene polymerization since the unique ability of lithium to provide high 1,4-polydiene microstructure is lost in polar media. The methodology for preparation of hydrocarbon-soluble, dilithium initiators is generally based on the reaction of an aromatic divinyl precursor with 2 moles of butyllithium. Unfortunately, because of the tendency of organolithium chain ends in hydrocarbon solution to associate and form electron-deficient dimeric, tetrameric, or hexameric aggregates, most attempts to prepare dilithium initiators in hydrocarbon media have generally resulted in the formation of insoluble, three-dimensionally associated species (40).

The reaction of *m*-diisoprenylbenzene with 2 moles of *t*-butyllithium in the presence of 1 equiv of triethylamine in cyclohexane at -20°C has been reported to form pure diadduct without oligomerization (eq. 13) (41). This initiator in the presence of 5 vol% of diethyl ether for the butadiene block has been used to prepare well-defined poly(methyl methacrylate)-*block*-polybutadiene-*block*-poly(methyl methacrylate).

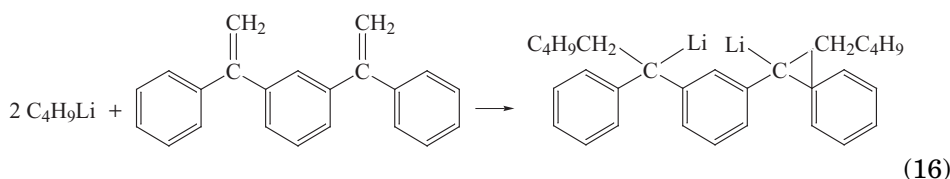


The reaction of pure *m*-divinylbenzene with *sec*-butyllithium in toluene at -49°C in the presence of triethylamine ($[(\text{C}_2\text{H}_5)_3\text{N}]/[\text{Li}] = 0.1$) has been reported to produce the corresponding dilithium initiator in quantitative yield (42). Polymerization of butadiene with this initiator in toluene at -78°C produced well-defined polybutadiene with high 1,4-microstructure (87%).

A useful, hydrocarbon-soluble, dilithium initiator has been prepared by the dimerization of 1,1-diphenylethylene with lithium in cyclohexane in the presence of anisole (15 vol%) as shown in equations 14 and 15 (43). Although the initiator was soluble in this mixture, it precipitated from solution when added to the polymerization solvent (cyclohexane or benzene). Therefore, the dilithium initiator was chain extended with approximately 30 units of isoprene to generate the corresponding soluble oligomer. This initiator was used to prepare well-defined polystyrene-*block*-polyisoprene-*block*-polystyrene and poly(α -methylstyrene)-*block*-polyisoprene-*block*-poly(α -methylstyrene) triblock copolymers with $>90\%$ 1,4-microstructure by sequential monomer addition.



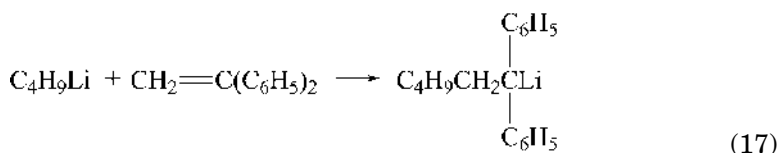
The addition reaction of 2 mol of *sec*-butyllithium with 1,3-bis(1-phenylethenyl)benzene (eq. 16) proceeds rapidly and efficiently to produce the corresponding dilithium species that is soluble in toluene or in cyclohexane (24,44). Although this dilithium initiator is useful for the preparation of homopolymers and triblock copolymers with relatively narrow molecular weight distributions, it is necessary to add a small amount of Lewis base or ≥ 2 equiv of lithium alkoxide (eg, lithium *sec*-butoxide) to produce narrow, monomodal molecular weight distributions.



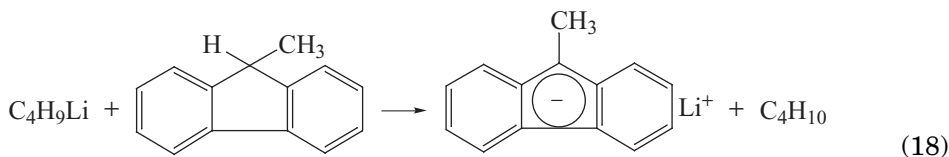
Functionalized Initiators. Alkylolithium initiators that contain functional groups provide versatile methods for the preparation of end-functionalized polymers and macromonomers (15,16). For a living anionic polymerization, each functionalized initiator molecule will produce one macromolecule, with the functional group from the initiator residue at one chain end and the active anionic propagating species at the other chain end. However, many

functional groups such as hydroxyl, carboxyl, phenol, and primary amine are not stable in the presence of reactive dienyllithium and styryllithium chain ends. Therefore, it is necessary to convert these functional groups into suitable derivatives, ie, protected groups, that are stable to the carbanionic chain ends and that can be removed readily after the polymerization. Examples of protected functional initiators include the hydroxyl-protected initiators, 1-lithium-6-(1-ethoxyethoxy)hexane, 6-(*t*-butyldimethylsiloxy)hexyllithium, and 3-(*t*-butyldimethylsiloxy)propyllithium, as well as a primary amine-protected initiator, 4-*bis*(trimethylsilyl)aminophenyllithium (45).

1,1-Diphenylmethylcarbanions. The carbanions based on diphenylmethane ($pK_a = 32$) (see Table 1) are useful initiators for vinyl and heterocyclic monomers, especially alkyl methacrylates at low temperatures (46). 1,1-Diphenylalkyllithiums can also efficiently initiate the polymerization of styrene and diene monomers that form less stable carbanions. Diphenylmethyl-lithium can be prepared by the metalation reaction of diphenylmethane with butyllithium or by the addition of butyllithium to 1,1-diphenylethylene, as shown in equation 17. This reaction can also be utilized to prepare functionalized initiators by reacting butyllithium with a substituted 1,1-diphenylethylene derivative. Addition of lithium salts such as lithium chloride, lithium *t*-butoxide, or lithium 2-(2-methoxyethoxy)ethoxide with 1,1-diphenylmethylcarbanions and other organolithium initiators has been shown to narrow the molecular weight distribution and to improve the stability of active centers for anionic polymerization of both alkyl methacrylates and *t*-butyl acrylate (47,48).



Fluorenyl Carbanions. Salts of fluorene ($pK_a \approx 23$) are more hindered and less reactive than many other organometallic initiators. Fluorenyl carbanions can be readily formed by metalation of fluorenes with alkali metal derivatives, as shown in equation 18. Carbanion salts of 9-methylfluorene are preferable to fluorene, since the latter generate chain ends that contain reactive, acidic fluorenyl hydrogens that can participate in chain transfer reactions. Fluorenyl salts are useful initiators for the polymerization of alkyl methacrylates, epoxide, and thiirane monomers.



Styrene and Diene Monomers

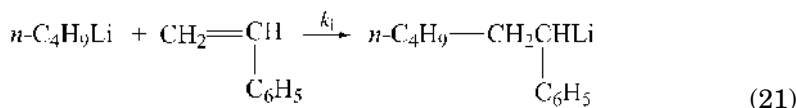
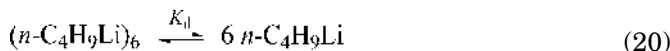
Kinetics of Polymerization.

Initiation Kinetics. The mechanism of initiation of anionic polymerization of vinyl monomers with alkyllithium compounds and other organometallic compounds is complicated by association and cross-association phenomena in hydrocarbon solvents and by the presence of a variety of ionic species in polar media (4,27,33,49). The kinetics of initiation are complicated by competing propagation and the occurrence of cross-association of the alkyllithium initiator with the propagating organolithium (50). Thus, only the initial rates provide reliable kinetic data.

Typical kinetics of the initiation reaction of *n*-butyllithium with styrene in benzene exhibit a first-order dependence on styrene concentration and approximately a one-sixth-order dependence on *n*-butyllithium concentration, as shown in equation 19.

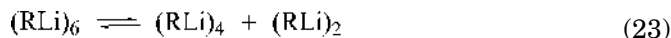
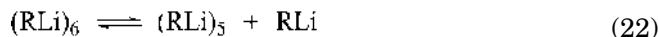
$$R_i = k_i(K_d/6)^{1/6}[\text{C}_4\text{H}_9\text{Li}]_0^{1/6}[\text{M}] \quad (19)$$

Since *n*-butyllithium is aggregated predominantly into hexamers in hydrocarbon solution, the fractional kinetic order dependency of the initiation process on the total concentration of initiator has been rationalized on the basis that unassociated *n*-butyllithium is the initiating species and that it is formed by the equilibrium dissociation of the hexamer as shown below:



The kinetic order for *sec*-butyllithium-initiated polymerization of styrene is close to 0.25 in benzene solution; this result is also consistent with initiation by unassociated *sec*-butyllithium, since *sec*-butyllithium is associated predominantly into tetramers in benzene solution.

The frequent coincidence of the fractional order with the degree of association supports the postulate that the initiating species is a small amount of reactive monomeric alkyllithium in equilibrium with the much larger concentration of the unreactive aggregated species. However, the correctness of this interpretation, ie, direct dissociation to monomeric, unassociated species, has been questioned (33). The experimentally observed energies of activation, eg, 75 kJ/mol (18 kcal/mol) for *n*-butyllithium initiation of styrene polymerization (51), appear to be too low to include the enthalpy of complete dissociation of the aggregates, which is estimated to require approximately 452 kJ/mol (108 kcal/mol) (52). An alternative is the incomplete or stepwise dissociation of the aggregate, for example, as shown in equations 22–25 for hexamers; equation 25 plus equation 24 would apply for tetramers.



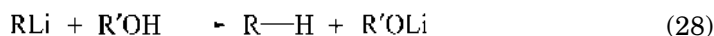
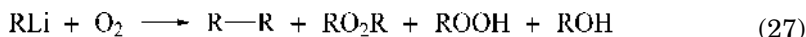
In aliphatic solvents the inverse correspondence between reaction order dependence for alkyllithium and degree of organolithium aggregation is not observed (49). In addition, the rates of initiation in aliphatic solvents are several orders of magnitude less than in aromatic solvents. Most reaction orders for alkyl-lithium initiators in aliphatic solvents are close to unity. These results suggest that in aliphatic solvents the initiation process may involve the direct addition of monomer with aggregated organolithium species (eq. 26) to form a cross-associated species.



The formation of cross-associated species would be expected to complicate the kinetics and lead to variable reaction orders as a function of conversion. The observation of pronounced induction periods has been ascribed to the enhanced reactivity of the mixed (ie, cross-associated) aggregated species. The effects of cross-association provide at least a partial explanation for the discrepancies reported in the literature for the kinetic order dependencies on alkyllithium initiator concentration; thus, only in the initial stages is it likely that a detailed interpretation of the mechanism is possible.

Lewis bases and alkali metal alkoxides have been used as additives to modify the initiation reaction with alkyllithium compounds. In the presence of THF, the initiation reaction kinetics of styrene with *sec*-butyllithium exhibit a first-order dependence on alkyllithium concentration. Lewis bases such as ethers and amines, when present in amounts comparable to the initiator concentration, dramatically increase the relative rate of initiation of styrene and diene polymerizations relative to propagation.

The effect of lithium alkoxides on alkyllithium-initiated polymerizations is important because these salts are ubiquitously present to some extent as impurities formed by the reactions with oxygen (13) (eq. 27) and hydroxylic impurities (eq. 28). In fact, it is common practice to utilize excess butyllithium, ie, more than the stoichiometric amount required to generate the required molecular weight, to scavenge impurities in the solvent and monomer feed.



The effects of lithium alkoxides on the rates of alkyllithium-initiation reactions depend on the solvent, the monomer, the alkoxide structure, the alkyllithium initiator, and the ratio of $[RLi]/[LiOR']$ (49,50). For *n*-butyllithium initiation of styrene in cyclohexane, the rate of initiation is increased at low relative concentrations of added lithium alkoxide $[t-C_4H_9OLi]/[C_4H_9Li] < 0.5$). At a ratio of 1/1, the rate is essentially the same as the control without alkoxide; beyond this ratio, the rate decreases continuously with increasing relative concentration of lithium alkoxide. In aromatic solvents, the initiation rate decreases with increasing relative concentrations of lithium alkoxide. Lithium alkoxides generally accelerate the rate of initiation by alkyllithiums (*n*-butyllithium and *sec*-butyllithium) for isoprene in hexane.

Propagation Kinetics. The kinetics of propagation for styrene and diene monomers in hydrocarbon solvents with lithium as the counterion is complicated by chain-end association (49,50,53). The kinetics of propagation can be investigated independently of initiation so that complications from cross-association with the initiator are absent. The reaction order dependence of the propagation rate on active center concentration is independent of the identity of the hydrocarbon solvent, aromatic or aliphatic, although the relative propagation rates, under equivalent conditions, are faster in aromatic versus aliphatic solvents.

Styrene Monomers. The anionic propagation kinetics for styrene (S) polymerization with lithium as counterion is relatively unambiguous. The reaction order in monomer concentration is first order as it is for polymerization of all styrene and diene monomers in heptane, cyclohexane, benzene, and toluene. The reaction order dependence on total chain-end concentration, $[PSLi]_0$, is one-half as shown in equation 29:

$$R_p = -d[S]/dt = k_{obs}[PSLi]_0^{1/2}[S] \quad (29)$$

The observed one-half kinetic order dependence on chain-end concentration is consistent with the fact that poly(styryl)lithium is predominantly associated into dimers in hydrocarbon solution. If the unassociated poly(styryl)lithium is the reactive entity for monomer addition, a simple dissociative mechanism can be invoked (equations 30 and 31). This mechanism leads to the kinetic equation shown in equation 32.



From equations 30 and 31, it can be seen that the observed rate constant for propagation, k_{obs} , is actually a composite of the propagation rate constant, k_p , and

the equilibrium constant for dissociation of the dimeric aggregates, K_d , raised to the one-half power (eq. 32).

$$\begin{aligned} R_p &= -d[S]/dt = k_p[\text{PSLi}][S] \\ &= k_p(K_d/2)^{1/2}[\text{PSLi}]_0^{1/2}[S] \\ &= k_{\text{obs}}[\text{PSLi}]_0^{1/2}[S] \end{aligned} \quad (32)$$

The measurement of the dissociation constants of the aggregates is difficult because of the low concentration of the unassociated species; thus, it is generally not possible to obtain directly a value for the propagation rate constant k_p (see, however, Refs. 54–56).

In contrast to this simple interpretation, the kinetic order dependence on chain-end concentration for propagation of styrene and *o*-methoxystyrene in toluene with alkylolithium initiators varies from 0.62 to 0.66 (56). Furthermore, recent neutron scattering data indicate that poly(styryl)lithium in benzene solution exhibits concentration-dependent degrees of aggregation involving predominantly dimers and tetramers, as well as small amounts of large-scale aggregates (57). These results suggest that the actual mechanism of propagation may be much more complicated than that depicted in equations 30 and 31 (see, however, Ref. 58).

A comparison of the observed propagation rate constants for styrene polymerization with different alkali metal counterions is shown in Table 2. Poly(styryl)sodium was presumably associated into dimers since kinetic orders of one-half were observed for the rate dependence on the active chain-end concentration. Poly(styryl)potassium exhibits intermediate behavior; dependence on chain-end concentration was one-half order at higher concentrations, but first order at low concentrations. Poly(styryl)rubidium and poly(styryl)cesium exhibit first-order dependencies on chain-end concentrations which is consistent with unassociated chain ends in cyclohexane. The counterion dependence is $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \gg \text{Li}^+$ in cyclohexane and $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ in benzene. The interpretation of these results is complicated by the fact that the complex observed rate constants (k_{obs}) reflect both the fact that the dissociation constant for the dimers increases with increasing cation size (no association for rubidium and cesium) and also the fact that the requisite energy associated with charge separation in the transition state would be less for the larger counterions.

Diene Monomers. The delineation of the mechanism of propagation of isoprene and butadiene in hydrocarbon solution with lithium as counterion is complicated by disagreement in the literature, regarding both the kinetic order dependence on chain-end concentration and the degree of association of the chain ends, as well as by apparent changes in kinetic reaction orders with chain-end concentration (53). For butadiene and isoprene propagation, reported reaction order dependencies on the concentration of poly(dienyl)lithium chain ends include 0.5, 0.33, 0.25, and 0.167. Kinetic studies of isoprene propagation with lithium as counterion in hydrocarbon solvents showed that the kinetic order dependence on chain-end concentration changed from 0.5 to either 0.25 or 0.17 as the chain-end concentration was varied from 10^{-2} to 10^{-6} mol/L (53,59,60). Comparison of these kinetic orders with the degrees of association of the poly(dienyl)lithium

Table 2. Kinetic Parameters for Styrene Propagation in Hydrocarbon Solvents^a

Counterion	Solvent	Temperature, °C	$[k_p(K_D/n)^{1/n}] (k_{\text{obs}}), \text{L}^{1/n}/(\text{mol}^{1/n} \cdot \text{s})$
Lithium	Benzene	30	1.55×10^{-2}
Lithium	Cyclohexane	40	2.4×10^{-2}
Sodium	Benzene	30	17×10^{-2}
Potassium	Benzene	30	180×10^{-2}
Potassium	Cyclohexane	40	30
Rubidium	Cyclohexane	40	22.5^b
Cesium	Cyclohexane	40	19^b

^aRef. 49.^bPropagation rate constant presumably for the unassociated species (see eq. 32); first-order dependence on active chain-end concentration observed.

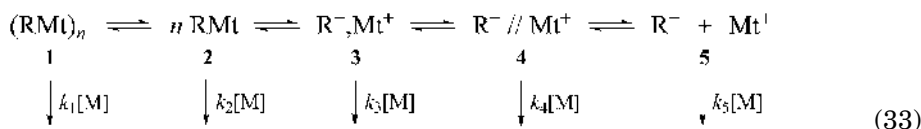
chain ends is complicated by the lack of agreement regarding the predominant degree of association of these species in hydrocarbon solution. Predominant degrees of association of both 2 and 4 have been reported by different research groups using the same techniques, ie, concentrated solution viscometry and light scattering (61–64). Recent evaluation of the association states of poly(butadienyl)lithium chain ends in benzene by small-angle neutron scattering, as well as both dynamic and static light scattering, indicates that dimeric and tetrameric aggregates are in equilibrium with higher order aggregates ($n > 100$) (65,66).

Relative Reactivities of Styrene and Dienes. The relative reactivities of dienes *versus* styrenes depend on the chain-end concentrations because of the differences in kinetic order dependencies on chain-end concentration. The relative rates of propagation at $[\text{PLi}] = \approx 10^{-3} M$ are in the order styrene > isoprene > butadiene. However at $[\text{PLi}] \leq \approx 10^{-4} M$, isoprene propagates faster than styrene (53).

Effects of Lewis Bases. The addition of small amounts of Lewis bases such as ethers and tertiary amines generally increases the rate of propagation in alkyllithium-initiated polymerizations. These Lewis bases decrease the average degree of association of the polymeric organolithium aggregates as determined by concentration solution viscosity measurements. In contrast, addition of strongly coordinating Lewis bases such as *N,N,N',N'*-tetramethylethylenediamine and pentamethyldiethylenetriamine can either increase or decrease the reaction rate for alkyllithium propagation of isoprene relative to hydrocarbon solution, depending on the chain-end concentration (67). This situation arises from the different reaction order dependencies on chain-end concentration, ie, 0.3 in hydrocarbon solution compared to 1.1 for the stoichiometric Lewis base complexes. The addition of lithium alkoxides generally decreases the rate of propagation, while addition of other alkali metal alkoxides increases the rate of polymerization in hydrocarbon solution.

Polar Solvents. A change in the reaction medium from hydrocarbon to polar solvent causes changes in the nature of the alkali metal carbanions that can be interpreted in terms of the Winstein spectrum of ionic species, as shown below (68,69). Thus, in addition to the aggregated (1) and unassociated (2) species that can exist in hydrocarbon solution, in polar solvents it is necessary to consider the intervention of free ions (5) and the contact (3) and solvent-separated (4)

ion-paired carbanion species, as shown below:



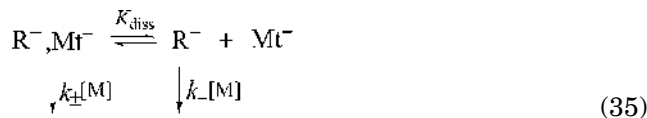
In general, as the polarity and solvating ability of the medium increases, more ionic species (a shift in the Winstein spectrum from left to right) are formed. In addition, each different chain-end species can react with monomer with its own unique rate constant.

In weakly polar solvents such as dioxane ($\epsilon = 2.21$), the kinetics of styrene propagation exhibit pseudo-first-order kinetics as illustrated in equation 34, where k_{obs} is the observed pseudo-first-order rate constant, k_p is the propagation rate constant, and $[\text{PS}^-\text{Mt}^+]$ represents the concentration of carbanionic chain ends that does not change for a living polymerization.

$$-d[\text{S}]/dt = k_{\text{obs}}[\text{S}] = k_p[\text{PS}^-\text{Mt}^+][\text{S}] \quad (34)$$

The values of k_p can be obtained by plotting k_{obs} versus $[\text{PS}^-\text{Mt}^+]$. The order of reactivity [rate constants in brackets are in units of L/(mol·s)] of alkali metal counterions is Li [0.9] < Na [3.4–6.5] < K [20–34] < Cs [5–24] (27). The trend of increasing reactivity with increasing ionic radius, as also observed in hydrocarbon solution, has been taken as evidence for contact ion pairs as the reactive propagating species. Similar behavior has been observed for isoprene polymerization in diethyl ether ($\epsilon = 4.34$); the propagation rate constant assigned to the lithium contact ion pair is 3.2 L/(mol·s) (70).

In more polar solvents such as THF ($\epsilon = 7.6$), a concentration dependence was observed for the plots of k_{obs} versus $[\text{PS}^-\text{Mt}^+]$; ie, k_p exhibits a linear dependence of $1/[\text{PS}^-\text{Mt}^+]^{1/2}$ (27). This dependence has been interpreted in terms of the participation of both ion pairs and free ions as active propagating species, as shown below:



where $k_{\pm}$ is the propagation rate constant for the ion pair species, k_- is the propagation rate constant for the free ion, and K_{diss} is the equilibrium constant for dissociation of ion pairs to free ions. The corresponding expression for k_p is shown below, recognizing that this k_p is only an apparent propagation rate constant.

$$k_p = k_{\pm} + k_- K_{\text{diss}}^{1/2} / [\text{P}^-\text{Mt}^+]^{1/2} \quad (36)$$

Plots of the apparent propagation rate constant versus $1/[\text{P}^-\text{Mt}^+]^{1/2}$ are shown in Figure 1. From this figure it can be deduced that the slopes of the lines decrease

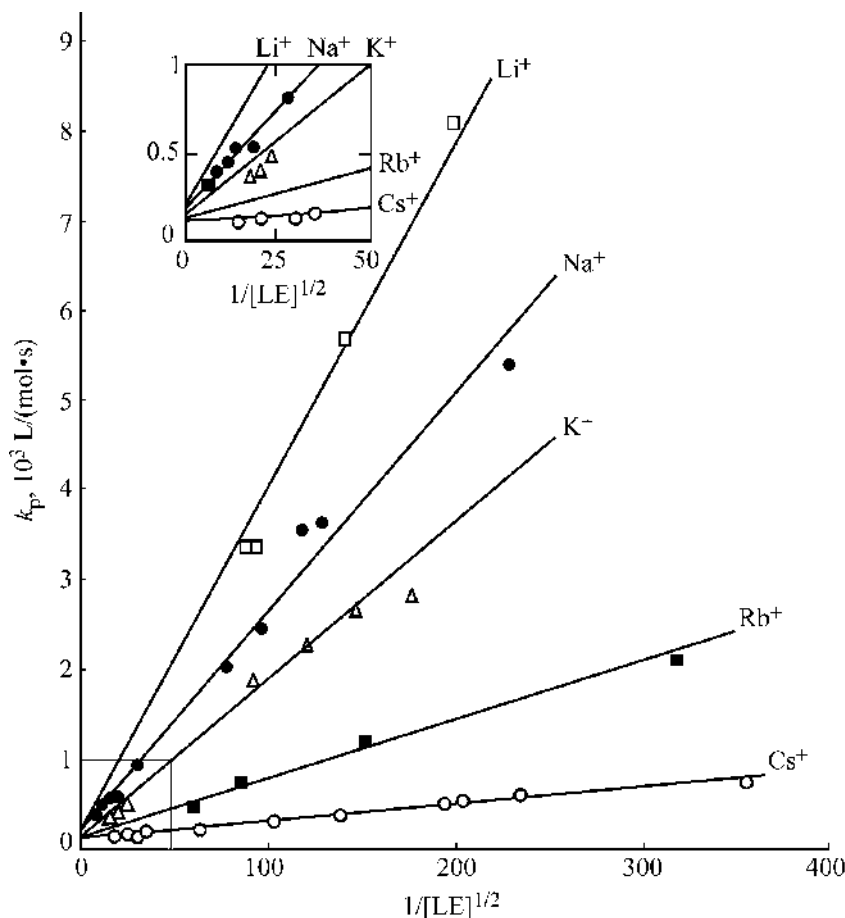


Fig. 1. Plots of the propagation constant k_p for salts of living polystyrene in THF vs $1/[LE]^{1/2}$. $\square$ Li^+ ; $\bullet$ Na^+ ; Δ K^+ ; $\blacksquare$ Rb^+ ; $\circ$ Cs^+ . $T = 25^\circ\text{C}$. From Ref. 27; reprinted by permission of Springer-Verlag.

as the cation size increases from lithium to cesium. Since k_- is independent of the cation, the variation of the slope with counterion reflects a decrease in K_{diss} as the counterion size increases. This is consistent with independent measures of the dissociation constants for free ion formation from both conductometric and kinetic studies. Figure 1 also shows that the intercepts, that represent $k_{\pm}$, also decrease with increasing cation size. Values of the propagation rate constant for free styryl anions are relatively insensitive to solvent; values for k_- of 0.65×10^5 and 1.3×10^5 L/(mol·s) have been reported at 25°C in THF (27). Corresponding values of $k_{\pm}$ vary from 160 L/(mol·s) for lithium to 22 L/(mol·s) for cesium ion in THF at 25°C . Similar results have been obtained for cumyl potassium-initiated polymerization of butadiene in THF; k_- had a value of 4.8×10^4 L/(mol·s) and $k_{\pm}$ was <1 L/(mol·s) at 0°C (71).

Although normal Arrhenius behavior was observed for k_- , anomalous increases of $k_{\pm}$ with decreasing temperature were observed in polar solvents such

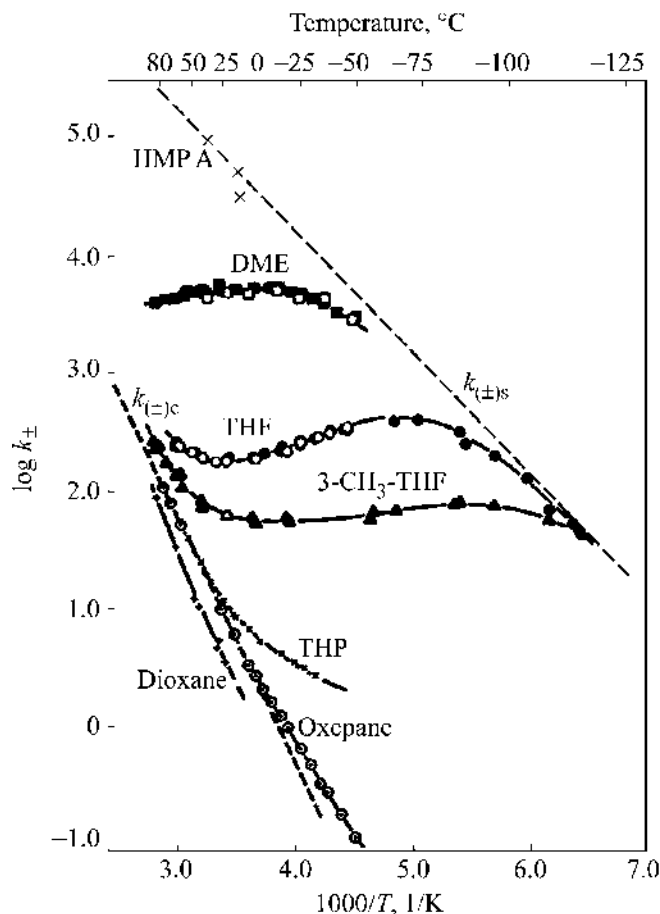
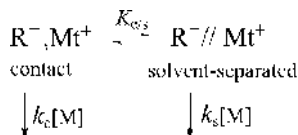


Fig. 2. Arrhenius plots of the propagation constants of ion pairs of poly(styryl)sodium in various solvents. The curves approach a common asymptote at low temperatures, interpreted as a linear Arrhenius plot referring to the propagation constant of solvent-separated ion pairs, and the curves approach again a common asymptote at high temperatures, interpreted as a linear Arrhenius plot referring to the propagation constant of tight ion pairs. From Ref. 27; reprinted by permission of Springer-Verlag.

as THF and dimethoxyethane (glyme), as shown in Figure 2 (27). These results have been explained in terms of a temperature-dependent equilibrium between contact and solvent-separated ion pairs, as shown below:



This equilibrium shifts from the less reactive contact ion pair to the more reactive solvent-separated ion pair as temperature is decreased because the contribution from the unfavorable (negative) entropy of dissociation ($T\Delta S$) decreases

Table 3. Ion Pair Rate Constants for Anionic Polymerization of Poly(styryl)sodium in Ethereal Solvents and the Equilibrium Constant and Thermodynamic Parameters for Ion Pair Equilibrium

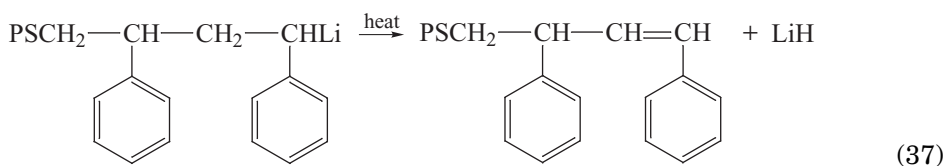
Solvent	k_c , L/(mol·s)	k_s , 10^4 L/(mol·s)	$K_{c/s}$ (25°C)	ΔH , kJ/mol ^a	ΔS , J/(mol·K) ^a
DME ^b	12.5	5.5	0.13	-23	-94
THF	34	2.4	2.25×10^{-3}	-27	-142
3-CH ₃ -THF ^c	20	12.4	5.8×10^{-4}	-21	-134
THP ^d	10.7	5.3	1.3×10^{-4}	-12.6	-117
Dioxane	5.5	—	$<10^{-5}$	—	—

^aTo convert J to cal, divide by 4.184.^b1,2-Dimethoxyethane.^c3-Methyltetrahydrofuran.^dTetrahydropyran.

and the enthalpy of dissociation is negative. As shown in Table 3, the values of k_c and k_s are not much dependent upon solvent, but the equilibrium constants $K_{c/s}$ are very dependent on the polarity of the solvent. These results also provide a rationalization for the effect of counterion on $k_{\pm}$ shown in Figure 1. Smaller cations such as lithium interact more strongly with solvent and form significant amounts of more reactive solvent-separated ion pairs.

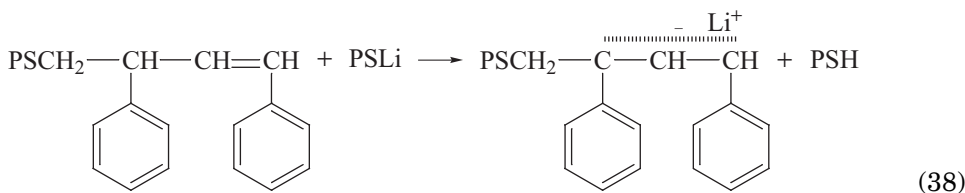
Termination Reactions. The categorization of a given polymerization system as living is based on results obtained on the laboratory time scale, ie, the absence of chain-termination or chain-transfer reactions occurring within the normal time required to complete the polymerization and carry out any subsequent chemical reactions with the active carbanionic polymer chain ends (6). In fact, the amount of spontaneous termination reactions in typical alkyllithium-initiated polymerizations of styrene and diene monomers depends on time, temperature, and whether polar additives are present (22,72,73).

Polymeric organolithium compounds exhibit good stability in hydrocarbon solution at ambient temperatures and for short periods of time at elevated temperatures (22,72). The principal mode of decomposition is loss of lithium hydride (β -hydride elimination) to form a double bond at the chain end, as illustrated below for poly(styryl)lithium.



Poly(styryl)lithium exhibits good stability over the duration of the polymerizations and beyond, ie, days, at ambient temperatures in hydrocarbon media. However, at elevated temperatures, it is observed that the initial uv absorption at 334 nm decreases and a new absorption is observed at 450 nm, assigned to a

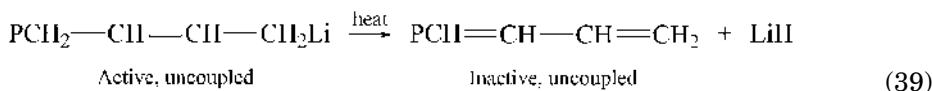
1,3-diphenylallyllithium species as shown below (22):

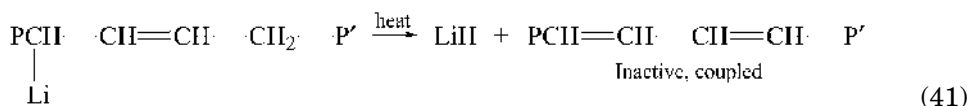
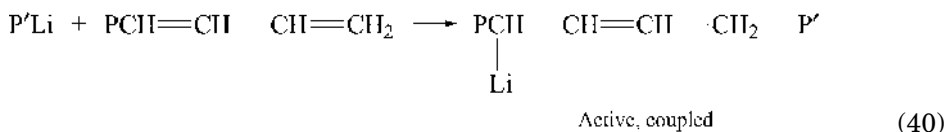


The rate constant for spontaneous decomposition was reported to be $4 \times 10^{-5} \text{ s}^{-1}$ at 65°C in cyclohexane (22,74). Analogous decomposition reactions have been observed for poly(styryl)sodium. The thermal stability of poly(α -methylstyryl)lithium is much lower than that of poly(styryl)lithium. The observed half-lives for spontaneous termination are 5 h and a few minutes at 25 and 60°C , respectively (75). However, the chain ends were stabilized with respect to spontaneous decomposition by the addition of TMEDA. The relative thermal stability of styryl carbanionic chain ends follows the order $\text{K} \gg \text{Na} > \text{Li}$ for the alkali metal counterions.

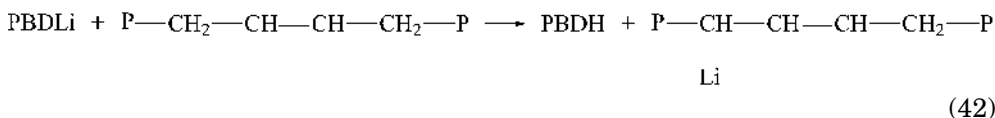
The carbanionic active centers based on 1,3-butadiene and isoprene, with lithium as counterion, generally possess good stability in hydrocarbon solvents at ambient temperatures. However, poly(dienyl)lithiums undergo complex decomposition reactions upon prolonged storage or heating at elevated temperatures. Poly(butadienyl)lithium in ethylbenzene exhibits an absorption maximum at 300 nm, which gradually decreases in intensity with the formation of absorption tails between 350 and 500 nm (22). Approximately 20% of the active centers were destroyed in less than 3 h at 100°C in ethylbenzene (76). The apparent first-order rate constant for decomposition of poly(butadienyl)lithium in hexane was estimated to be $1.9 \times 10^{-5} \text{ s}^{-1}$ at 93°C and a chain-end concentration of 2.2 mequiv of poly(butadienyl)lithium per 100 g of solution (25 wt% polymer) (74). The corresponding first-order rate constant for chain-end decomposition of poly(isoprenyl)lithium at 93°C was estimated to be $6.7 \times 10^{-5} \text{ s}^{-1}$ (74). Although the differences are not large, the relative order of increasing stabilities of chain ends toward thermal degradation is poly(α -methylstyryl)lithium $\ll$ poly(styryl)lithium $<$ poly(isoprenyl)lithium $<$ poly(butadienyl)lithium as estimated by chain-end titration data.

Size exclusion chromatography (sec) analyses of the thermal decomposition products of poly(dienyl)lithiums in heptane at 80°C have shown that the chain-end decomposition is accompanied by formation of species which have double and triple the molecular weight of the original living polymer (77). After heating for 46 h at 80°C in heptane, a 12 wt% yield of coupled products was observed for poly(isoprenyl)lithium; after heating for 27 h at 80°C in heptane, a 19wt% yield of coupled products was observed for poly(butadienyl)lithium. The following reactions illustrate the type of reactions proposed to explain the formation of dimeric products:





Evidence also suggests that athermal metalation of the backbone can occur as shown below:



It would be expected that this in-chain metalation coupled with elimination of lithium hydride would lead to in-chain diene units which would have even more reactive allylic hydrogens for further metalation-elimination-coupling sequences that would promote thermal decomposition, branching, and ultimately gel formation.

Polymeric organolithium compounds exhibit limited stability in ether solvents analogous to alkyllithium compounds. Living carbanionic polymers react with ether solvents such as THF in a pseudo-first-order decay process and the rate decreases in the order $Li > Na > K$. For example, a $10^{-5} M$ solution of poly(styryl)lithium in THF at $25^\circ C$ exhibited a rate of decay of a few percent per minute, but poly(styryl)cesium was found to be exceptionally stable (78). Metalation and decomposition reactions can also occur in the presence of amines such as TMEDA.

Chain-Transfer Reactions. Chain-transfer reactions to polymeric organoalkali compounds can occur from solvents, monomers, and additives that have pK_a values lower or similar to those of the conjugate acid of the carbanionic chain end (72). Relatively few monomers that undergo anionic polymerization exhibit chain transfer to monomer. Chain transfer has been well documented for the anionic polymerization of 1,3-cyclohexadiene. The chain-transfer constant (k_{tr}/k_p) was calculated to be 2.9×10^{-2} at $20^\circ C$ and 9.5×10^{-3} at $5^\circ C$ in cyclohexane (79). Although chain transfer would be expected for *p*-methylstyrene, controlled polymerizations can be effected when the temperature is maintained at room temperature or below. The observations of broad molecular weight distributions and a low molecular weight tail by sec analysis have provided evidence for chain transfer during the anionic polymerization of *p*-isopropyl- α -methylstyrene (80).

The kinetics of chain transfer to ammonia have been investigated for potassium amide-initiated polymerization of styrene in liquid ammonia at $-33.5^\circ C$. The calculated chain-transfer constant (k_{tr}/k_p) was 2.34×10^{-4} (81). The

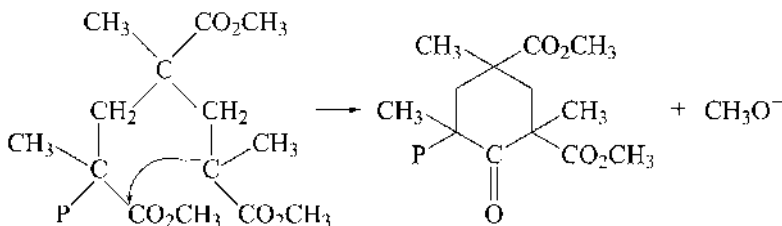
chain-transfer reaction of poly(styryl)lithium with toluene at 60°C was investigated during the polymerization of styrene with the use of ^{14}C -labeled toluene. The calculated chain-transfer constant ($k_{\text{tr}}/k_{\text{p}}$) was 5×10^{-6} (82). A much larger chain-transfer constant ($k_{\text{tr}}/k_{\text{p}} = 1.28 \times 10^{-4}$) was found for analogous transfer from toluene to poly(styryl)sodium. Chain-transfer reactions are promoted by Lewis bases. A chain-transfer constant of 0.2 was reported for the telomerization of butadiene initiated by metallic sodium in a toluene/tetrahydrofuran mixture at 40°C (83). Significant chain-transfer effects have also been reported for alkyllithium-initiated polymerizations using alkenes as solvents. Allenes and alkynes act as modifiers in alkyllithium-initiated polymerizations that have the effects of lowering rates of reaction and polymer molecular weights. Although these carbon acids can terminate chain growth, the ability of the resulting metalated chain-transfer product to reinitiate chain growth has only been demonstrated for 1,2-butadiene (84).

Polar Monomers

Polar Vinyl Monomers. The anionic polymerization of polar vinyl monomers is often complicated by side reactions of the monomer with both anionic initiators and growing carbanionic chain ends, as well as chain-termination and chain-transfer reactions. However, synthesis of polymers with well-defined structures can be effected under carefully controlled conditions. The anionic polymerizations of alkyl methacrylates and 2-vinylpyridine exhibit the characteristics of living polymerizations under carefully controlled reaction conditions and low polymerization temperatures to minimize or eliminate chain-termination and chain-transfer reactions. The proper choice of initiator for anionic polymerization of polar vinyl monomers is of critical importance to obtain polymers with predictable, well-defined structures. As an example of an initiator that is too reactive, the reaction of methyl methacrylate (MMA) with *n*-butyllithium in toluene at -78°C produces approximately 51% of lithium methoxide by attack at the carbonyl carbon (85).

Methyl Methacrylate. The most generally useful initiator for anionic polymerization of MMA and related compounds is 1,1-diphenylhexyllithium which is formed by the quantitative and facile addition of butyllithium with 1,1-diphenylethylene (DPE) (eq. 17) (46). Using this initiator in THF at -78°C, it is possible to polymerize MMA to obtain polymers and block copolymers with predictable molecular weights and narrow molecular weight distributions. Controlled polymerizations are not effected in nonpolar solvents such as toluene, even at low temperatures. Other useful initiators for polymerization of MMA are oligomers of (α -methylstyryl)lithium whose steric requirements minimize attack at the ester carbonyl group in the monomer. These initiators are also useful for the polymerization of 2-vinylpyridine (see METHACRYLIC ESTER POLYMERS).

The principal termination reaction in the anionic polymerization of MMA is a unimolecular backbiting reaction with the prepenultimate ester group to form a six-membered ring, β -keto ester group at the chain end, as shown below:



The rate of this backbiting reaction decreases with increasing size of the counterion.

A dramatic development in the anionic polymerization of acrylate and methacrylate monomers was the discovery that by addition of lithium chloride it was possible to effect the controlled polymerization of *t*-butyl acrylate (86). Thus, using oligomeric (α -methylstyryl)lithium as initiator in THF at -78°C , the molecular weight distribution (M_w/M_n) of the polymer was 3.61 in the absence of lithium chloride but 1.2 in the presence of lithium chloride ($[\text{LiCl}]/[\text{RLi}] = 5$). In the presence of 10 equiv of LiCl, *t*-butyl acrylate was polymerized with 100% conversion and 95% initiator efficiency to provide a polymer with a quite narrow molecular weight distribution ($M_w/M_n = 1.05$). More controlled anionic polymerizations of alkyl methacrylates are also obtained in the presence of lithium chloride. Other additives, which promote controlled polymerization of acrylates and methacrylates, include lithium *t*-butoxide, lithium (2-methoxy)ethoxide, and crown ethers (47,48). The addition of lithium chloride also promotes the controlled anionic polymerization of 2-vinylpyridine.

The kinetics of anionic polymerization of MMA are complicated by chain-end association effects and the involvement of both free ions and ion pairs as propagating species. Lithium ester enolates are highly aggregated even in THF; association numbers range from 2.3 to 3.5 (87). Because of chain-end association, a dependence of propagation rate constants on chain-end concentration has been observed for lithium and sodium counterions. The propagation rate constant for the free ions at -75°C in THF is $4.8 \times 10^5 \text{ L}/(\text{mol}\cdot\text{s})$ (88). The propagation rate constants for ion pairs vary in the order $\text{Cs} \approx \text{K} \approx \text{Na} \gg \text{Li}$. This is consistent with the conclusion that contact ion pairs are the predominant propagating species. The ion pair rate constants for lithium and potassium as counterions in THF at -40°C are 100 and 750 $\text{L}/(\text{mol}\cdot\text{s})$, respectively (89).

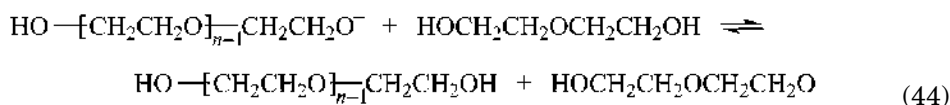
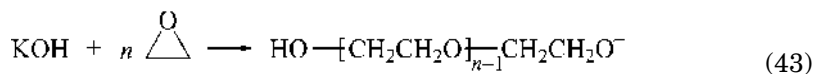
The kinetic effects of lithium chloride on anionic polymerization of alkyl acrylates and methacrylates have been carefully examined (47,48,90,91). Added lithium chloride decreases the rate of propagation but has little effect on the rate of termination. In the absence of lithium chloride, free ions as well as associated and unassociated species can participate in the propagation event. By a common ion effect, the role of free ions is minimized by addition of lithium chloride. In the absence of lithium chloride, the rate of interconversion between tetrameric aggregates, dimeric aggregates, and unassociated ion pairs is slow relative to propagation resulting in broader molecular weight distributions. Lithium chloride decreases the amount of aggregated species and forms cross-associated complexes with the lithium ester enolate ion pairs. Most important, the equilibration among

these lithium chloride cross-aggregated species is fast relative to propagation so that narrow molecular weight distributions can be obtained.

Heterocyclic Monomers. A variety of heterocyclic monomers can be polymerized by anionic ring-opening polymerizations. The types of anionically polymerizable heterocyclic monomers include oxiranes (epoxides), thiacyclopropanes, thiacyclobutanes, lactones, lactides, lactams, anhydrides, carbonates, and siloxanes (92). Among these heterocyclic monomers, the anionic polymerizations of epoxides have been examined most extensively.

Ethylene Oxide. The anionic polymerization of ethylene oxide is complicated by association phenomena and the participation of ion pair and free ion intermediates in the propagation reactions (see POLYETHERS). Simple lithium alkoxides are strongly associated into hexamers and tetramers even in polar media such as THF and pyridine (93). As a consequence, lithium alkoxides are unreactive as initiators for the anionic polymerization of oxiranes. Association effects can be minimized by effecting polymerizations in alcohol media or in dipolar aprotic solvents.

The potassium hydroxide-initiated polymerization of ethylene oxide in alcoholic solvents such as diethylene glycol produces low molecular weight polyols ($M_w \approx 600-700$) with broad molecular weight distributions because of chain-transfer reactions with alcohol that occur throughout the polymerization, as shown below (98):

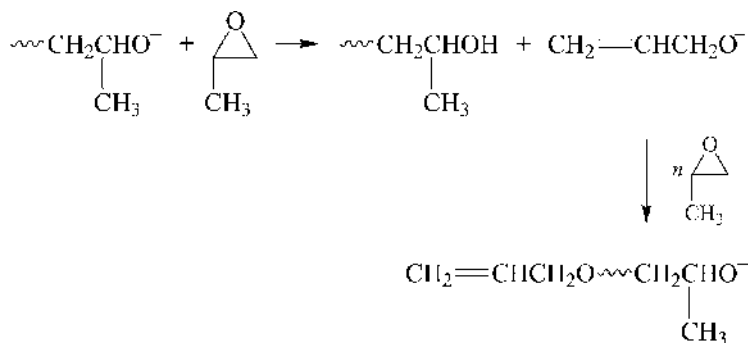


“Living polymerizations with reversible chain transfer” (6) can be effected for alkoxide-initiated polymerizations of ethylene oxide in the presence of alcohol ($[\text{ROH}]/[\text{NaOR}] \approx 10$) in solvents such as dioxane (95,96). Narrow molecular weight distributions are obtained because, although there is formally a chain-transfer reaction between OH-ended polymers and alkoxide-ended polymers, the equilibrium between these two types of chain ends is rapid and reversible such that all chains participate uniformly in chain growth as described in Reference 97.

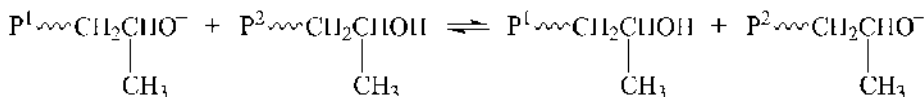
Association phenomena and the presence of both ion pairs and free ions as propagating species complicate the kinetics of sodium alkoxide-initiated polymerizations of ethylene oxide even in dipolar aprotic solvents such as HMPA ($\epsilon = 26$). However, living polymerizations occur in dipolar aprotic solvents and in ethers such as THF, although the rates are much slower in ethers. The rates of propagation increase with increasing radius of the cation. The rates of propagation of ethylene oxide are also accelerated in the presence of cation complexing agents such as crown ethers and cryptands. Although the cryptated ion pairs are somewhat less reactive than the uncomplexed ion pairs, cryptands promote dissociation of the ion pairs to form free ions that

are 70 times more reactive than the ion pairs (98). Because of the concentrated charge on oxygen, contact ion pairs predominate. The propagation rate constants in THF at 20°C for the cesium ion pair and the free ion are 7.3 and 100 L/(mol·s) (98). An optimized, living polymerization procedure utilized *N*-carbazolylpotassium as initiator in THF at 20°C in the presence of crown ether (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane); narrow molecular weight distribution polymers with controlled molecular weights as high as 266,000 g/mol could be obtained (99).

Propylene Oxide. The anionic ring-opening polymerization of propylene oxide is much slower than the analogous polymerization of ethylene oxide (see POLYETHERS). The propagation rate constant at 40°C in neat propylene oxide is 1.9×10^{-4} L/(mol.s) (100). The anionic ring-opening polymerization of propylene oxide using hydroxide or alkoxide initiators is not a living polymerization. Chain transfer to monomer competes with propagation to limit the maximum molecular weight attainable and to broaden the molecular weight distribution, as shown below.



Thus, chains are formed that have the unsaturated allyloxy end group. The chain-transfer constant (k_{tr}/k_p) is approximately 0.01; thus, the molecular weight attainable is theoretically limited to approximately 6×10^3 g/mol (101). However, molecular weights as high as 13,000 g/mol have been obtained for polymerization of neat propylene oxide with potassium as counterion in the presence of 18-crown-6 ether. Under these conditions, chain-transfer constants as low as 8×10^{-4} have been reported (102). This is due to the rapid equilibration between hydroxyl-ended chains and alkoxide-ended chains, that ensures uniform growth of all chains even after chain transfer, as shown below:



However, chain transfer to monomer will still broaden the molecular weight distribution and prevent molecular weight control even when reversible chain transfer among growing species occurs. This rapid and reversible chain transfer is used to prepare branched polypropylene oxide polymers. Initiation of propylene oxide polymerization with an alkali metal alkoxide and a triol such as glycerol

will produce the corresponding polypropylene oxide with an average functionality of three.

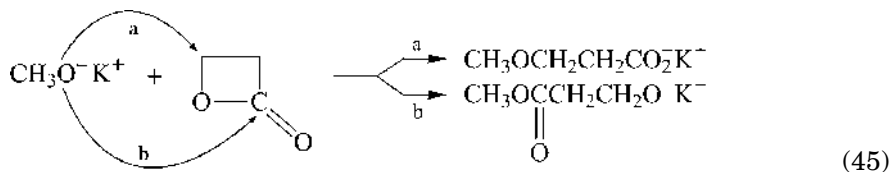
The anionic polymerization of propylene oxide initiated by potassium alkoxide or hydroxide occurs predominantly (95%) by cleavage of the O—CH₂ bond. For bulk polymerization at 80°C, approximately 4% head-to-head placements occur. However, there is no stereocontrol in this alkoxide-initiated ring opening and the resulting polymer is nontactic (103).

Chain-transfer reactions to monomer occur with other homologues of propylene oxide. The reactivity of higher epoxides decreases as expected on the basis of steric hindrance effects on nucleophilic attack at the oxirane carbons.

Propylene Sulfide. The anionic polymerization of propylene sulfide is a living polymerization that proceeds in the absence of termination and chain transfer (96) (see POLY(ALKYLENE SULFIDE)S). The regiochemistry of addition corresponds to regular head-to-tail addition without detectable amounts of head-to-head or tail-to-tail additions. The polymer stereochemistry is nontactic. The kinetics of propagation of propylene sulfide initiated by carbazylsodium in THF at chain-end concentrations $<10^{-3}$ M are not complicated by chain-end association effects. The reported propagation rate constants for contact ion pairs and free ions at -40°C were 1×10^{-3} and $1.7 \text{ L}/(\text{mol}\cdot\text{s})$, respectively (96). The ion pair rate constants for the corresponding [2.2.2]cryptate-solvated sodium thiolate were more than two times larger than the corresponding free ion rate constants in THF at -39°C (98).

Lactones.

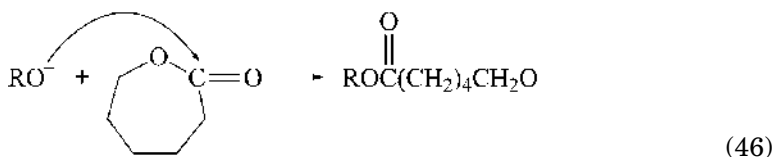
β -Propiolactone. The anionic polymerizations of the β -lactones and ϵ -lactones have been extensively investigated (104). Living characteristics are observed for the polymerization of β -propiolactone using a dibenzo-18-crown-6 ether complex of sodium acetate as the initiator in dichloromethane (105). Depending on the reactivity of the initiator, either acyl-oxygen cleavage or alkyl-oxygen cleavage can occur to form the corresponding alkoxide or carboxylate anions, respectively, as illustrated below for initiation with potassium methoxide that results in both modes of ring opening.



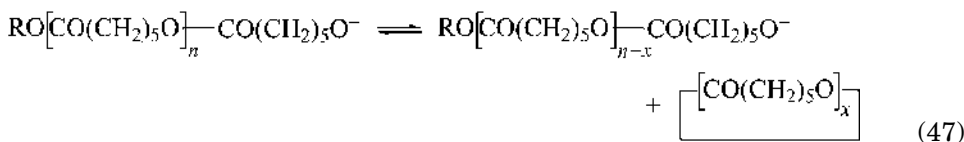
Only alkyl-oxygen cleavage is observed for initiation with potassium acetate. Regardless of the initiator, all propagating species eventually become carboxylate anions because in each subsequent propagation step a fraction of the alkoxide anions are converted to carboxylate anions. The kinetics of these polymerizations are complex. Both complexed ion pairs and free ions are involved in the propagation reactions and the free ion rate constants depend on monomer concentration. The relative reactivity of complexed ion pairs and free ions is temperature-dependent. Above the inversion temperature of -35°C , free ions are more reactive than ion pairs, but below this temperature, the ion pairs are more

reactive. At 30°C in DMF, the observed (average) propagation rate constant is 0.13 L/(mol·s) (106). The anionic polymerization of α,α -dialkyl- β -propiolactones such as pivalolactone (α,α -dimethyl- β -propiolactone) initiated with carboxylate anions exhibits the main characteristics of living polymerizations.

ϵ -Caprolactone. The anionic polymerization of ϵ -lactones, especially ϵ -caprolactone, is generally complicated by intramolecular cyclization reactions and redistribution reactions that prevent control of molecular weight and lead to broader molecular weight distributions (104). Alkoxides and not carboxylates are active initiators for polymerization of ϵ -caprolactone consistent with the identification of the alkoxide anion as the propagating species, as shown below:



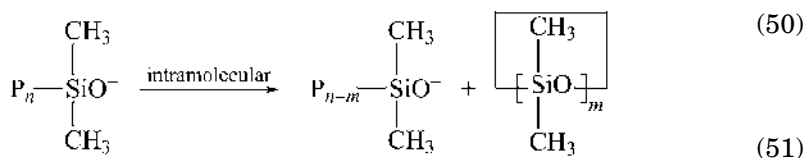
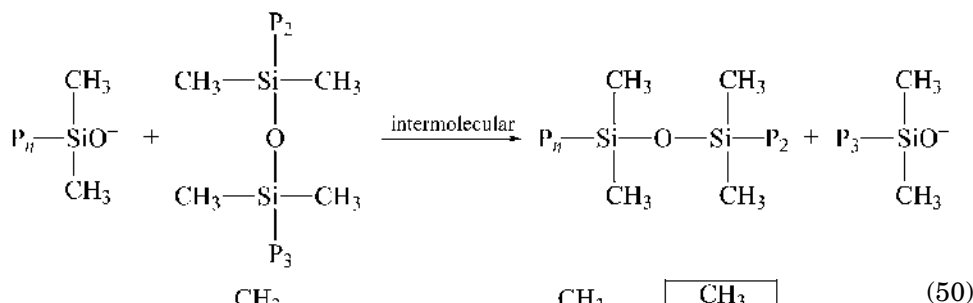
Chain-end association complicates the kinetics of polymerization. Evidence for aggregation of lithium and sodium alkoxides, but not for potassium alkoxides, in THF has been found. The propagation rate constants in THF at 20°C for the free ions and ion pairs are 3.5×10^2 and 4.8 L/(mol·s) (107). The anionic polymerization of ϵ -caprolactone leads to the formation of considerable amounts of oligomers as by-products. In dilute solution no high polymer is formed. In bulk polymerization, more than one-third of the equilibrium distribution of products are oligomers that have been identified to be cyclic (see eq. 47). The intermolecular analogue of this reaction (transesterification) leads to scrambling of the polymer molecular weights and a molecular weight distribution that broadens with time.



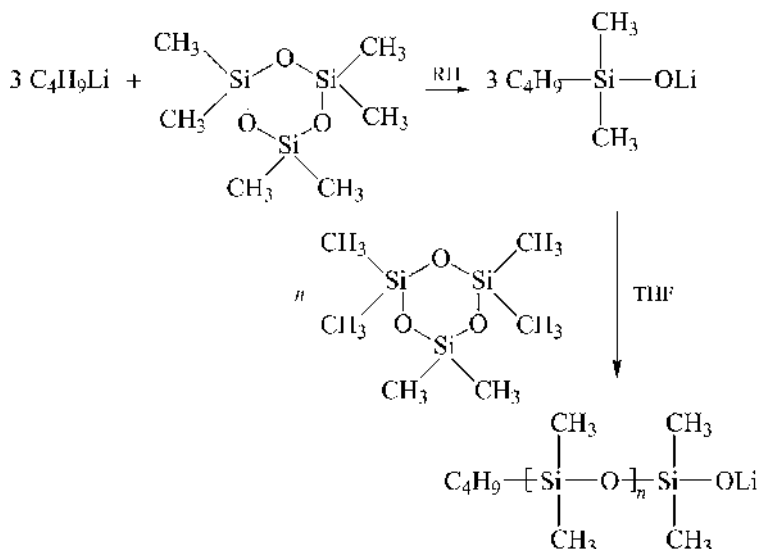
Polymerizations with lithium as counterion minimize backbiting reactions at short reaction times.

Cyclic Carbonates. Aliphatic, cyclic carbonates such as 5,5-dimethyl-1,3-diox-2-one can be polymerized using alkyllithium compounds as initiators in hydrocarbon solution to high molecular weight polymers (108,109). Ring-chain equilibration is promoted at long reaction times and in THF as solvent. At -10°C in toluene, *sec*-butyllithium-initiated polymerization of 5,5-dimethyl-1,3-diox-2-one proceeds via a lithium alkoxide-propagating species

can be described as an equilibration among these various components; in addition to reaction with the monomer, the growing silanolate chain ends react with all siloxane bonds via intramolecular cyclization and intermolecular chain transfer, as shown below:



In contrast to the polymerization of D_4 , the anionic polymerization of D_3 with lithium as counterion is a living polymerization which produces polydimethylsiloxanes with well-defined structures. Useful initiators include lithium silanolates or the product from the reaction of 3 moles of butyllithium with D_3 in hydrocarbon solvent, as shown below. It is noteworthy that no polymerization occurs in the absence of a Lewis base promoter such as THF, glymes, DMSO, or HMPA.



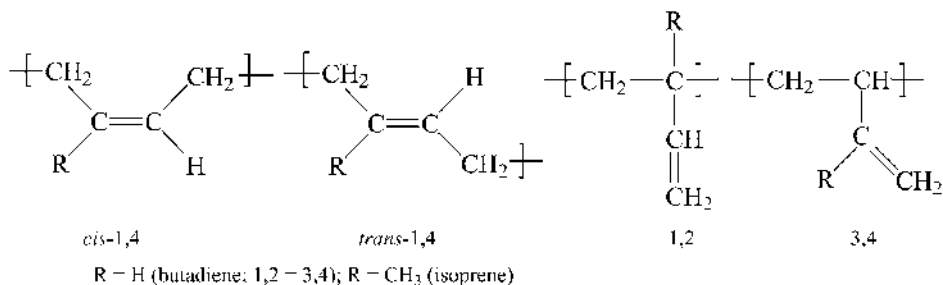
The kinetics of polymerization of cyclosiloxanes are complicated by chain-end association. Complexation of counterions with cryptands disrupts the

aggregates. For the lithium [2.1.1]cryptand complex in aromatic solvent at 20°C, the propagation rate constants for D₃ and D₄ are 1.4 and 4×10^{-3} L/(mol·s), respectively (98) (see SILICONES).

Stereochemistry

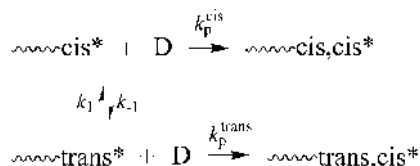
Polydienes.

Polydienes in Hydrocarbon Solvents. One of the most important synthetic and commercial aspects of anionic polymerization is the ability to prepare polydienes with high 1,4-microstructure using lithium as the counterion in hydrocarbon solution (115,116). The key discovery was reported in 1956 by scientists at the Firestone Tire and Rubber Co., that polyisoprene produced by lithium metal-initiated anionic polymerization had a high (>90%) *cis*-1,4 microstructure analogous to natural rubber (26). In general, conjugated 1,3-dienes [CH₂=C(R)-CH=CH₂] can polymerize to form four isomeric microstructures as shown below:



The stereochemistry of the anionic polymerization of isoprene and butadiene depends on the counterion, monomer concentration, chain-end concentration, solvent, temperature, and the presence of Lewis base additives (see BUTADIENE POLYMERS; ISOPRENE POLYMERS). The effect of counterion on polybutadiene stereochemistry is illustrated by the data in Table 4, which shows that lithium is unique among alkali metal counterions in producing polybutadiene with high 1,4 microstructure. Similar results have been reported for the stereochemistry of the anionic polymerization of isoprene (see Table 5) except that the stereochemistry with lithium as the counterion in neat isoprene is 94% *cis*-1,4 and 6% 3,4 compared with 35% *cis*-1,4, 52% *trans*-1,4, and 13% 1,2 for analogous polymerization of butadiene. From the data in Table 6, it is possible to delineate the effects of monomer concentration, chain-end concentration, monomer concentration, and solvent. The highest *cis*-1,4 microstructures are obtained in the absence of solvent, ie, with neat monomer, at low concentrations of initiator ($\approx 10^{-6}$ M). High *cis*-1,4 enchainment is also favored by the use of aliphatic versus aromatic solvents at low concentrations of initiator; however, the total amount of 1,4 microstructure (*cis* + *trans*) is relatively insensitive to solvent and chain-end concentration. In general, temperature is not an important variable for polydienes prepared in hydrocarbon solution, with lithium as the counterion; however, relatively large effects of pressure have been reported.

A comprehensive hypothesis has been proposed to explain the effects of the concentrations of active chain ends and monomer on polydiene microstructure (123). Based on studies with model compounds and the known dependence of polydiene microstructure on diene monomer (D) and chain-end concentrations as shown in Table 6, the mechanistic hypothesis shown below was advanced.



It was proposed that isomerization of the initially formed cis form of the active chain end occurs competitively with monomer addition at each step of the reaction (123,124). Thus, when the concentration of monomer is high relative to the chain-end concentration, the first-order isomerization of the cis form does not compete effectively with monomer addition. However, at low concentrations of monomer relative to chain ends, the isomerization does compete and significant amounts of the trans form will be in equilibrium with the cis form.

The kinetic order dependence on the active chain-end concentration is approximately 0.25 for diene propagation, while the kinetic order dependence on the active chain end concentration is approximately one for cis–trans isomerization of

Table 4. Effect of Counterion on Polybutadiene Microstructure for Neat Polymerizations^a

Counterion	Temperature, °C	Microstructure (%)		
		<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
Lithium	70	35	52	13
Sodium	50	10	25	65
Potassium	50	15	40	45
Rubidium	60	7	31	62
Cesium	60	6	35	59

^aRef. 117.

Table 5. Effect of Counterion on Polyisoprene Microstructure for Neat Polymerizations^a

Counterion	Temperature, °C	Microstructure (%)			
		<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	3,4
Lithium	25	94	—	—	6
Sodium	25	—	45	7	48
Potassium	25	—	52	8	40
Rubidium	25	5	47	8	39
Cesium	25	4	51	8	37

^aRefs. 117 and 118.

Table 6. Microstructure of Polydienes in Hydrocarbon Media Using Organolithium Initiators

Initiator concentration, <i>M</i>	Solvent	Temperature, °C	Microstructure (%)			Reference
			<i>cis</i> -1,4	<i>trans</i> -1,4	3,4	
<i>Polyisoprene</i>						
6×10^{-3}	Heptane	−10	74	18	8	119
1×10^{-4}	Heptane	−10	84	11	5	
8×10^{-6}	Heptane	−10	97	—	3	
5×10^{-6}	Heptane	25	95	2	3	120
9×10^{-3}	Benzene	20	69	25	6	121
5×10^{-6}	Benzene	25	72	20	8	120
1×10^{-2}	Hexane	20	70	25	5	121
1×10^{-5}	Hexane	20	86	11	3	
3×10^{-3}	None	20	77	18	5	
8×10^{-6}	None	20	96	—	4	
			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	
<i>Polybutadiene</i>						
8×10^{-6}	Benzene	20	52	36	12	
5×10^{-1}	Cyclohexane	20	53 ^a		47	122
1×10^{-5}	Cyclohexane	20	68	28	4	121
3×10^{-2}	Hexane	20	30	60	8	
2×10^{-5}	Hexane	20	56	37	7	
3×10^{-3}	None	20	39	52	9	
5×10^{-6}	None	20	86	9	5	

^aTotal 1,4 content (*cis* + *trans*).

the chains ends (53,116). Thus, while the unassociated chain ends add monomer, isomerization of the chain ends occurs in the aggregated state. Since aggregation is favored by increasing chain-end concentrations, high 1,2 microstructure is observed (47% for butadiene) for high chain-end concentrations ($[PBDLi] = \approx 0.1 M$) and high *cis*-1,4 microstructure (86% for butadiene) is obtained at low chain-end concentrations ($\approx 10^{-6} M$).

The microstructure of anionic polymerization of other poly(1,3-diene)s with lithium as counterion in hydrocarbon media is also predominantly 1,4 (115). However, higher amounts of *cis*-1,4 microstructures are obtained with more sterically hindered diene monomers. Thus, using conditions which provide polyisoprene with 70% *cis*-1,4, 22% *trans*-1,4, and 7% 3,4 microstructure, 2-*i*-propyl-1,3-butadiene and 2-*n*-propyl-1,3-butadiene provide 86% and 91% *cis*-1,4 enchainment, respectively. Both 2-phenyl-1,3-butadiene (92% *cis*-1,4) and 2-(triethylsilyl)-1,3-butadiene (100% *cis*-1,4) also exhibit high *cis*-1,4 enchainment.

Polydienes Polar Solvents. In polar media, the unique, high 1,4 stereospecificity, with lithium as counterion, that is observed in hydrocarbon media is lost and large amounts of 1,2-poly(butadiene) and 3,4-poly(isoprene) enchainments are obtained (see Tables 7 and 8). Tables 7 and 8 show that there is a tendency toward higher 1,4 content with increasing size of the counterion in polar

Table 7. Effects of Polar Solvents on Polybutadiene Microstructure^{a, b}

Solvent	Counterion	Temperature, °C	Microstructure (%)		
			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
THF	Lithium	0	6	6	88
THF	Lithium	-78	~0	8	92
THF	Sodium	0	6	14	80
THF	Sodium	-78	~0	14	86
THF	Potassium	0 or -78	5	28	67
(C ₂ H ₅) ₂ O	Lithium	0	8	17	75
(C ₂ H ₅) ₂ O	Sodium	0	7	23	70
(C ₂ H ₅) ₂ O	Potassium	0	11	34	55
Dioxane	Lithium	15	—	13	87
Dioxane	Sodium	15	—	15	85
Dioxane	Potassium	15	—	45	55
Dioxane	Cesium	15	—	59	41
Dioxane	Free ion	15	—	22	78

^aRefs. 125 and 126.^bFree ion formation was suppressed for the measurements in THF and (C₂H₅)₂O by the addition of tetraphenylboride salts (triphenylcyanoboron for potassium).**Table 8. Effects of Polar Solvents on Polyisoprene Microstructure**

Solvent	Counterion	Temperature, °C	Microstructure (%)					Reference
			<i>cis</i> -1,4	<i>trans</i> -1,4	Total 1,4 content (<i>cis</i> + <i>trans</i>)	1,2	3,4	
THF	Lithium	30			12	29	59	127
THF	Sodium	0			11	19	70	128
DME ^a	Li, Na, K, Cs	15			24–26	28–33	44–48	129
(C ₂ H ₅) ₂ O	Lithium	20			35	13	52	130
(C ₂ H ₅) ₂ O	Sodium	20			17	22	61	
(C ₂ H ₅) ₂ O	Potassium	20			38	19	43	
(C ₂ H ₅) ₂ O	Cesium	20			52	16	32	
Dioxane	Lithium	15	3	11		18	68	126
Dioxane	Potassium	15	4	32		14	50	
Dioxane	Free ion	15	<1	24		32	44	

^a1,2-Dimethoxyethane.

media. The highest 1,2 content in polybutadiene and the highest amounts of 1,2 and 3,4 enchainments in polyisoprene are obtained with lithium and sodium. The highest 1,4 enchainments are observed for cesium as counterion in polar media. Higher 1,4 contents are also obtained in less polar solvents such as dioxane.

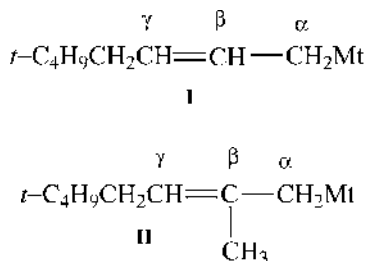
There are several important structural differences for polydienyl anions in polar media versus hydrocarbon solvents: (1) chain ends are generally not associated into higher aggregates in polar media compared to hydrocarbon; (2) the charge distribution of unsymmetrical allylic anions is a function of solvent, counterion, and temperature; (3) the kinetic and equilibrium distribution of chain-end configurations can vary with solvent and counterion; (4) the distribution of contact ion pairs, solvent-separated ion pairs, and free ions can vary with solvent, counterion, and temperature.

Table 9. Calculated Charges on Allyl Carbon Atoms of Neopentylallyl- and Neopentylmethylallyl-alkali Metal Compound^a

Counterion	Solvent	Calculated charges on allylic carbon atoms			Σ (total)
		α	β	γ	
Neopentylallyl-alkali metal (I)					
Li	C ₆ H ₆	0.79	−0.13	0.22	0.88
	THF	0.69	−0.15	0.40	0.94
Na	THF	0.65	−0.12	0.49	1.02
K	THF	0.59	−0.11	0.53	1.01
Rb	THF	0.55	−0.11	0.53	0.97
Cs	THF	0.51	−0.12	0.52	0.91
Neopentylmethylallyl-alkali metal (II)					
Li	C ₆ H ₆	0.80	−0.14	0.19	0.85
	THF	0.73	−0.15	0.34	0.92
Na	THF	0.69	−0.12	0.38	0.95
K	THF	0.61	−0.09	0.44	0.96
Rb	THF	0.58	−0.09	0.47	0.96
Cs	THF	0.54	−0.10	0.45	0.89

^aRef. 131.

Using the relationship that the chemical shift per electron corresponds to 114 ppm/electron, the calculated charge distributions for neopentylallyl-alkali metal I and neopentylmethylallyl-alkali metal II compounds have been calculated and the results are shown in Table 9 (131).



Compounds I and II can be regarded as models for butadienyl and isoprenyl carbanionic chain ends, respectively. The data in Table 9 show that while the negative charge is more localized on the alpha (α) carbon in hydrocarbon solution for the lithium derivatives, in polar media there is less charge on the alpha (α) carbon and more charge on the gamma (γ) carbon in all allyl organoalkali compounds. The presence of more negative charge on the gamma (γ) carbon provides a partial explanation for the formation of predominantly side-chain vinyl microstructure in polar media; however, lithium with the least charge on the gamma carbon gives the highest 1,2 enchainment and cesium with high charge on the gamma carbon gives the highest 1,4 enchainment. It has been suggested that a highly solvated lithium cation in ether solvents, which is situated closer to the alpha carbon in the allylic anion, may block reaction with monomer at this position and lead to

Table 10. Effects of Temperature and Concentration of Lewis Base on Vinyl Content of Polybutadiene in Hexane

Base	[Base]/[Li]	1,2 Microstructure (%)				Reference
		5°C	30°C	50°C	70°C	
Triethylamine	30	—	21	18	14	133
	270	—	37	33	25	
Diethyl ether	12	—	22	16	14	
	180	—	38	29	27	
Tetrahydrofuran	5	—	44	25	20	
	85	—	73	49	46	
Diglyme	0.1	—	51	24	14	
	0.8	—	78	64	40	
<i>N,N,N',N'</i> -Tetramethylethylenediamine	0.6	—	73	47	30	134
	0.4	78	—	—	—	
	6.7	85	—	—	—	
	1.14	—	76	61	46	
Bispiperidinoethane	0.5	91	50	44	21	135
	1	99.99	99	68	31	

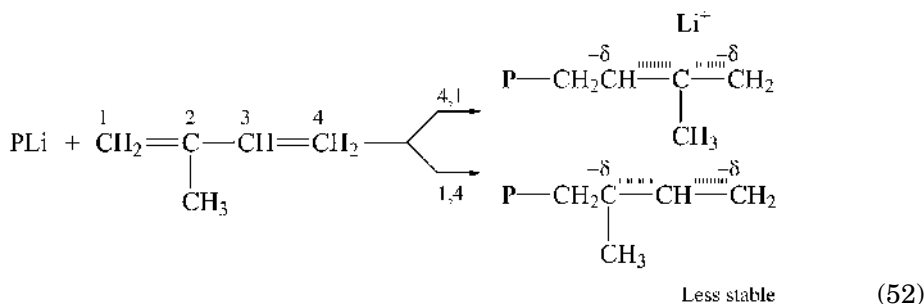
preferential attack at the less hindered gamma position to form 1,2-butadiene units (132).

Sterically hindered, 2-alkyl-substituted dienes form high 1,4 microstructure in polar media as well as in hydrocarbon media (115). Butyllithium-initiated polymerization of 2-isopropyl-1,3-butadiene in diethyl ether produces a polymer with 81% *cis*-1,4 and 19% *trans*-1,4 microstructure. Similarly, >90% 1,4 microstructure is observed in THF for butyllithium-initiated polymerization of 2-triethylsilyl-1,3-butadiene, 2-trimethoxysilyl-1,3-butadiene, 1-phenyl-1,3-butadiene, 1-pyridyl-1,3-butadiene, and 2-phenyl-1,3-butadiene.

Polar Modifier Effects. Small amounts of Lewis base additives in hydrocarbon media can exert dramatic effects on polydiene microstructure as shown by the data in Table 10. Lewis bases which interact most strongly with lithium produce the highest amount of 1,2 microstructure. For example, there is a correlation between the enthalpies of interaction of Lewis bases with polymeric organolithium compounds and the ability of these bases to promote 1,2 enchainment (136). The highest vinyl contents for polybutadiene are obtained with the most strongly coordinating ligands such as the bidentate bases, TMEDA and DIPIP (bispiperidinoethane). To obtain significant amounts of vinyl microstructure with weak donor-type bases such as diethyl ether and triethylamine, they must be present in large amounts relative to lithium. In contrast, the strongly coordinating bases produce high vinyl polybutadiene microstructure at low base to lithium atom ratios ($R = [\text{Base}]/[\text{Li}] = 1-2$).

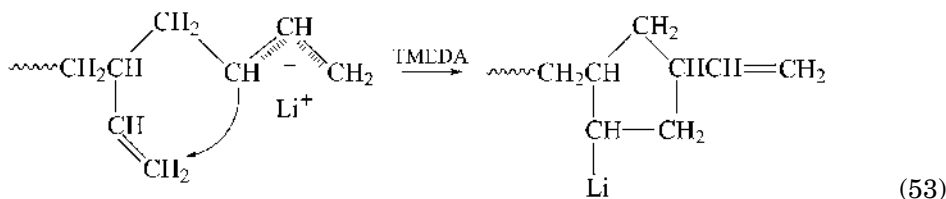
An interesting effect of Lewis bases on diene microstructure is the fact that in the presence of strongly coordinating bases such as TMEDA, 1,2 units are observed for polyisoprene. For example, the microstructure of polyisoprene formed in the presence of TMEDA ($[\text{TMEDA}]/[\text{Li}] = 1$) in cyclohexane corresponds to 21% 1,4, 12% 1,2, and 67% 3,4 (137). The formation of 1,2 units requires the formation

of the less stable 1,4 chain ends versus 4,1 chain ends as shown in equation 52:



With lithium as counterion in neat monomer or in hydrocarbon solvent, no 1,2 enchainment is detected (see Tables 5 and 6).

Another interesting and surprising phenomenon observed in alkyllithium-initiated polymerization of butadiene in the presence of TMEDA is that cyclization to form in-chain vinylcyclopentane units (up to 60%) is observed when the butadiene monomer is introduced into the reactor at low rates (eq. 53) (138).



Under such conditions, propagation does not effectively compete with cyclization; similar results are obtained with bispiperidinoethane. With respect to the mechanistic requirements for this type of cyclization, it was reported that batch polymerization in THF/TMEDA (92/2, v/v) at 0°C showed no evidence of these cyclic units although the vinyl content was almost 90%. This reaction forms a relatively unstable 2° alkyllithium from a resonance-stabilized allylic lithium, which would appear to be energetically unfavorable. However, it should be noted that this process also converts a π bond into a more stable σ bond as in any vinyl polymerization. The generality of this cyclization process in monomer-starved systems was demonstrated by showing that significant amounts of cyclization are observed using sodium as counterion in the presence of TMEDA and also with lithium complexed only with THF.

The ability to prepare polydienes with variable microstructures is an important aspect of alkyllithium-initiated anionic polymerization. The main consequence of the change in microstructure is that the glass-transition temperatures of the corresponding polymers are higher for polymers with more side-chain vinyl microstructure. For example, the glass-transition temperature of polybutadiene is an almost linear function of the % 1,2 configuration in the chain as shown in Figure 3 (139). Thus, while *cis*-1,4-polybutadiene has a glass-transition

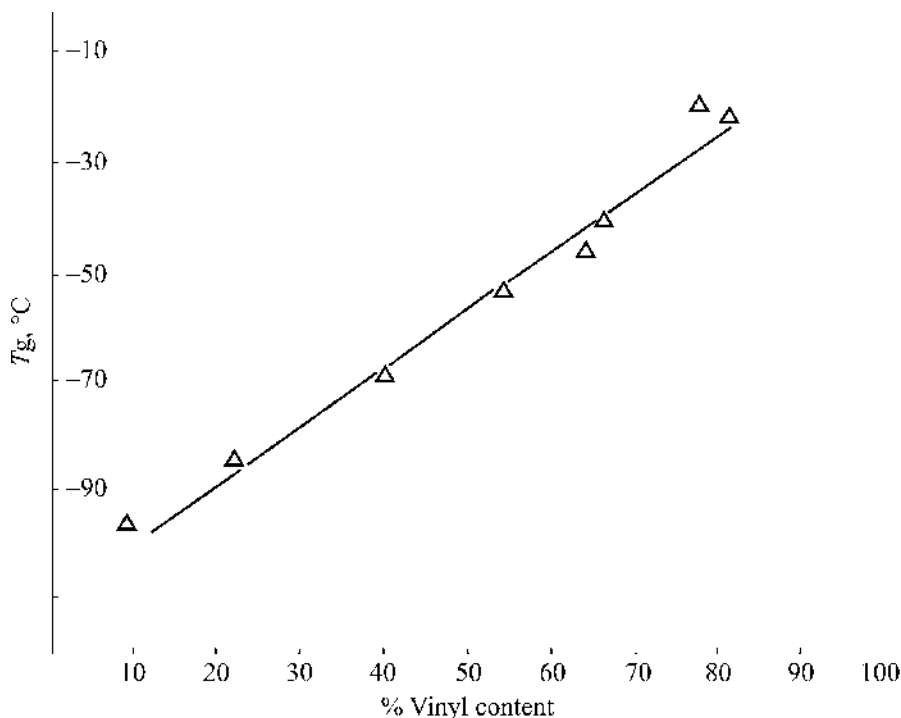


Fig. 3. Variation of T_g with vinyl (1,2) content for polybutadiene. From Ref. 139; reprinted by permission of Plenum Press.

temperature of -113°C , 1,2-polybutadiene has a glass-transition temperature of -5°C (140). This has practical consequences because polybutadienes with medium vinyl contents (eg, 50%) have glass-transition temperatures ($\approx -60^{\circ}\text{C}$) and properties which are analogous to styrene-butadiene rubber. Analogously, the glass-transition temperature of *cis*-1,4-polyisoprene is approx -71°C , a polyisoprene with 49% 3,4 enchainment exhibited a T_g of -36°C (141).

Methacrylate Stereochemistry. Like the anionic polymerization of dienes, the anionic polymerization of alkyl methacrylates, especially MMA, is dependent on the counterion, solvent, and to a certain extent temperature (116,142,143). In general, the stereochemistry of the anionic polymerization of alkyl methacrylates in toluene solution with lithium as the counterion is highly isotactic (68–99%) and the isotacticity increases with the steric requirements of the alkyl ester group as shown in Table 11. Isospecificity for polymerizations in toluene is also observed for alkyl sodium initiators (67% mm), but not for potassium or cesium alkyls in toluene. Sterically hindered Grignard reagents, in particular *t*-butylmagnesium bromide or isobutylmagnesium bromide prepared in ether, provide controlled, living polymerizations and highly isotactic polymers (86.7 and 92.5% mm, respectively), provided that excess magnesium bromide is present to shift the Schlenk equilibrium (eq. 54) in favor of RMgBr .

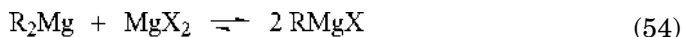


Table 11. Stereochemistry of Anionic Polymerization of Alkyl Methacrylates in Toluene Solution

Alkyl ester	Initiator	Temperature, °C	Microstructure (Triads, %)			Reference
			mm	mr	rr	
CH ₃	DPHLi ^a	-78	86	10	4	85
	C ₄ H ₉ Li		68	19	13	
	Amyl-Na		67	25	9	
	Octyl-K		39	36	25	
	Fluorenyl-Cs		6	50	44	
	<i>t</i> -C ₄ H ₉ Li/(C ₂ H ₅) ₃ Al ^b		0	10	90	
C ₂ H ₅	DPHLi ^a	-70	89	10	1	144
<i>t</i> C ₄ H ₉	C ₄ H ₉ Li		90	5	5	147
(C ₆ H ₅) ₂ CH	C ₄ H ₉ Li		99	1	0	148
(C ₆ H ₅) ₃ C	C ₄ H ₉ Li	-78	96	2	2	149
CH ₃	<i>t</i> -C ₄ H ₉ MgBr		96.7	3	0.3	
	<i>n</i> -C ₄ H ₉ MgBr		11	15.3	73.7	
	<i>i</i> -C ₄ H ₉ MgBr		92.5	5.4	2.1	
	(<i>t</i> -C ₄ H ₉) ₂ Mg		1.4	19.2	79.4	
	(C ₆ H ₅ CH ₂) ₂ Mg		63	24	13	
	<i>t</i> -C ₄ H ₉ Li/Al(BHT)-(iB) ₂ ^c	0	2	26	72	151
	<i>t</i> -C ₄ H ₉ Li/Al(ODBP) ₂ -CH ₃ ^d	-78	11.6	67.8	20.6	152

^a1,1-Diphenylhexyllithium.^b[Al]/[Li] ≥ 2.^c*t*-Butyllithium/(2,6-di-*t*-butyl-4-methylphenoxy)diisobutylaluminum ([Al]/[Li] ≥ 1).^d*t*-Butyllithium/bis(2,6-di-*t*-butyl-phenoxy)methylaluminum ([Al]/[Li] ≥ 2).

In contrast, using di-*t*-butylmagnesium, prepared in ether, PMMA was obtained with predominantly syndiotacticity (79% rr). Highly isotactic PMMA is obtained for ether-free dibenzylmagnesium-initiated polymerization in toluene. Ate-type complexes of *t*-butyllithium with trialkylaluminums ([Al]/[Li] ≥ 2) effect living and highly syndiotactic (≥90% rr) polymerization of MMA in toluene. Analogous complexes of *t*-butyllithium with (2,6-di-*t*-butyl-4-methylphenoxy)-diisobutylaluminum ([Al]/[Li] ≥ 1) at 0°C in toluene generate PMMA with predominantly syndiotactic placements (71–75% rr). In contrast, the ate complex of *t*-butyllithium with bis(2,6-di-*t*-butylphenoxy)methylaluminum forms predominantly heterotactic PMMA (67.8% mr) and poly(ethyl methacrylate) (87.2% mr at -78°C; 91.6% mr at -95°C).

As shown in Table 12, in polar media highly syndiotactic PMMA is formed for free ions and with lithium and sodium as counterions; for sodium, syndiospecificity is observed only in more polar solvents such as dimethoxyethane or in the presence of strongly solvating ligands such as cryptands. Lithium is the smallest alkali metal cation and the most strongly solvated; the equilibrium constants for formation of free ions and solvent-separated ion pairs are largest for lithium and smallest for cesium. Since cesium and potassium have a tendency to form heterotactic placements, it is proposed that contact ion pairs result in predominantly heterotactic placements while solvent-separated ion pairs and free ions form

Table 12. Stereochemistry of Anionic Polymerization of Alkyl Methacrylates in Polar Solvents

Alkyl ester group	Counterion	Solvent	Temperature, °C	Microstructure (Triads, %)			Reference
				mm	mr	rr	
CH ₃	Li	THF	−85	1	15	84	153
			−45	1	22	77	89
			−35	6	32	62	154
			−57	1	16	83	89
	Na	Dioxane	13	10	35	55	154
			−51	4	38	58	155
		THF	−47	22	52	26	89
			−55	2	21	77	156
		[222], DME	−98	1	19	80	89
			−60	9	52	39	153
	K	Dioxane	13	14	56	30	154
			−53	5	52	42	157
	Cs	THF	−66	3	37	60	156
			−98	1	20	79	89
	Free ion	DME	−98	1	20	79	89
			−78	0.2	9.6	90.2	143
	Mg ^a	THF	−78	0.2	9.6	90.2	143
			−78	2	11	87	148
(C ₆ H ₅) ₂ CH	Li	THF		94	4	2	
(C ₆ H ₅) ₃ C							
(CH ₃) ₃ C	Li		−40	12	49	39	89
			−48	6	65	29	
			−42	4	51	45	
			−55	4	17.5	78.5	143

^aPolymerization initiated by *n*-C₄H₉MgBr in the presence of 2 equiv of TMEDA.

predominantly syndiotactic placements in polar media. These results are general for a variety of alkyl methacrylates; even diphenylmethyl methacrylate gives 87% syndiotactic triads in THF with lithium as counterion at −78°C. However, the exception is trityl methacrylate which forms 94% isotactic triads under the same conditions and also in toluene.

A variety of stereoregulating mechanisms have been invoked to explain the stereochemistry of anionic polymerization of alkyl methacrylates (158–160). As discussed earlier (161), although syndiotactic diads are thermodynamically slightly favored over isotactic diads, the free-energy differences are so small that the formation of stereoregular chains must be kinetically controlled. The kinetic control arises from the differences in free energies of activation ($\Delta\Delta G^\ddagger = \Delta G_{\text{iso}}^\ddagger - \Delta G_{\text{syndio}}^\ddagger$) with respect to addition of a monomer unit to form an isotactic versus a syndiotactic diad. Relatively small activation energy differences can lead to large differences in the stereochemistry of propagation. Thus, a change in free energy of activation difference of only 5.4 kJ/mol (1.3 kcal/mol) can change the stereochemistry from 50/50 = iso/syndio to 90/10 = iso/syndio. Since only limited tools are available to predict or understand the physical and chemical basis of such factors as solvation, particularly those associated with small energy differences of this order of magnitude, it is prudent to limit phenomenological interpretations of these stereochemical effects. Thus, any explanation of the

Table 13. Stereochemistry of Polystyrenes Prepared with Anionic Initiators^a

Counterion	Solvent	Temperature, °C	Stereochemistry		
			mm	mr	rr
Li	THF	−78	0.10	0.32	0.58
		20	0.12	0.37	0.51
	Toluene	−20	0.13	0.42	0.45
		20	0.07	0.41	0.52
K	THF	−78	0.09	0.34	0.57
Cs	THF	−78	0.14	0.35	0.51
Na	Toluene	10	0.15	0.40	0.45
K			0.22	0.37	0.41
Rb			0.21	0.44	0.35
Cs			0.24	0.41	0.35

^aRefs. 162 and 163.

predominantly syndiotactic polymerization stereochemistry in THF with lithium as the counterion (84% rr at −85°C) is tempered by the fact that the stereochemistry for the free-radical polymerization of MMA is also highly syndiotactic (78.5% at −55°C) (139). Many factors such as polar monomer coordination and interaction of the counterion with the chain end and with the penultimate groups have been invoked to explain the formation of isotactic polymers in non-polar media. The coordination of the penultimate ester group with the lithium ester enolate group at the chain end would dictate a meso placement. This simple picture, however, does not take into account the fact that these lithium ester enolates are highly associated in hydrocarbon solution and in polar media such as THF (87).

The control of PMMA stereochemistry is important because the glass-transition temperature of PMMA strongly depends on the microstructure (143). The measured T_g for 99% mm PMMA is reported to be 50°C, and the T_g for PMMA with 96–98% rr triads is 135°C. To obtain a PMMA with higher upper use temperature, polymers with the highest syndiotactic microstructure are required.

Styrene Stereochemistry. The effect of counterion, solvent, and temperature on the stereochemistry of anionic polymerization of polystyrene is shown in Table 13. The principal conclusion is that the stereoregularity of polystyrenes prepared by anionic polymerization is predominantly syndiotactic and that the stereoregularity is surprisingly independent of the nature of the cation, the solvent and the temperature, in contrast to the sensitivity of diene stereochemistry to these variables.

When small amounts of water were deliberately added to butyllithium in hydrocarbon solution, it was possible to prepare polystyrene with as much as 85% polymer that was insoluble in refluxing methyl ethyl ketone and identified as isotactic polystyrene by x-ray crystallography (164). Isotactic polystyrene (10–22% crystalline) can be prepared when lithium *t*-butoxide is added to *n*-C₄H₉Li initiator and the polymerization in hexane (styrene/hexane = 1) is effected at −30°C (165). This polymerization becomes heterogeneous and is quite slow (after 2–5 days, 50% monomer conversion; 20–30% conversion to isotactic polymer).

Vinylpyridines. The stereochemistry of anionic polymerization of 2-vinylpyridine is predominantly isotactic for most polymerization conditions as shown by the data in Table 14 (166). The coordination of the penultimate pyridyl nitrogen with the magnesium ester enolate at the chain end has been invoked to explain the high meso triad content for initiation by Grignard-type reagents in hydrocarbon solution. The absence of this interaction for 4-vinylpyridine results in almost atactic polymer stereochemistry.

Copolymerization

Relatively few comonomer pairs undergo anionic copolymerization to incorporate significant amounts of both monomers into the polymer chains (167). In general, the comonomer that is most reactive (lowest pK_a value for the conjugate acid of the propagating anion; see Table 1) will be incorporated to the practical exclusion of the other comonomer. Comonomer pairs that can be effectively copolymerized include styrenes with dienes and methacrylates with acrylates, ie, comonomer pairs with similar reactivity.

Anionic copolymerizations have been investigated by applying the classical Mayo–Lewis treatment that was originally developed for free-radical chain reaction polymerization (168). The copolymerization of two monomers (M_1 and M_2) can be uniquely defined by the following four elementary kinetic steps, assuming that the reactivity of the chain end (M_1^- or M_2^-) depends only on the last unit added to the chain end; ie, there are no penultimate effects.

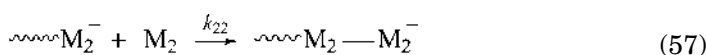
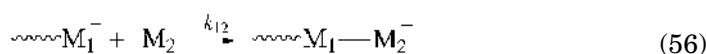
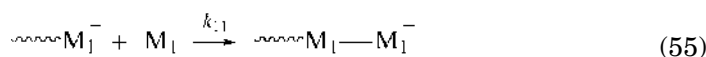


Table 14. Stereochemistry of Poly(2-vinylpyridine)s Prepared with Anionic Initiators^a

Counterion	Solvent	Temperature, °C	Stereochemistry		
			mm	mr	rr
Li	Toluene	−78	0.69	0.21	0.10
^b	THF	−78	0.44	0.44	0.12
^c			0.56	0.36	0.08
			0.26	0.51	0.23
Mg	Toluene	25	0.76	0.18	0.06
	THF	25	0.37	0.56	0.07
Rb	THF	−78	0.50	0.36	0.14

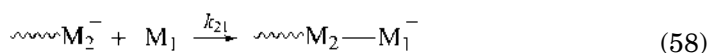
^aRef. 166.

^b[LiB(C₆H₅)₄]/[I] = 2.0.

^cPoly(4-vinylpyridine).

Table 15. Anionic Copolymerization Parameters in Hydrocarbon Solution with Alkylolithium Initiators

M ₁	M ₂	Solvent	Temperature, °C	r ₁	r ₂	Reference
Butadiene	Styrene	None	25	11.2	0.04	169
		Benzene	25	10.8	0.04	
		Cyclohexane	25	15.5	0.04	
		Hexane	0	13.3	0.03	
			25	12.5	0.03	
			50	11.8	0.04	
		THF	−78	0.04	11.0	
			0	0.2	5.3	
			25	0.3	4.0	
		Diethyl ether	25	1.7	0.4	
		Triethylamine	25	3.5	0.5	
		Anisole	25	3.4	0.3	
		Diphenyl ether	25	2.8	0.1	
	Isoprene	Hexane	20	2.72	0.42	170
	1,1-Diphenylethylene	Benzene	40	54	~0	171
Isoprene	Styrene	THF	0	0.13	~0	172
		Benzene	30	7.7	0.13	
		Toluene	27	9.5	0.25	
		Cyclohexane	40	16.6	0.046	
		THF	27	0.1	9	
		1,1-Diphenylethylene	40	37	~0	
		THF	0	0.12	~0	
		THF	0	0.12	~0	
Styrene	1,1-Diphenylethylene	Benzene	30	0.7	~0	177
		THF	30	0.13	~0	



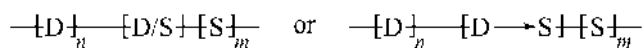
From these four basic kinetic equations, the Mayo–Lewis instantaneous copolymerization equation can be derived as shown below:

$$\frac{d[\text{M}_1]}{d[\text{M}_2]} = \frac{[\text{M}_1](r_1[\text{M}_1] + [\text{M}_2])}{[\text{M}_2](r_2[\text{M}_2] + [\text{M}_1])} \quad (59)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and $d[\text{M}_1]/d[\text{M}_2]$ represents the instantaneous copolymer composition. The monomer reactivity ratios r_1 and r_2 represent the relative reactivity of each growing chain end for addition of the same monomer compared to crossover to the other monomer. Representative monomer reactivity ratios for anionic copolymerizations are listed in Table 15. The applicability of standard copolymerization theory to anionic polymerization has been considered in detail. Equations 55–58 represent an oversimplification since the chain ends are aggregated in hydrocarbon solution and there is a spectrum of ion pairs and free ions in polar media.

In most copolymerizations, $r_1 \neq r_2$ and one monomer is preferentially incorporated into the initially growing polymer. This leads to a depletion of the preferentially incorporated monomer in the feed and the composition of the copolymer formed changes with conversion. For systems undergoing continuous initiation, propagation, and termination, the resulting compositional heterogeneity is intermolecular; ie, the copolymer formed initially is different from the copolymer formed at the end of the reaction. However, in living anionic copolymerization, all of the compositional heterogeneity arising from the disparity in monomer reactivity ratios is incorporated into each growing polymer chain.

Tapered Block Copolymers. The alkyllithium-initiated copolymerizations of styrene with dienes, especially isoprene and butadiene, have been extensively investigated and illustrate the important aspects of anionic copolymerization. As shown in Table 15, monomer reactivity ratios for dienes copolymerizing with styrene in hydrocarbon solution range from approximately 8 to 17, while the corresponding monomer reactivity ratios for styrene vary from 0.04 to 0.25. Thus, butadiene and isoprene are preferentially incorporated into the copolymer initially. This type of copolymer composition is described as either a *tapered block copolymer* or a *graded block copolymer*. The monomer sequence distribution can be described by the structures below:



First there is a diene-rich block; a middle block follows, which is initially richer in butadiene with a gradual change in composition until eventually it becomes richer in styrene; a final block of styrene completes the structure. For a typical copolymerization of styrene and butadiene (25/75, wt/wt), the solution is initially almost colorless, corresponding to the dienyllithium chain ends and the rate of polymerization is slower than the homopolymerization rate of styrene, as shown in Figure 4. The homopolymerization rate constants for styrene, isoprene, and butadiene are $1.6 \times 10^{-2} \text{ L}^{1/2}/(\text{mol}^{1/2} \cdot \text{s})$, $1.0 \times 10^{-3} \text{ L}^{1/4}/(\text{mol}^{1/4} \cdot \text{s})$, and $2.3 \times 10^{-4} \text{ L}^{1/4}/(\text{mol}^{1/4} \cdot \text{s})$, respectively (49). After approximately 70–80% conversion, the solution changes to orange-yellow, which is characteristic of styryllithium chain ends. At the same time, the overall rate of polymerization increases (inflection point). Although the percent conversion at which the inflection point is observed does not appear to depend on solvent, the time to reach this percent conversion is quite solvent-dependent, as shown in Figure 4. Analysis of the copolymer composition indicates that the total % styrene in the copolymer is less than 5% up to approximately 75% conversion (see Fig. 5) (50). When these samples are analyzed by oxidative degradation by ozonolysis, polystyrene segments (corresponding to polystyrene blocks in the copolymer) are recovered only after the inflection point is reached as shown in Figure 5. For a 75/25 (wt/wt) feed mixture of butadiene/styrene, 80% of the styrene is incorporated into the tapered block copolymer as block styrene.

The kinetics of copolymerization provide an explanation for the copolymerization behavior of styrenes with dienes. One useful aspect of living anionic copolymerizations is that stable carbanionic chain ends can be generated and the rates of their crossover reactions with other monomers measured

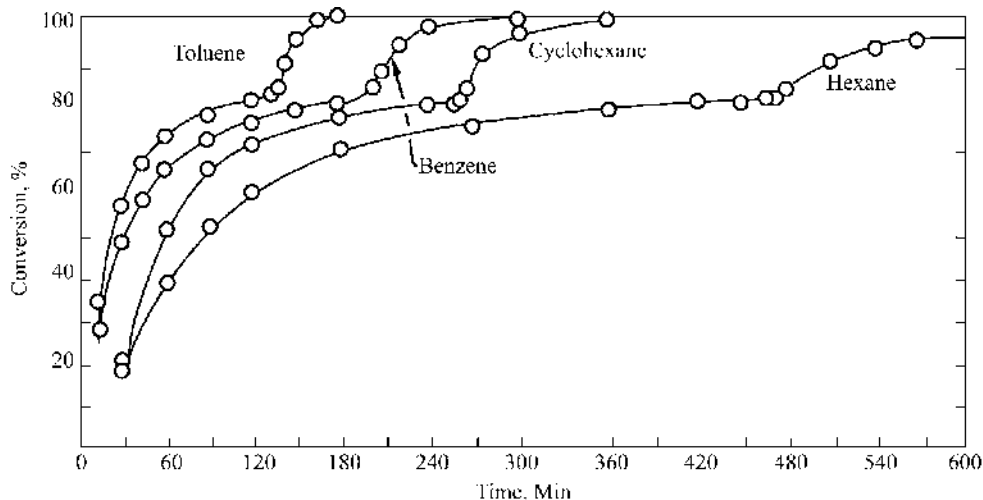
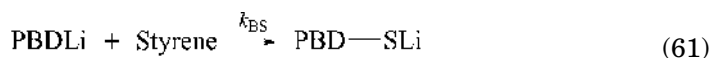
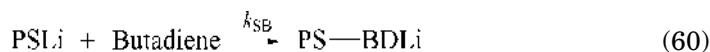


Fig. 4. Copolymerization of butadiene and styrene in different solvents at 50°C. Parts of butadiene/styrene/solvent/*n*-butyllithium = 75/25/1000/0.13 (2.0 mmol). From Ref. 50; reprinted by permission of the Rubber Division of the American Chemical Society.

independently of the copolymerization reaction. Two of the four rate constants involved in copolymerization correspond at least superficially to the two homopolymerization reactions of butadiene and styrene, eg, k_{BB} and k_{SS} , respectively. The other two rate constants can be measured independently as shown in equations 60 and 61:



Kinetic results of a number of independent kinetic studies can be summarized as follows for styrene–butadiene copolymerization (49,178):

$$[1.1 \times 10^2 \text{ L}/(\text{mol}\cdot\text{s})] \gg [4.5 \times 10^{-1} \text{ L}/(\text{mol}\cdot\text{s})] > [8.4 \times 10^{-2} \text{ L}/(\text{mol}\cdot\text{s})] > [6.6 \times 10^{-3} \text{ L}/(\text{mol}\cdot\text{s})]$$

This kinetic order contains the expected order of homopolymerization rates, ie, $k_{SS} > k_{BB}$. The surprising result is that the fastest rate constant is associated with the crossover reaction of the poly(styryl)lithium chain ends with butadiene monomer (k_{SB}); conversely, the slowest reaction rate is associated with the crossover reaction of the poly(butadienyl)lithium chain ends with styrene monomer (k_{BS}). Similar kinetic results have been obtained for styrene–isoprene copolymerization.

In polar media, the preference for diene incorporation is reduced as shown by the monomer reactivity ratios in Table 15. In THF, the order of monomer reactivity ratios is reversed compared to that in hydrocarbon media. The monomer

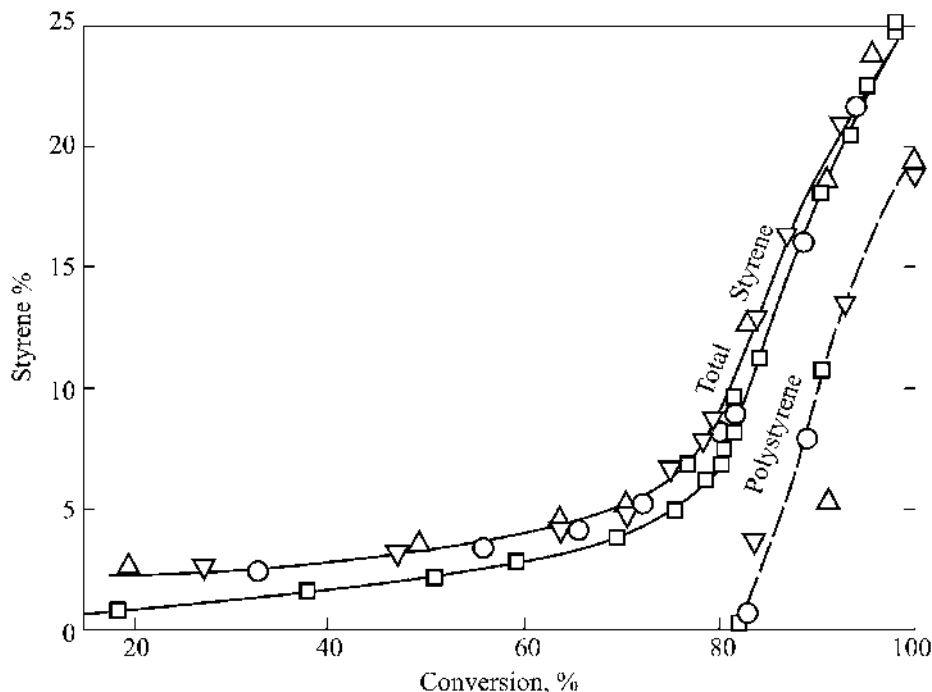


Fig. 5. Copolymerization of styrene from butadiene–styrene (75/25) at 50°C. □ Hexane; Δ cyclohexane; ▽ benzene; ○ toluene. From Ref. 50; reprinted by permission of the Rubber Division of the American Chemical Society.

reactivity ratios for styrene are much larger than the monomer reactivity ratio for dienes.

The counterion also has a dramatic effect on copolymerization behavior for styrene and dienes (38). It is particularly noteworthy that the monomer reactivity ratios for styrene ($r_S = 0.42$) and butadiene ($r_B = 0.30$) are almost equal for copolymerization in hydrocarbon at 30°C using an organosodium initiator; however, butadiene is incorporated predominantly as vinyl units (60% 1,2). In contrast, initial styrene incorporation is observed for analogous organopotassium initiators ($r_S = 3.3$) and butadiene ($r_B = 0.12$).

Tapered butadiene–styrene copolymers are important commercial materials because of their outstanding extrusion characteristics, low water absorption, good abrasion resistance, and good electrical properties. Tapered block copolymers are used for wire insulation and shoe soles (after vulcanization) as well as for asphalt modification (179).

Random Styrene–Diene Copolymers. Random copolymers of butadiene (SBR) or isoprene (SIR) with styrene can be prepared by addition of small amounts of ethers, amines, or alkali metal alkoxides with alkyllithium initiators. Random copolymers are characterized as having only small amounts of block styrene content. The amount of block styrene can be determined by ozonolysis or, more simply, by integration of the ^1H nmr region corresponding to block polystyrene segments ($\delta = 6.5\text{--}6.94$ ppm) (180). Monomers reactivity ratios of

$r_B = 0.86$ and $r_S = 0.91$ have been reported for copolymerization of butadiene and styrene in the presence of 1 equiv of TMEDA ($[TMEDA]/[RLi] = 1$) (181). However, the random SBR produced in the presence of TMEDA will incorporate the butadiene predominantly as 1,2 units. At 66°C, 50% 1,2-butadiene microstructure will be obtained for copolymerization in the presence of 1equiv of TMEDA (134). In the presence of Lewis bases, the amounts of 1,2-polybutadiene enchainment decreases with increasing temperature.

In general, random SBR with a low amount of block styrene and low amounts of 1,2-butadiene enchainment (<20%) can be prepared in the presence of small amounts of added potassium or sodium metal alkoxides. Using 0.2 equiv of sodium 2,3-dimethyl-2-pentoxide, the monomer reactivity ratios for alkyllithium-initiated SBR were found to be $r_B = 1.1$ and $r_S = 0.1$ (182). The resulting copolymer had only 5% block styrene and 18% 1,2-vinyl microstructure. The unique copolymerization behavior in these mixed alkali metal alkoxide/organolithium systems may be due to the formation of cross-associated adducts.

Commercial anionically prepared, random SBR polymers (solution SBR) prepared by alkyllithium-initiated polymerization typically have 23% *cis*-1,4, 49% *trans*-1,4, and 28% vinyl microstructure compared to 10% *cis*-1,4, 70% *trans*-1,4, and 20% vinyl microstructure for emulsion SBR with the same comonomer composition. Solution SBRs typically have branched architectures to eliminate cold flow. Compared to emulsion SBR, solution random SBRs require less accelerator and give higher compounded Mooney viscosity, lower heat buildup, increased resilience, and better retread abrasion index (179). Terpolymers of styrene, isoprene, and butadiene have been prepared using a chain of single-stirred reactors, whereby the steady-state concentration of each monomer and Lewis base modifier at any degree of conversion can be controlled along the reactor chain (183).

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ANNEALING

Introduction

The annealing of plastics can be defined as a secondary process wherein the plastic is brought to a certain temperature, kept there for a time, and then cooled to

room temperature. The primary reasons for annealing include the reduction or removal of residual stresses and strains, dimensional stabilization, reduction or elimination of defects, and improvement of physical properties (1).

In the plastics industry, annealing has been applied primarily to thermoplastic polymers, block copolymers, and amorphous or semicrystalline polymer blends (2–56).

Although the main effect of annealing is to increase the density of the plastic, work indicates that other changes occur as well (57–64). The annealing of semicrystalline polymers may change the crystal structure, the degree of crystallinity, the perfection of the crystals, and the orientation of both the crystalline and amorphous material (2–22).

The annealing of polymer blends and block copolymers may result in enhanced phase and microphase separation, and may also change the surface of the materials, making them more or less susceptible to stress crazing and stress cracking (23–39). The same problem may occur in amorphous and crystalline plastics.

In most cases, the induced stresses and orientation may be insignificant, and no annealing is required if proper processing conditions have been used during fabrication. However, annealing becomes necessary when the molded parts are excessively stressed, when maximum dimensional stability and heat resistance are required, or when certain properties must be enhanced. Improper annealing may also cause deterioration in performance.

Theoretical Background

In all forming operations, such as injection molding (qv) or extrusion (qv), frozen-in orientation and residual stresses arise from two sources. The first is the flow-induced stresses (shear and normal), which occur during flow through restricted channels and lead to the orientation of the polymer chains; if these stresses do not completely relax during the subsequent cooling period, they appear as frozen-in birefringence and flow stresses in the plastic. In the case of injection molding, extensional flow of the melt front also causes birefringence. The second source is the differential density or shrinkage and the viscoelastic behavior of the plastic during nonuniform cooling through a glass-transition or a crystallization temperature, resulting in thermal stresses and birefringence. Recent work suggests that coupling between these various stresses occurs during cooling and annealing. The degree of coupling appears to depend upon molecular conformers and is not yet completely understood. The frozen-in strain pattern in injection-molded parts is more complex than in extruded film or sheet.

Stresses may be induced in polymeric glasses by cooling from above their glass transition. This is best understood by reference to the volume–temperature curves in Figure 1. If the polymer is cooled rapidly from temperature T^* to some temperature T_1 , then its outer surface is transformed to a rigid glass while the core is still above its glass transition. The result is differential contraction between the outer surface and the core because of their different thermal coefficients of expansion. The volume–temperature behavior of the skin is represented by the line ABC in Figure 1. Since the surface is restrained from shrinking by

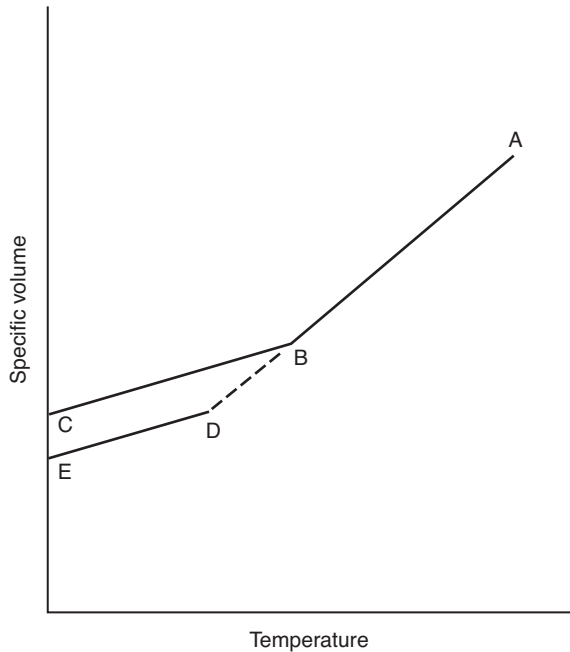


Fig. 1. Hypothetical curves for the specific volume–temperature behavior of fast and slowly cooled amorphous plastics. ABC = fast cooling; ADE = slow cooling.)

the core, it is in a state of tension. The core cools more slowly and follows the line ADE. During this cooling period, skin and core undergo a reduction in volume accompanied by changes in the stress profiles.

Inasmuch as the core ultimately shrinks more than the skin, the resultant stress profile is inverted, as shown by curve A in Figure 2, ie, the skin is in a state of compression and the core in a state of tension. If high packing pressures are required to fill the mold, when the part is removed, it swells and the residual stress profile shifts to that shown by curve B.

It is well known that during injection molding a solid layer is formed when the polymer melt front reaches the mold wall. The thickness of this layer is determined by the mold, the melt temperature, the mold temperatures, and the flow rate. The remaining space in the mold is subsequently filled by passage of the melt through this outer layer. These layers, in contrast to the core, are quenched in position and do not have time to undergo significant relaxation.

From several detailed studies, an expression for the expected residual stress profile has been derived using the method of finite elements:

$$\Delta\sigma_i = \left(\frac{1}{1-\mu} \right) [(\alpha_i \Delta T_i + \Delta\varepsilon) E_i - \Delta\sigma_{i,\text{vol}}] - \Delta P$$

where i denotes the i th section, α the thermal coefficient of expansion, μ Poisson's ratio, E the elastic modulus (stress relaxation), $\Delta\sigma$ the residual stress, and $\Delta\varepsilon$ the shrinkage (65). The first term in square brackets describes the stresses caused by the thermal gradient, and the second, the stress relaxation. The last term, ΔP ,

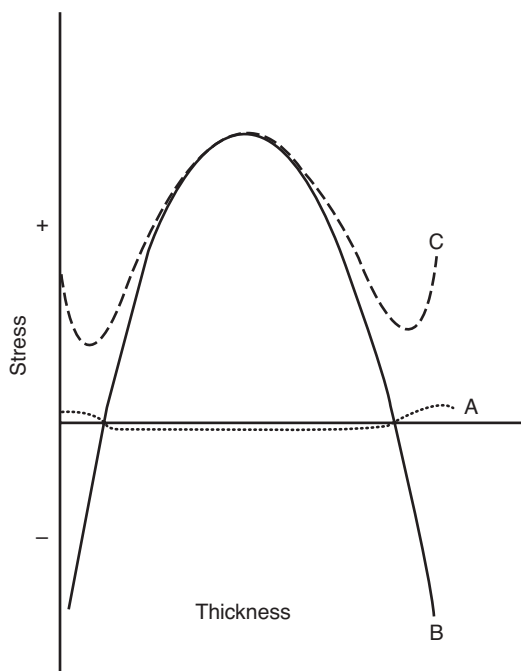


Fig. 2. Curve A shows the expected stress distribution through the thickness of an amorphous thermoplastic after the surface has been quenched below its glass transition, while the core is still above its glass transition; curve B depicts the new stress distribution through the thickness of the sample described after the entire sample has been cooled below its glass transition and has reached equilibrium; curve C depicts the stress distribution through the thickness of an amorphous thermoplastic that was molded at an elevated packing pressure, cooled below its glass transition, and removed from the mold.

is the hydrostatic stress that the plastic is exposed to during molding and before the opening of the mold. Under normal molding conditions, ie, low pressures and high temperatures, the residual stresses are compressive at the surface and tensile in the interior. High molding pressures and longer holding times can lead to an inversion of the stress profile, ie, tensile at the surface and compressive in the interior. More complicated profiles have been observed, but they are not understood.

In the case of semicrystalline polymers, densification results from crystallization and, as in the case of the glassy polymers, changes occurring in the skin and in the core cause stresses. However, the situation is more complex because of the different mechanisms of crystallization, ie, row nucleation, and the fact that secondary crystallization may occur minutes, hours, or days later (2–23).

In the case of polymer blends and block copolymers, densification may be the result of phase separation, microphase separation, crystallization, or simple glass formation. Such materials obviously exhibit more complex behavior because of these different densification modes, which can be affected by fabrication conditions and the thickness and geometry of the part and the plastic (24–31).

In forming parts by injection molding, variations in part thickness can enhance shear stresses and pressure differentials that may cause internal flow (66).

Vacuum thermoforming and other thermoforming procedures can lead to orientation and thermal stresses. Internal stresses are also introduced during the machining (qv) of molded parts, ie, during cutting, drilling, and sawing. Stresses may also be introduced when parts are welded by a linear vibration process or bonded by strong adhesives. These stresses act like the frozen-in stresses set up during forming operations.

Failure Modes

Molded thermoplastics containing residual stresses and frozen-in orientation undergo stress crazing or stress cracking when placed in the wrong environment or momentarily exposed to certain liquids; these conditions represent the primary modes of plastics failure. Systematic studies of the morphology of crazes by various experimental techniques indicate that they are composed of drawn fibrils and voids (a foam structure) with dimensions on the order of 10–20 nm. It has also been shown that the stress-strain behavior of crazes is elastoplastic and that crazes precede brittle failure (66). Empirical correlations of the tendency toward crazing have been suggested, and it appears that this phenomenon is a reflection of the glass transition of the plastic, its yield stress, and its cohesive energy density (67).

In contrast to stress crazing, stress cracking seems to be related to the onset of crystallization within amorphous materials or to changes between contiguous crystalline phases. Thermooxidative and photolytic scission of tie chains between crystalline components can also result in stress cracking.

Principles

Initially, annealing of plastics was of industrial interest, but it has become of serious concern to scientists and engineers in academic and government laboratories, and has been named physical aging (1,61,62). Although the work has focused on the behavior of glasses, it increases understanding of the behavior of semicrystalline polymers, block copolymers, and polymer blends because of the development of new experimental techniques to monitor the changes.

For example, Fourier-transform ir has been used to monitor the conformer population in poly(ethylene terephthalate) (PET) during annealing, and it was observed that the percentage of the gauche population changes dramatically, but the amount of trans isomer remains essentially constant. Correspondingly, solid-state nmr on PET indicates that the motion of methylene groups becomes more restricted upon annealing (60). Volumetric, mechanical, calorimetric, and optical methods have been used to monitor structural relaxation processes. Poly(vinyl acetate), poly(methyl methacrylate), bisphenol A polycarbonate, poly(ethylene terephthalate), and poly(vinyl chloride) have been studied by these techniques. New theories and models have emerged to explain the thermodynamics and the relaxation behavior of such systems. Although free

volume, ie, the difference in volume of a glass at equilibrium and as received, had long been used to explain annealing, the newer theories invoke molecular conformers and their interactions with the local environment (68–78). Molecular modeling and computer simulation of the formation and aging of glasses have also been discussed, but differences exist between experiment and simulation.

The typical behavior of amorphous polymers, such as poly(vinyl acetate), polystyrene, poly(methyl methacrylate), and bisphenol A polycarbonate is shown in Figure 1. The upper curve (ABC), obtained by rapid cooling (quenching), results in a material of lower density than that obtained by slow cooling (ADE). The lower density of the quenched material was previously interpreted in terms of free volume, but is now associated with the freezing-in of higher energy states. As a result, the tendency of material to return to a lower energy state is impeded by the high viscosity of the polymer, 1 Pa·s (10 P). The glass transition of the quenched polymer is higher than that of the slowly cooled one.

There are two points of view with regard to the static and kinetic properties of glass-forming polymers. The first one, involving the concept known as free volume, has been used for several decades to interpret physical measurements. Several definitions of free volume have been proposed and are interconnected in that all involve an excess volume. For example, free volume has been defined in terms of a van der Waals hard-sphere model, in terms of the fluctuations in volume and energy, in terms of mobility coefficients, and in terms of the volume differences of the glass and liquid or the glass and its crystal. The main reason for its acceptance have been its simplicity and utility in correlating large amounts of data.

A theory proposes that the underlying mechanisms reflect a single sub-molecular event, which couples with the local environment to yield a complex relaxation spectrum. This theory may provide a “molecular connection” to bulk phenomena, such as the formation and relaxation behavior of glasses. For example, parameters evaluated from dielectric data have been used to calculate the volumetric relaxation behavior of a glass (78). The interpretation of stress relaxation, creep, and mechanical transitions has also been reported (61).

The annealing of semicrystalline plastics may change the degree of crystallinity, the size and orientation of the crystallites, their contiguous structural morphology, and number of tie chains between the crystallites (4).

When a semicrystalline polymer is cooled below its crystallization temperature, the onset of crystallization is controlled by the temperature interval below the melting point and the formation of critical nuclei or the presence of foreign nuclei (16).

Growth of the nuclei can occur by deposition of polymer chains on the nuclei surface, followed by folding into a structure like a fireman’s hose or by a vertical alignment like a box of spaghetti. In either case, tie chains occur between the crystallites. For clean materials, the rates of nucleation and growth generally follow bell-shaped curves between the melting point and the glass transition of the polymer. The temperatures at which the maximum rates of nucleation and growth occur may be widely separated. For example, if poly(chlorotrifluoroethylene) or poly(butylene terephthalate) are thermally quenched from above their melt temperature T_m to below their glass transition

T_g , nuclei are formed, but little, if any, crystallization occurs. Upon annealing, crystallites grow and the mechanical properties change significantly.

If nucleating agents have been added to the crystalline polymer, crystallization may occur just below the crystallization temperature, may be much faster, and may result in smaller crystallites more uniformly dispersed in the plastic, which tends to make the plastic zone flexible and more resistant to stress cracking (16). The nucleation and growth of new phases have been discussed in terms of the classical Flory-Huggins theory (62).

In many cases, the annealing of polymer blends and block copolymers involves the same principles discussed for glassy and crystalline polymers. However, polymer blends that undergo phase separation and block copolymers that undergo microphase separation are more complex, because the degree of phase separation and the morphology of the blends are affected by the processing conditions, the mode of separation, and, obviously, the annealing conditions (25,66).

Commercial polymer blends and block copolymers typically contain other low and intermediate molecular-weight additives, such as plasticizers, flame re-tardants, and uv and thermal stabilizers. During annealing, phase and micro-phase separation may be enhanced, and bleeding of the additives may be observed. The morphologies of polymer blends and block copolymers can be affected by processing and quenching conditions. If the melt viscosities of the polymers are not matched, compositional layering perpendicular to the direction of flow may occur (66,67). As in the case of crystalline polymers, the skin may be different both in morphology and composition (64). Annealing may cause more significant changes in the skin than in the interior (4).

Equipment

The equipment used for annealing is similar to that used for preheating thermoplastic sheets, rods, or tubes before shaping. Depending on the annealing medium, ie, liquid or air, different heating units are used.

The equipment for liquid baths, ie, water, oils, or waxes, consists of tanks or troughs that should be of suitable size. To ensure uniform heating and maintain the required annealing temperature, a proper recirculating system and adequate temperature control should be provided. The temperature-control system should consist of a sensing element, a controller that interprets the information received from the sensing element, and a heating or cooling element regulated by the controller. Provision must be made for removing or recycling the liquid to prevent temperature build-up or localized hot spots.

When air is the heating medium, circulating-air or air-flow ovens have proved most suitable. An air-flow oven consists typically of two compartments: in one, the air is heated to the required temperature by gas or electricity, and in the other, the material is heated by hot air at the annealing temperature for the required time. To avoid dead spaces or hot spots, the hot air is rapidly circulated through the two compartments with compressors or blowers. If the temperature is carefully controlled in every part of the oven, the material can be left in the oven for a considerable time without undue deterioration.

The other methods of heating require convection ovens, infrared ovens, and dielectric heating devices. However, the air-flow ovens are preferable, despite their low heating rates. For the annealing of large shapings, air-flow ovens are almost essential, because the temperature must be uniform throughout. To secure uniform temperature, careful design of racks and ease of parts handling are very important. The clamping necessary for holding or suspending the parts in the oven should not exert too high a pressure, or deformation or distortion occurs during annealing.

A proper design should permit free air circulation to avoid formation of pockets of dead air where solvent vapors can accumulate. It should also provide for bleeding some air and admitting fresh air to permit air exchange. This prevents the accumulation of fumes and solvent vapors, if cemented parts are annealed.

After annealing, cooling must be very slow and gradual to avoid reintroducing stresses and thus defeating the purpose of annealing. Slow cooling is accomplished by immediately packing the parts in such a way as to provide adequate insulation or by allowing the parts to cool in the air oven or in a liquid bath with the heat turned off.

Occasionally, as in the case of films, annealing is done on hot rolls moving very slowly. This process is limited to minimum thicknesses of 3 mm, since thinner materials are distorted. In blown-film extrusion, the film is cooled by air flowing through the annealing chamber (a tube placed between the die and the air ring). The cooling rate is controlled in such a way that the film surface can level out; rapid cooling preserves surface roughness developed during extrusion.

Methods

Theoretically, the most desirable annealing temperatures for amorphous plastics, some polymer blends, and block copolymers is above their glass transition, where the relaxation of stress and orientation is the most rapid. However, the required temperatures may cause excessive distortion and warping. To anneal as quickly as possible, the plastic is heated to the highest possible temperature at which dimensional changes owing to strain release are within permissible ranges. This temperature can be determined by placing the plastic part in an air oven or liquid bath and gradually raising the temperature by intervals of 3–5°C until the maximum allowable change in shape or dimension occurs. This distortion temperature is dictated by thermomechanical processing history, geometry, thickness, weight, and size. The annealing temperature should then be fixed about 5°C lower.

The time necessary for annealing at the distortion temperature varies with the thickness and geometry of the part, the annealing medium, and the degree of relief required. Optimum annealing conditions must be determined by experiment.

When a plastic part is annealed, volume changes depend upon the thermomechanical history, the annealing temperature and time, and the plastic's properties. In general, densification occurs, but may be preceded by a rarefaction.

If the specific volume–temperature curves for various thermal histories are available, the time and temperature necessary to produce a given density can be

estimated from the relation

$$\frac{V_e - V}{V_e - V_t} = \exp - (kt) \left(\frac{1}{1-n} \right)$$

where V_e is the equilibrium volume, V the starting volume, V_t the volume at time t , k a rate constant, and n a number between 0 and 1.

The annealing of crystalline polymers, polymer blends, and block copolymers may create changes in the degree of crystallinity or perfection of crystals and the degree of phase or microphase separation.

In these systems, crystallization and phase and microphase separation are based on two mechanisms: the first, ie, nucleation and growth, involves the formation of critical nuclei or the presence of heterogeneous nuclei on which growth may occur, and the second, ie, spinoidal decomposition, involves a small fluctuation in density or composition spread sinusoidally at some characteristic wavelength over the body. In this case, the phases grow at a uniform distance apart in the body.

Annealed plastics tend to be stiffer and more brittle than the unannealed, but this may depend upon the plastic, the fabrication conditions, and the annealing process. Under unfavorable conditions, annealing can be deleterious.

Cooling rates vary with thickness. In general, higher cooling rates can be used for thin sections, lower rates for thicker ones. Cooling rates for crystalline polymers, polymer blends, and block copolymers are somewhat less critical than for amorphous plastics.

Additives (qv) modify flow and impact resistance and increase uv or oxidative resistance. Performance can be impaired or enhanced as a result of changes in phase or microphase separation, morphology, or residual stress and frozen-in orientation.

Media

The medium affects annealing time. In a liquid medium, short times are required, because the heat transfer is much faster than in air. In addition, a more uniform distribution of temperature is achieved without additional labor cost when the molded part is immediately placed into the bath. Annealing time is, of course, also affected by the thermal properties of the liquid and the annealed article. There are, however, disadvantages to liquid media. Frequently spotting occurs, which cannot be overcome without extra cost. Using oil may present difficulties in handling, and wiping the articles may be required. Although hot air is widely used, immersion in liquid often gives better results. In fact, some plastics, such as nylon and acetal resins, cannot be annealed in hot air because of possible oxidation. These are usually annealed in an oil bath through which an inert gas is bubbled.

A suitable annealing liquid should have an adequate heating range and stability, as well as complete inertness to the annealed plastic. The liquid should also be free of noxious fumes and should not present a fire hazard. Water is a good annealing liquid, but its boiling point is often too low. A small amount of

detergent is usually added to promote wetting and rapid draining. For maximum dimensional stability, the liquid bath should have a temperature 25–30°C above the temperature at which the articles are to be used.

Effectiveness

Annealing is a secondary finishing operation that requires time, equipment, energy, and personnel. For maximum effectiveness, conditions should be determined carefully using quality-control methods. A common procedure is to monitor the process in a solvent-induced stress-crazing or stress-cracking test, in which samples are exposed to a liquid or mixture of liquids. The degree of strain or stress needed to cause failure with a given liquid is calibrated with Bergen jigs. However, such tests can only be performed on simple parts. The strip-removal method and determination of the birefringence have also been used. Strip removal was developed in the early 1950s. Its difficulties are created by the need to section samples carefully without modifying the intrinsic stresses imposed by the cutting process and to evaluate the elastic moduli of the skin and core. On the other hand, birefringence measurement is nondestructive and more easily performed, but is currently limited to transparent or translucent materials. Determination of stress requires a separation of the contribution of the thermal and orientational birefringence. Determination of the stress-optical or the stress-fringe coefficient is also required; in some materials, this coefficient is dependent upon the degree of orientation.

Other techniques, such as dsc, sonic modulus, infrared dichroism, fluorescence depolarization, and Brillouin scattering may provide additional data (50,79–87).

Examples

In general, manufacturers of thermoplastics provide recommended annealing procedures. However, because they have little control over the mold design, the processing conditions, the use of regrind, etc, their technical manuals contain a disclaimer. Consequently, data from the technical literature have been chosen for discussion here.

Bisphenol A polycarbonate, developed in the mid 1950s, is an optically clear thermoplastic. In contrast to poly(methyl methacrylate) and polystyrene, it is ductile. However, when annealed below its glass transition, the notched Izod impact strength fell from 854 J/m (16 ft-lb/in.) to 107 J/m (2 ft-lb/in.) for 3-mm samples. Early studies concentrated on possible physical, chemical, and morphological changes. For example, it was found that irradiation causes a decrease in the molecular weight and in the Izod impact strength. Later work demonstrated that annealing increases density, tensile yield stress, flexural yield stress, and glass-transition temperature, but reduces impact strength, elongation, and creep rate (49,85,86). Dynamic mechanical spectra of annealed samples show a small peak just below the glass transition, whereas dsc indicates an excess enthalpy just above the glass transition (56). Fatigue-crack propagation studies on

annealed samples indicate a change in effective fracture toughness and that the fatigue properties are strongly affected. The rate at which these properties change depends upon the annealing temperature and the molecular weight of the resin (49,67). More recent studies have centered on residual stresses, shear and dilational processes, crazing, and the use of fracture mechanics.

Early annealing studies of semicrystalline polymers addressed films in which the degree of crystallinity and the orientation of the crystallites were considered of primary importance. Subsequent work on injection-molded parts of polypropylene, an ethylene-propylene copolymer, and poly(butylene terephthalate) have revealed that complex skin, skewed zone, and core are altered by annealing (3). In the case of poly(butylene terephthalate), the skin was shown to be of lower density, and correspondingly, of lower crystallinity than the core (4). Upon annealing, the skin density increased.

The annealing of polymer blends has not yet been extensively studied. The work on blends of bisphenol A polycarbonate and copolyesters best exemplifies the effects of annealing on a number of properties. It indicates that densification may occur by two different mechanisms: normal densification of a glass and crystallization. The observed degree of crystallization after annealing depends upon the initial blend composition, and the annealing temperature and time, modulus, yield strength, and Izod impact strength are affected (25).

Economic Aspects

Annealing, as a secondary operation adding to the cost of the fabrication of thermoplastic parts, is considered only if there is evidence of part failure caused by residual stress, frozen-in orientation, or objectionable dimensional changes. Every effort should be made by the fabricator to minimize the introduction of excessive stresses and orientation during fabrication through the use of correct mold designs and proper molding conditions. With the development of faster processing equipment, computer controls, and a better understanding of the effects of processing, annealing will continue to play an important role in plastics technology.

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ANTIFOAMING AGENTS

Introduction

Foams are generated by incorporation of air into a liquid by mechanical ways such as agitation, mixing, recirculation, and air bubbling, by physical ways such as pressure variation and change in gas solubility, by chemical ways such as gas creation during reactions, or by biochemical ways such as microorganism respiration or decomposition. In food and beverage, cosmetics, or detergent applications, stable foam is desired to bring sensorial pleasure, ease of application, or give the perception of effective cleaning. Foam is stabilized by the presence of surface-active components. Foam stabilization is caused by electrical double layers created by ionic surfactants, surface dilatational viscosity, and the Gibbs–Marangoni effect, which results from elasticity of the surface acting as a restoring force to the lamellae (1,2). In many industrial applications, however, it is vital to control or eliminate foam, as it can affect dramatically the process efficiency or the quality of the finished product in its subsequent application.

The control or reduction of foam formation can be achieved by thermal or mechanical ways such as centrifugation, pressurization, and ultrasonic treatment. Chemical foam control agents, also called antifoams or defoamers, are widely used and are very effective in many applications. These agents are also sometimes referred to as foam inhibitors, foam suppressants, suds inhibitors, deaerators, or air release agents. Antifoams (3) are chemical agents that are dispersed into the foaming solution to prevent the formation of excessive

foam. Defoamers (3) are usually described as substances that are sprayed over and rapidly collapse the existing foam. Although some good defoamers like alcohols are sometimes ineffective antifoams, good antifoams can sometime show weak defoaming effect as well. Despite these varying performances, many applications require both preventive and control functions, and, in practice, the same types of materials are used for both defoaming and antifoaming. For this reason, the general term *antifoams*, as used in this article, is meant to encompass all product types and degrees of action encountered with such process aids.

The most obvious use of antifoams as process aids is to increase holding capacity of vessels and improve the efficiency of distillation or evaporation equipment. They are also used to improve filtration, dewatering, washing, and drainage of suspensions, mixtures, or slurries. Examples of industrial operations that benefit from the use of antifoams include oil well pumping; gas scrubbing at petrochemical plants; polymer and chemical synthesis and processing, particularly in monomer stripping; textile dyeing and finishing; leather processing; paint and adhesive manufacture; phosphoric acid production; control of wastewater and sewage; food preparation, notably the refining of sugar; brewing of beer; and penicillin production by fermentation. Among the finished products that are improved in quality or efficacy by the proper inclusion of antifoams are lubricants, particularly cooling lubricants in metal working; diesel fuel, hydraulic and heat-transfer fluids; paints and other coatings; adhesives; inks; detergents; and antifatulent tablets.

The use of vegetable and mineral oils as antifoams has been known for a long time. However, most modern antifoams are complex, formulated specialty chemicals whose composition is often proprietary. Numerous reviews of the field have appeared, notably the comprehensive book on the subject by Garrett (4). Other useful reviews include some on foam control principles (3,5,6), coating applications (7), and silicones (8,9).

An antifoam has to meet the following basic requirements to be effective:

- (1) It must be insoluble in the foaming system under the process conditions.
- (2) It must have lower surface tension than the foaming medium.
- (3) It must be rapidly dispersed in the foaming system.

Beside these basic physical requirements, additional industrial requirements have also to be satisfied, such as

- (1) good cost in use or price–performance ratio,
- (2) high efficiency at low dosage level,
- (3) ease of handling and use (delivery in water-based emulsion or in powder form),
- (4) insensitivity to process conditions (pH, temperature, water hardness),
- (5) it must be inert and give no adverse effect on the production quality (no deposits, no reactions, and no defects on the treated product),

- (6) toxicological and ecological safety, and
- (7) regulatory acceptability.

Antifoam Components

Modern antifoams contain numerous ingredients to meet the diverse product requirements for which they are formulated, including a variety of active ingredients in both solid and liquid states. Antifoam compounds can be used as such in some applications, but in many cases, these antifoam active components are predispersed into formulated products to allow easy handling and to provide maximum efficiency and minimum risks of adverse effects like scaling or deposition problems. Antifoams can be formulated as dispersion into an organic solvent for nonaqueous applications, as oil-in-water emulsion for aqueous foaming systems or as granulated powder to deliver the antifoam as a dry mix, for instance, into washing machine detergent powder or into cement. Antifoam active components and their delivery systems are described in this section.

Antifoam Active Components and Categories. Various types of antifoams are used. They are categorized according to the nature of the antifoam active components and their delivery systems. There is no universal antifoam solution. Each application will require a careful selection of the antifoam to meet all the technical, economical, safety, and regulatory requirements. Antifoam active components can be categorized according to their composition in terms of nonpolar or polar components, as hydrocarbon oil-based antifoams, silicone antifoams, and surfactant antifoams. In some applications, antifoams are also categorized as solid antifoam particles, oil-containing particles, and particle-free antifoams; the last is particularly of interest in applications where the presence of solid hydrophobic particles can affect the application operation, for instance, by generating surface defects during application of paints and coating or by giving fouling problems in the ultrafiltration operations of fermentation processes.

The main ingredients used as antifoam active components are summarized in Table 1. Not all antifoams contain all classes of components; some complex formulations contain several different materials in a particular category, for example, combinations of silicones and organic oils with silica or organic hydrophobic particles and polyethers to further enhance the antifoam efficiency (10).

Hydrophobic Antifoams.

Hydrophobic Oil Antifoams. In nonaqueous systems, particularly in oil and gas applications, polydimethylsiloxane (PDMS) and fluorosilicones without hydrophobic particles are found to be very effective because of their low surface tension, low surface viscosity, and insolubility. Their good thermal stability is also very advantageous (15).

Hydrophobic Oil/Particles Antifoams. The most widely and commonly used category of antifoams is based on a combination of insoluble oils and hydrophobic solid particles. The mixtures of oil and hydrophobic solid particles have usually much higher efficiency than the two components taken separately (3,4).

The role of the hydrophobic oil and hydrophobic particles is discussed in the section Mechanisms of Action. The hydrophobic solid has to be very well dispersed

Table 1. Antifoam Categories

Hydrophobic antifoams		
Hydrocarbons	Oil: • Paraffins, mineral oil, polybutylene, kerosene, and other paraffinic and naphthenic mineral oils • Natural oils: linseed oil, corn oil, soybean oil, peanut oil, sunflower oil, tall oil, castor oil, and lard oil	Particulates: • Hydrocarbon waxes: mineral, paraffin, synthetic, natural, and microcrystalline waxes • Amides waxes: amines, sulfoamides: ethylenediamine distearamide, melanine resins, and urea derivatives
Silicones	• Fluorocarbons (11) Oil: • PDMS • Organosiloxanes with longer alkyl or with aryl groups • Fluorosilicones (12)	• Fluorocarbons Particulates: • Hydrophobic silica: treated fumed silica, treated precipitated silica and silica treated during the antifoam compounding • Silicone resins
Amphiphilic antifoams		
Surfactants	Polyethers: • Poly(oxyalkylene) surfactants: polyoxyethylene/polyoxypropylene block copolymers, polymers, and derivatives (13) • Silicone polyethers Molecular defoamers: • Acetylenic glycols (14) and branched fatty alcohols • Fluorinated surfactants	
Fatty acids, alcohols, and esters	Fatty acids/soaps: Organic phosphates and derivatives	Calcium/magnesium salt of fatty acids and calcium/magnesium salts of organic phosphates Long chain fatty alcohols, acids, and esters

in the system. An optimized level of hydrophobicity is also needed to achieve optimal antifoam effectiveness (16). Two main classes of oil/particle antifoams are found commercially.

Organic-Based Antifoams. Organic antifoams are usually composed of organic (mineral or vegetable) oil combined with organic hydrophobic particulates (hydrocarbon waxes, amides) or hydrophobic silica. This category of antifoams is

effective in a range of temperatures below the melting point of waxes. Although less efficient than silicone-based antifoams, it provides a very low cost antifoam solution and is still used in many aqueous-based applications such as wastewater treatment, detergents, and pulp and paper. Organic antifoams generally have low viscosity and can be used as such in many applications. Amide solid particles are particularly important commercially; one example is the use of ethylene bis stearamide (EBS) as a component of latex paint and paper pulp black liquor antifoam (17).

Silicone-Based Antifoams. Silicone antifoams (9) are generally based on mixtures of PDMS and hydrophobic silica. This is a category of antifoams that is largely used in many applications and studied for the elucidation of the mechanisms of action and the roles of each component (18). Many factors affect the antifoam's performance: the characteristics of the hydrophobic particles, the silicone oil, the foaming system, and process conditions.

The hydrophobic particles are generally hydrophobized silica. Silica is hydrophilic by nature due to the presence of silanol groups at the surface. Fumed or precipitated silica are hydrophobized by the reaction of these silanol groups with alkylchlorosilanes or siloxane oligomers or polymers at 300–400°C. Hydrophobic silica can also be produced by treatment with alcohols, fatty amines, and hydrocarbon waxes. The level of silica treatment, silica porosity, and particle size are important factors for the antifoam performance (16,19). The development of hydrophobic silica is widely acknowledged as one of the most significant advances in antifoam technology. They are used with a considerable variety of liquid components including hydrocarbons, polyethers, and silicones. Pure silicone solids, such as silicone resins, are used in antifoam formulations as solid particles or in combination with hydrophobic silica (20,21).

Polyorganosiloxanes other than PDMS can also be used in applications that require, for instance, better compatibility or increased insolubility. In inks and coatings, for example, silicones substituted with longer alkyl groups such as decyl or dodecyl, aryl groups, or hydrophilic moieties (such as polyoxyalkylene groups) have better compatibility and decrease surface defects. Light crude oil extraction sometimes requires antifoams with increased insolubility, such as polyorganosiloxanes substituted by trifluoropropyl groups (22).

Amphiphilic Antifoams.

Surfactant Antifoams: Polyoxyalkylene Derivatives. This category of antifoams is based on polyoxyethylene (A)/polyoxypropylene (B) block copolymers (23,24). The copolymers can be ABA or BAB structures or condensed with polyamines, polyalcohols or fatty alcohols, or acids groups. These compounds have surface-active properties linked to the presence of hydrophilic and hydrophobic parts. Antifoaming occurs for insoluble polyoxyalkylene derivatives. However, when the hydrophilic polyoxyethylene moieties are predominating, the compounds are soluble in water and are adsorbed at the foam film surface and, in some case, acting rather as foam stabilizer at low temperature, but functioning as antifoam when the temperature is raised to or above their cloud point; the decrease of hydration of the polyether chains above the cloud point products become insoluble and these products act as antifoams (25,26). Polyoxyethylene/polyoxypropylene block copolymers are commercially available from BASF

as Pluriol, Pluronic, and Plurafax or from Dow Chemical Company under Tergitol L trade name. The use of "soluble" foam control agents has increased in recent years because the absence of solid particulates can have advantages and products meeting the biodegradability regulatory requirements that are now available. These types of antifoams are largely used in fermentation, textile treatment, automatic dishwashing, and food processing. For example, copolymers of polyoxyethylene and polyoxypropylene are used to reduce foaming during the acid-gas-scrubbing process (27), fermentation, and food processing (4,28,29). High molecular weight adducts of propylene oxide and polyhydric alcohols such as glycerol and pentaerythritol have also been reported to have useful antifoaming properties (30), as well as fatty alcohol adducts (31).

Silicone antifoam's performance can be enhanced by nonionic surfactants in potato medium (32). Silicone polyethers are also widely used as antifoams (8); low hydrophilic-lipophilic balance (HLB) silicone polyethers are effective additives in inks and coatings and are sometimes used in combination with PDMS-silica-based antifoam as formulation aids and performance enhancer.

Molecular Defoamers: Gemini Surfactants. Contrary to conventional defoamers, molecular defoamers are not macroscopically physically incompatible or insoluble with the foaming system. Foam destabilization occurs by displacement of the foam-stabilizing surfactants and weakening of the lateral cohesive strength of the interfacial foam film, which increases the rate of bubble collapse. Molecular defoamers are based on Gemini-type surfactants such as acetylenic glycols (14), like 2,4,7,9-tetramethyl-5-decyne-4,7-diol (trade name Surfynol 104). Such defoamers have applications in water-based coatings, agricultural chemicals, and other areas where excellent wetting is needed. Some highly branched aliphatic alcohols can be classified in this category as well.

Calcium/Magnesium Salts of Organic Acids (Soap). Fatty carboxylic acids and soaps of chain length C12–C22 are also used as antifoams in applications such as detergents. The antifoam effect results from the formation of insoluble calcium soap and is very sensitive to pH, water hardness, and detergent composition like the type of builder used (4,33). Mixtures of fatty carboxylic acids are still quite largely used as foam control in liquid detergents. In the same category, organic phosphates like tributylphosphate and its derivatives containing polyoxyethylene were reported in detergent application (4) and in combination with other components in cement (34).

Long-Chain Fatty Alcohols, Acids, and Esters. Suspensions of long-chain fatty alcohols, acids, and ester waxes are effective antifoams in foaming systems with low concentrations of surfactants, such as papermaking processes (35,36) and food-processing applications systems. This category of antifoams forms hydrophobic solid particles and gives effective antifoaming under temperature conditions below its melting point. Mixtures of various carbon chain lengths are usually most effective, as they generate a partially molten system similar to the oil/particle dual antifoam system. Long chain fatty acids can also be associated with calcium and magnesium to form insoluble soaps that act as "gel-particle" antifoams (37).

Antifoam Delivery Systems. The antifoam must be rapidly and well dispersed in the foaming media to effectively reach and disrupt the foam lamella. Antifoams are insoluble in the foaming media, and the most modern high

efficiency silicone antifoam compounds have generally very high viscosities, which make them extremely difficult to disperse as such in the process. Antifoams are generally predispersed on a carrier to provide an easy-to-handle, readily dispersible system for delivering the active antifoam components to the foaming system and also to tie the complex antifoam formulation together. Sometimes, the carrier is used simply as an extender to lower the cost of the final product. For nonaqueous applications, the carrier is usually a low viscosity nonpolar liquid. Any of the usual paraffinic, naphthenic, aromatic, chlorinated, or oxygenated organic solvents can be used, but aliphatic hydrocarbons are the most common. For aqueous foaming applications, water-dispersible carriers are used: They can be based on polar organic liquids, water itself, or water-dispersible/soluble solid particulates. When a nonaqueous liquid is used as the dispersion media, the product is generally referred to as an antifoam concentrate. When water is used as a carrier fluid, the antifoam product is typically an oil-in-water emulsion. With growing concern over unrecovered solvents, this has become a preferred type of antifoam formulation. Such products usually require preservatives to prevent bacterial spoilage in storage and thickeners to reduce the emulsion phase separation. The optimal particle size for the antifoam droplets strongly depends on the foaming system, but is generally in the range of 5–30 μm (9,18,38). Droplets that are too large lead to a reduced number of antifoam droplets distributed in the foaming systems and require a higher dosage. Droplets that are too small would reduce the antifoam efficiency, as explained later in the Mechanisms of Action section (18). The particle size distribution can be controlled by the shear and the temperature during the dispersion process and maintained by the addition of emulsifiers and thickeners. Examples of emulsifying agents used for oil-in-water antifoam emulsions are fatty acid esters and metallic soaps of fatty acids: fatty alcohols and sulfonates, sulfates, and sulfosuccinates; sorbitan esters; ethoxylated alcohols/carboxylic esters, and silicone–polyether copolymers. Examples of thickeners used in antifoam emulsions are those based on cellulose, such as xanthan gum, carboxymethylcellulose, and hydroxyethylcellulose; carboxylic polymers (as Carbopol) are also commonly used.

The dispersion must be stable in various aspects and conditions where it is used: There should be no deterioration of the performance, no change in the physical aspect, no phase separation, and no drift in viscosity. The dispersion must also be compatible and stable in the application systems, with no negative effect on the final product when it is added to the system. In paints, coatings and inks, or liquid detergent applications, the antifoam has to be formulated to provide a finished product formulation that is stable, also showing no separation or deterioration of the antifoaming performance during its processing or storage. The formulated antifoam must resist process conditions such as shear, temperature, water hardness, and pH variations. When the antifoam is delivered in a solid powder like laundry detergent powder or cement, it must not wet the powder or affect its free-flowing characteristics and it has to be protected from other chemicals such as surfactants, bleaching, or alkaline agents. Water-soluble and -insoluble inorganic or organic solid sorbent carriers used are sodium sulfate, sodium carbonate, sodium tripolyphosphate, methylcellulose, starches, zeolites, silica, and so on. To preserve the integrity of the antifoam formulation, the particles are further encapsulated by a coating usually based on polymers of ethoxylates, acrylates, carboxylates, vinyl alcohols, and so on. These polymers are also

commonly called binders; they not only bind the antifoam droplet on the carrier by a protective coating but also the carrier particles together, providing a powder with desired granulometry and allowing disruption on contact with water and release of the antifoam active in the foaming system such as the washing process. Organic waxes are very often used in detergent-granulated antifoams to delay the release of the antifoam and provide foam control throughout the washing cycle.

Mechanisms of Action

Foam is essentially dispersion of gas enclosed within a liquid. Each bubble–bubble interaction occurs in a thin film through which liquid constantly travels under the influence of gravity and agitation. Three films form a curved triangular channel, which is known as a *Plateau border*. Four Plateau borders meet at angles of 109.6° to form a *vertex*. Foams are thermodynamically unstable. To understand how defoamers operate, the various mechanisms that enable foams to persist must first be examined. Four main explanations for foam stability are (1) surface elasticity, (2) viscous drainage retardation effects, (3) reduced gas diffusion between bubbles, and (4) other thin-film stabilization effects from the interaction of the opposite surfaces of the films. The stability of a single foam film can be explained on the basis of the Gibbs elasticity (E), which results from the reduction in the equilibrium surface concentration of adsorbed surfactant molecules when the film is extended (39). This increases the equilibrium surface tension that acts as a restoring force. The Gibbs elasticity is defined in equation 1, where σ is surface tension and A is the surface area of the film:

$$E = 2A d\sigma/dA \quad (1)$$

In a foam where the films are interconnected, the related time-dependent Marangoni effect is more relevant. A similar restoring force to expansion results because of transient decreases in the surface concentration (increases in surface tension), which is caused by the finite rate of surfactant adsorption at the surface. Such nonequilibrium surface tension effects are best described in terms of dilatational moduli (ε^*). The complex dilatational modulus ε^* of a single surface is defined in the same way for the Gibbs elasticity as in equation 2 (the factor 2 is halved as only one surface is considered):

$$\varepsilon^* = A d\sigma/dA \quad (2)$$

In a dilatational experiment, where the surface is periodically expanded and contracted, ε^* is a function of the angular frequency (ω) of the dilatation, as shown in equation 3, where ε_d is the dilatational elasticity and η_d is the dilatational viscosity:

$$\varepsilon^*(i\omega) = |\varepsilon| \cos\theta + i|\varepsilon| \sin\theta = \varepsilon_d(\omega) + \omega\eta_d(\omega) \quad (3)$$

A stable foam possesses both high surface dilatational viscosity and elasticity (40). In principle, defoamers should reduce these properties.

Both high bulk and surface shear viscosity delay film thinning and stretching deformations that precede bubble bursting. The development of ordered structures in the surface region can also have a stabilizing effect. Liquid crystalline phases in foam films enhance stability (41). In water–surfactant–fatty alcohol systems, the alcohol components may serve as a foam stabilizer or a foam breaker, depending on the concentration (41). Alcohol/surfactant ratios less than that corresponding to the liquid crystalline phase enhance film stability; higher ratios produced by contact with alcohol droplets disrupt this phase and result in film instability. Liquid-phase defoamer components may dilute or destroy such stabilizing phases, or they may simply contribute to lower surface shear viscosities than the foam-stabilizing surfactant (profoamer). For example, the very low surface shear viscosity of PDMS (42) is often cited as a contributing factor to its effectiveness in defoamer compositions. On the other hand, too rigid a surface will also be prone to the rupture. Thus, dilatational moduli that are too high will also result in foam instability, as in the case of diesel fuel antifoaming with a fluorosilicone antifoam agent (43).

Reduced gas diffusion between bubbles delays collapse by retarding changes in bubble size and the resulting mechanical stresses. Consequently, single films persist longer than the corresponding foam, but it seems to be a minor factor in practical defoaming situations. The same is true of other thin-film stabilization effects from the interaction of the opposite surfaces of the film. These comprise both electric double-layer repulsion for ionic surfactants and entropic repulsion of polymer chains at the surface for nonionic materials. These effects are of paramount importance in determining the stability of very thin (less than 10 nm) films, but in practice the real challenge is usually to defoam films of at least several hundred nanometers in thickness, where such effects have not been significant. All these mechanisms except high bulk viscosity require a stabilizer in the surface layers of foam films. Accordingly, most theories of antifoaming are based on the replacement or modification of these surface-active stabilizers. This requires defoamers to be yet more surface active; most antifoam oils have surface tensions in the range of 20–30 mN/m, whereas most of organic surfactant solutions and other aqueous foaming media have surface tensions between 30 and 50 mN/m. This is illustrated in Table 2.

In addition to have a lower surface energy than the foaming medium, antifoams must be not only insoluble in that medium but also readily dispersible in it. Five basic processes involved in the rupture of foam films by antifoams are entering, spreading, bridging-dewetting and/or bridging-stretching, and rupture (Fig. 1).

The entering, bridging, and spreading processes are governed by the entering coefficient E , the bridging coefficient B , and the spreading coefficient S , defined in equations 4–6, respectively, where σ_f is the surface tension of the foaming medium, σ_a is the surface tension of the antifoam, and σ_{af} is the interfacial tension between them:

$$E = \sigma_f + \sigma_{af} - \sigma_a \quad (4)$$

$$B = \sigma_f^2 + \sigma_{af}^2 - \sigma_a^2 \quad (5)$$

$$S = \sigma_f - \sigma_{af} - \sigma_a \quad (6)$$

Table 2. Surface Tensions of Surfactants and Defoamers

Material	Surface tension, mN/m or dyn/cm ^a	Temperature, °C	Reference
Surfactants			
Sodium lauryl sulfate (C ₁₂ H ₂₅ SO ₄ ⁻ Na ⁺)	39.5	25	(44)
Sodium 12-butoxydodecyl sulfate (C ₄ H ₉ OC ₁₂ H ₂₄ SO ₄ ⁻ Na ⁺)	44.0	25	(44)
Lauryl pyridinium bromide (C ₁₂ H ₂₅ C ₅ H ₅ N ⁺ Br ⁻)	41.2	30	(44)
Lauryl alcohol ethoxylate C ₁₂ H ₂₅ (OC ₂ H ₄) _n OH	36.3	23	(44)
Alkyl phenol ethoxylate <i>para-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OC ₂ H ₄) _n OH	33.5	25	(44)
Surfactant/defoamer			
Surfynol 104 ^b	33.1	25	(14)
Pluronic L62 ^c	42.8	25	(45)
Defoamers			
Poly(oxypropylene) ^d	31.2	22	(46)
Polydimethylsiloxane ^e	20.2	20	(46)
Kerosene	27.5	29	(47)
Mineral oil (MWP paraffin)	28.8	20	(48)
Corn oil	33.4	20	(49)
Peanut oil	35.5	20	(49)
Tributyl phosphate	25.1	20	(50)

^aSurfactant values are at the critical micelle concentration in aqueous solution; surfactant/defoamer values are at 0.1% concentration in aqueous solution.

^bSurfynol 104 is an acetylenic glycol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, marketed by Air Products and Chemicals, Inc.

^cPluronic L62 is a poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene) copolymer marketed by BASF AG.

^dMolecular weight 3000.

^eMolecular weight 3900.

The lower the value of σ_a , the more likely it is that E , B , and S are positive, indicating a thermodynamic requirement for the to occurrence of processes. The requirement for a positive E and B to have antifoaming activity is well established (3,4,8,38): If E and B are negative, the foam film is stable and no film rupture is effective. The requirement for a positive spreading coefficient S has also been speculated (51–53), but it is debatable. Garrett and co-workers (54) demonstrated that positive S is not a necessary condition for having the antifoaming activity.

The most recent and significant progress in the understanding of the antifoam mechanism, the role of oil, and particles, as well as the mechanisms of deactivation, was reported by Denkov's group of the Laboratory of Chemical Physics and Engineering at the University of Sofia in Bulgaria (18). The authors showed that there is no direct relationship between the magnitude of the E , B , or S coefficients with the antifoam activity. They categorized the activity of antifoams

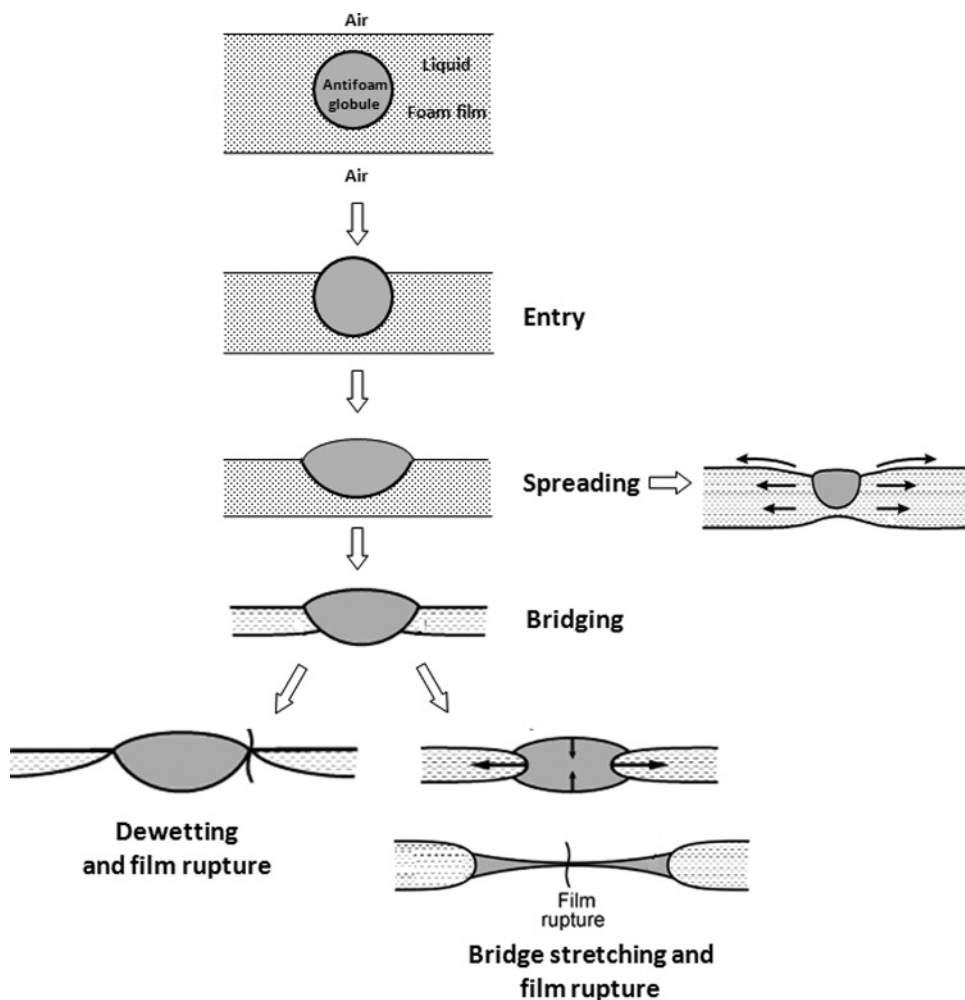


Fig. 1. Schematic presentation of the possibilities for foam film destabilization. The antifoam globule enters at the air–liquid interface ($E > 0$). Spreading occurs, and the globule forms a lens that further bridges the foam film ($B > 0$). Two different scenarios of foam film rupture are possible: If the process of bridge dewetting is faster than bridge deformation, a bridging–dewetting mechanism could be realized; if the bridge deformation is faster, a bridging–stretching mechanism is realized. Reprinted from Ref. (18) with permission of the American Chemical Society.

depending on their so-called “entry barriers”: The energy barrier prevents the emergence of the preemulsified antifoam globule at the solution surface. This surface is also described as an asymmetric film or a pseudoemulsion film (3). Fast antifoams have low entry barriers and in less than 10 s leave a clean liquid surface layer once the agitation was stopped. Slow antifoams have higher entry barriers and require more than 5 min to destroy the foam. Fast antifoams act on the thick foam film layer. Slow antifoams are collected and trapped in the Plateau borders: compressed while the film is becoming thinner and eventually break the foam film when the compression capillary pressure exceeds the entry

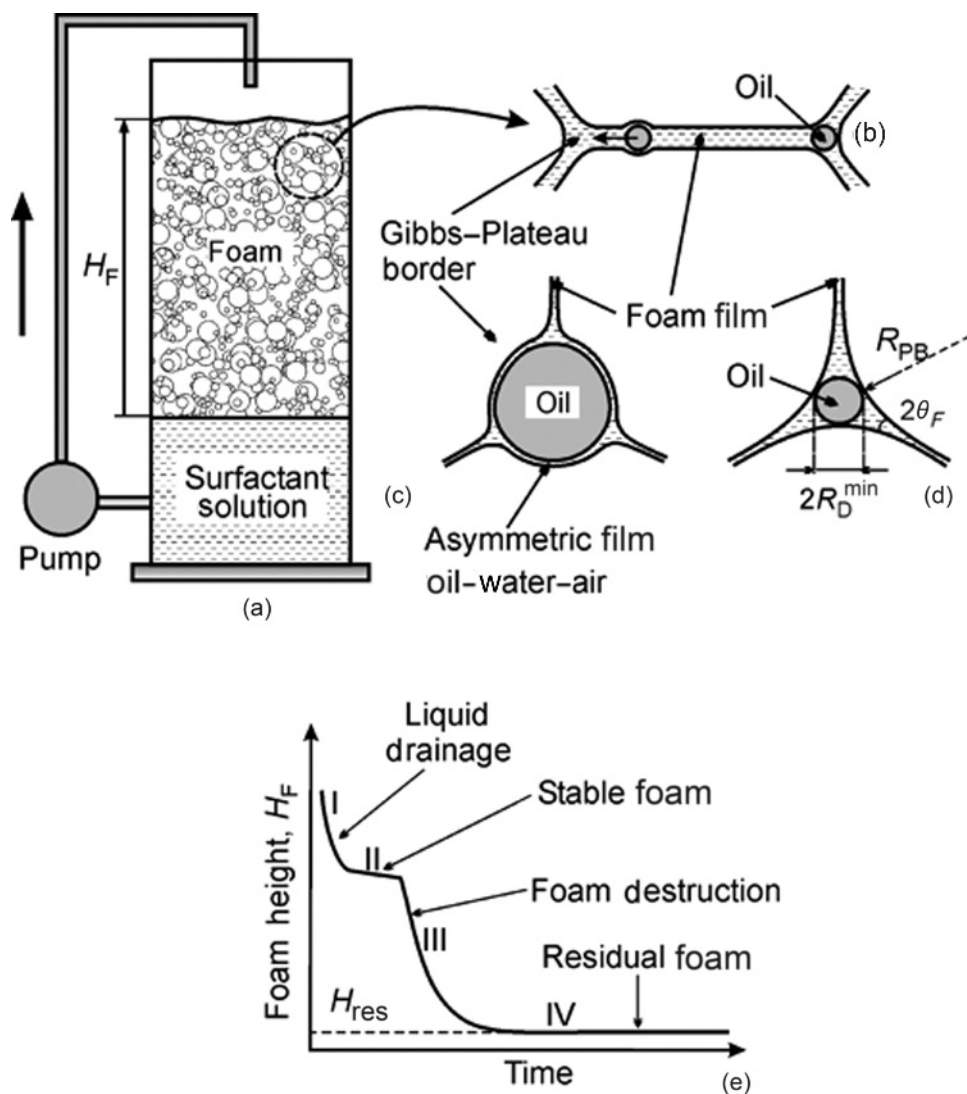


Fig. 2. Schematic presentation of foam destruction by the globules of slow antifoams (a and b). The oily globules rapidly leave the foam films and enter the neighboring Plateau borders (PBs) soon after foam agitation is stopped. (c) Water drainage from the foam leads to gradual narrowing of the PBs. The large drops are compressed by the PB walls and asymmetric oil-water-air films are formed. When the compressing capillary pressure exceeds the drop entry barrier, P_C^{CR} , the asymmetric film ruptures and the drop enters the PB wall and causes rupture of the neighboring foam films. (d) Drops of radius smaller than $R_D^{\min}$ remain uncompressed and cannot induce foam destruction. (e) Stages of foam evolution in the presence of slow antifoam. Reprinted from Ref. (18) with permission of the American Chemical Society.

barrier (18) (Fig. 2). For slow antifoams, the size of the antifoam globules strongly influences the foam decay times, as well as the height of the residual foam layer (18) (Fig. 2).

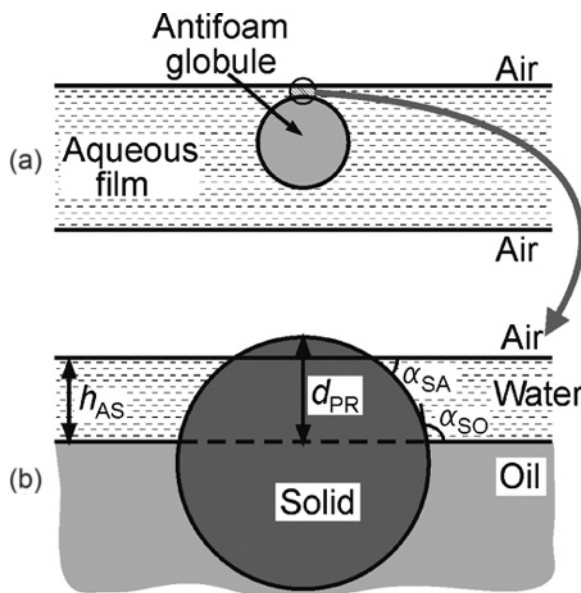


Fig. 3. (a) When an antifoam globule approaches the foam film surface, asymmetric oil–water–air film is formed. (b) If the protrusion depth, d_{PR} , of the solid particle is larger than the thickness of the asymmetric film, h_{AS} , and the condition for dewetting, $\alpha_{SA} + \alpha_{SO} > 180^\circ$, is satisfied, the solid particle pierces the air–water interface and induces rupture of the asymmetric film. The particle assists the oil globule entry—this is the so-called “pin” effect of solid particles. Reprinted from Ref. (18) with permission of the American Chemical Society.

The role of the hydrophobic particles in fast antifoam compounds has been shown to destabilize the asymmetric pseudoemulsion film (3,4,21,55) and facilitate the entry of the droplet at the surface by reducing the barrier of entry (18,56). The role of the particle hydrophobicity is of great importance at the antifoam entry barrier (18,57). Figure 3 shows the action of the solid particle on the protrusion of the asymmetric film and allowing the antifoam globule to pierce the air–liquid interface. A protrusion by the solid particle occurs if the three-phase contact angles α_{SA} (solid–water–air) and α_{SO} (solid–water–oil) satisfy the condition given below:

$$\alpha_{SA} + \alpha_{SO} > 180^\circ \quad (7)$$

Solid particles in mixed compounds should be sufficiently hydrophobic to satisfy equation 7. However, particles that are too hydrophobic might have an insufficient protrusion depth (d_{PR}) in the aqueous phase to enter the air–liquid interface. Therefore, there is an optimal hydrophobicity for the solid particles to minimize the entry barrier of mixed oil particle antifoams (58).

It has also been demonstrated that exhausted or deactivated oil–silica antifoams segregate into two distinct populations of globules (silica-free and silica-enriched), neither of them being active antifoams (59,60). In addition, the spread oil layer disappears from the foam solution surface. The antifoam can be reactivated by addition of fresh oil without silica (59), which allows the entering, bridging, and spreading mechanisms to function again, carrying particles

that can then bridge, stretch/dewet, and collapse the foam film. The presence of a spread oil layer on the solution surface leads to significantly lower entry barriers than in an exhausted system in which all the oil is emulsified into the liquid phase with complete depletion of the oil layer at the foaming solution surface (61). Figure 4 presents the deactivation of the oil–silica antifoam, the role of spreading of the oil layer at the surface, and the reactivation of exhausted antifoam by addition of the oil layer at the surface.

The above mechanism of antifoam action has also been shown to be valid for more complex systems. The barrier of entry can explain the lack of antifoam activity of silica in the silicone oil antifoam in foaming systems that are stabilized by bulky surfactants, forming a very thick adsorption foam layer and asymmetric film such as alkylpolyglucosides, some fatty acid sorbitan esters, and fatty alcohol polyglycol ethers referred to as Brij and Span series (18,62), and macromolecular surface-active compounds such as proteins and biosurfactants (63). In such systems, the protrusion depth of the solid silica particle present in the antifoam compounds was insufficient to enter into the asymmetric film and penetrate the surface. It has been shown that surfactants can destabilize protein foams by a so-called “orogenic displacement” of proteins (63), a mechanism by which the protein is removed and displaced from the interface by small surfactant molecules. Efficient antifoaming can be achieved by combining this effect with silica particles containing silicone antifoam (32). The antifoaming mechanism of calcium soap-forming solid particles has also been related to the facilitation of the oil droplet entry; again, the synergy of the oil and solid hydrophobic particles was proved (33).

Applications

Pulp and Paper. The critical and troublesome foaming problems of the pulp and paper industry have led to the use of antifoams. It is the world's biggest single user of defoaming agents (37,64). Early use of large amounts of kerosene or fuel oil has resulted in ecological and cleanliness concerns compared to effective formulated antifoams. Foams are encountered at every stage from pulping, through paper fabrication and coating, to printing. A variety of wastewater streams are generated, which are very prone to foaming because of the presence of dissolved soaps. Specific antifoam products are often tailored for each different stream. The so-called black liquor antifoams were the first commercial hydrophobic silica in hydrocarbon oil products, replacing EBS and were then extended to other industries. The use of these antifoams has allowed some kraft pulp mills to exceed original designed capacity and reduce deposits problems. Although they are still used in the industry, the oil-based antifoams have been substantially replaced in the past 20 years by silicone-based products. These provide less deposits problems, superior stability, and foam control efficiency, particularly at extreme temperature and pH conditions typical of pulp-washing operations. In papermaking processes, fatty alcohols and fatty acid ester derivative dispersions are more commonly used as deaerators. Polyalkylene glycols are also used in the wet-end, size press, and coating units of the paper process.

Fermentation. The efficient production of penicillin, yeasts, enzymes, lactic acids, or bioethanol by fermentation requires antifoams to control gas

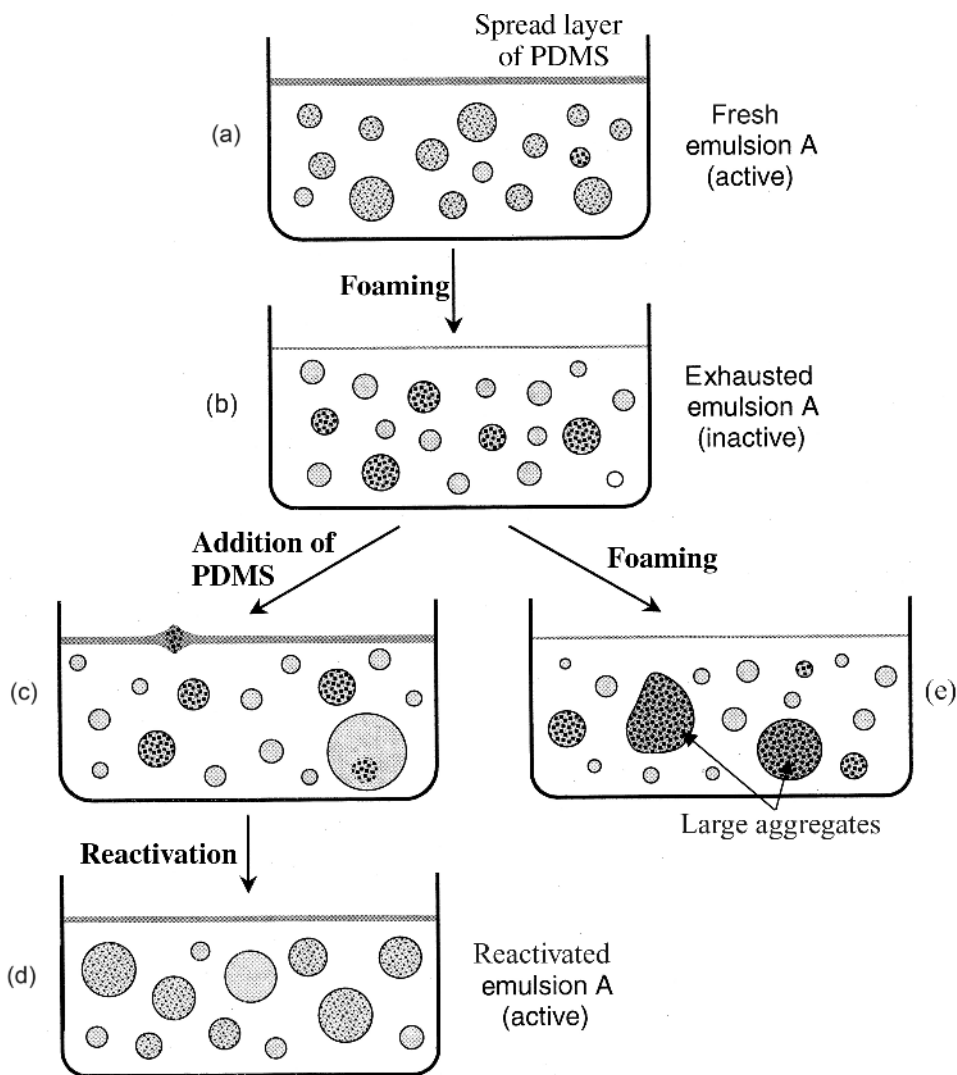


Fig. 4. Schematic presentation of the processes of antifoam exhaustion and reactivation of emulsion A. **(a)** An initially active (fresh) emulsion A contains globules of optimal silica/oil ratio; a layer of spread oil is formed on the surface of the surfactant solution. **(b)** The foam destruction by the antifoam globules leads to gradual segregation of oil and silica into two inactive populations of globules (silica-free and silica-enriched); the spread oil layer disappears from the solution surfaces the antifoam becomes inactive. **(c)** The introduction of a new portion of oil leads to restoration of the spread oil layer and to redistribution of silica, so that active silica globules are formed again the antifoam is reactivated. **(d)** The macroaggregates (see the text) appear as a result of aggregation of the silica-enriched globules. **(e)** Reprinted from Ref. (59) with permission of the American Chemical Society.

evolution during the reaction (28). Most cell cultures generate foam-stabilizing agents such as proteins, carbohydrates, or biosurfactants, and the presence of foam can severely impact the performance of a bioreactor. This application requires a very careful selection and dosage of the antifoam to avoid negative effects on the oxygen transfer, the metabolism and growth rate of

microorganisms, or the subsequent purification stage like in the downstream ultrafiltration stage where the antifoam can give potential fouling of the membranes. In modern yeast production facilities, the antifoams are introduced by means of automatic electrode-activated devices. The most commonly described antifoams in this application are silicone-based oil and emulsions, polyoxyalkylene polymers and ester derivatives, natural oils such as soybean oil and lard oil, or mixtures of these (28). Novel antifoaming agents tailored for fermentation processes have been recently described: Fluorocarbon–hydrocarbon surfactants were found to be effective at very low dosage while giving a higher physical oxygen transfer coefficient than the traditional silicone antifoam (12).

Paints, Coatings, and Inks. Foam problems occur both during the preparation of paints and coatings and in their application. The use of ball mills and other equipment for pigment dispersion provides ideal condition for mixing in air, and the presence of surfactants in the formulations generates persistence of the foams. Foam in a pigment-grinding process lowers the mechanical shear and reduces the coloring and shielding functions of the expensive pigments. These problems may be controlled during manufacturing by mechanical means, but an antifoam is almost always required for foam control during application because application methods vary considerably, for example, roller, brush, dip, or spray methods. The proper choice and minimum use of surfactants such as dispersants, flow agents, and wetting agents can minimize but not eliminate the use of antifoams to prevent pigment separation or surface defects during applications such as cratering, pinholes, fisheyes, and orange peel. In addition to the final dried film appearance, the antifoam must not detract from other properties such as color acceptance, gloss, adhesion, and recoatability. The wide variety of paint types explains the large number of different antifoams that are used in this industry (65). Suitable antifoam must be selected carefully depending on the paint type, either water borne or solvent borne, and the applied process, such as pigment grinding and coating.

Oil and Gas. There are a variety of uses for antifoams in oil recovery. They are used in some of the materials used in oil extraction, such as in drilling muds and cement lining, and also directly with the crude oil itself. In its natural state, crude oil contains dissolved gases held by high reservoir pressure. When this live crude oil is extracted and passed into the low pressure environment of a gas–oil separator, the dissolved gases are liberated and can cause troublesome foaming that leads to oil losses via the gas stream and downstream equipment damage (66). Foaming is a problem in other petrochemical operations including distillation, cracking, coking, and asphalt processing. Antifoams are also used in the downstream petroleum market in lubricating oils and diesel fuel. The principal antifoams used in the treatment of nonaqueous foams in the oil industry (67) are silicones (low solubility in hydrocarbons and effective at low concentrations), fluorosilicones (greater resistance to chemical attack and solubilization), and silicone glycols (eg, in diesel fuel).

Cleaning: Laundry and Automatic Dishwashing. Antifoams are part of the composition of many detergents and cleaning products. This is largely due to the automation of cleaning equipment and the need to operate it optimally. Recent changes in detergent composition (68) and washing machine design also have a significant impact on the need for foam control in these applications (69,70). It is a considerable challenge to incorporate antifoams into a detergent in such a way

that the foam-control properties do not drift with time. The antifoam composition has to survive storage with the surfactants, builders, bleaches, and other auxiliary agents, and yet function properly as soon as the detergent is added to the wash water. In powdered laundry detergents used in washing machines, the antifoam is granulated by agglomeration on a powder carrier and encapsulated by using film-forming polymers and/or organic waxes in the agglomeration process (69,71). In liquid laundry detergents, stabilization of the antifoams to maintain a uniform dispersion is technically challenging and very sensitive to the detergent formulation; it requires density matching and specific colloid stabilization such as specialty emulsifiers or particulate stabilizing aids (69,72). Although foaming should be controlled at acceptable levels in laundry washing machines, it must be completely avoided in automatic dishwashers because foaming can totally suppress the washing efficiency by reducing the water pressure needed to rotate the spraying arms. Adequate silicone-based solutions have been recently developed, which maintain proper machine operation and enable flexibility in dishwasher detergent formulations (73).

Wastewater Treatment. Antifoams are used extensively to treat wastewater in many municipal and industrial treatment facilities and also in mining and mineral processing. Benefits are aesthetic, environmental, and economic. Aeration basins are free of unsightly, troublesome foam, and water and energy are conserved by allowing more efficient use of mechanical equipments. Most foaming problems occur either at the biological treatment step or the effluent discharge step (74). Aeration is necessary in biological treatments to allow microorganisms to breathe, but the agitation produces foam. Antifoams that do not disrupt this process must be selected. Some of the upstream processes may depend on foaming and other surface-active phenomena such as flotation and flocculation steps, and care must also be taken to use antifoams that do not interfere with these processes if treated streams are recycled. Effluent foam discharge is illegal in some countries including the United States, where the Environmental Protection Agency (EPA) prohibits discharge of floatable materials in the effluent stream (74).

Metal Working Fluid. The metal working industry has been encountering considerable foaming problems with the cutting oils and coolants that are sprayed onto the tool-work piece interface to provide cooling, controlled lubrication, corrosion protection, and increased tool life. These coolants are provided as mineral oil/emulsifier concentrates, which are diluted with water by the user. For many years, this industry tolerated the foam difficulty in its many milling, drilling, grinding, rolling, and drawing operations, but now uses antifoams such as formulated silicones and dispersions of fatty amides in mineral oils. Calcium soaps are also used as foam inhibitors in coolants. They are formed as a finely divided suspension of insoluble particles when the soaps present in the cooling lubricant concentrate react with hardening agents added to the dilution water.

Polymerization/Latices. Foam is often a particular problem in the production of polymers. There are numerous situations where foam can reduce the production capacities of vats and vessels and cause problems in pumps, meters, and other equipments, particularly distillation and evaporation equipments. Foam is frequently a problem when stripping off a monomer from a polymer.

Examples are in the production of styrene–butadiene and acrylonitrile–butadiene rubber latices. These latices are stabilized by surfactants that greatly contribute to foaming problems. Another problem area is in the stripping of unreacted monomer from poly(vinyl chloride) suspensions. In this process, vinyl chloride, a gas at room temperature, is liquefied by pressure, emulsified in water with surfactants and catalysts, and heated to bring about polymerization. The recovery of unpolymerized monomer by distillation from this mixture produces a severe foaming problem.

Construction. Polymer dispersions in cements, mortars, and plastics are being increasingly used in the construction industry (75). Their plasticizing effect allows reduced amounts of water to be used, and they also confer strength and adhesion benefits in certain situations. The emulsifiers and dispersants used in these products can result in air entrainment problems with a detrimental effect on the ultimate stability of the construction. Powdered antifoams that can be directly added to the cement are commonly used. They have usually high surface area; highly absorbent inorganic fillers that have been treated with liquid antifoam compositions similar to the products are used in low foaming detergents. For the latex manufacturers, the other solution to this problem is to formulate low foaming polymer dispersions with appropriate antifoams having good long-term stability.

Textiles. Antifoams are required in the jet dyeing of textiles (76,77). This process, which is mainly used with polyester fibers, is carried out at elevated temperature and pressure and involves pumped recirculation of the dyeing medium from the reservoir through the jets. When the operation is complete and the pressure released, severe foaming can result in the absence of an effective antifoam. Foam control is also needed in other dyeing processes (76), such as continuous dyeing and beck dyeing. For example, in the dyeing of knitted fabrics of textured polyester fibers, foaming of the dye liquor can float the material, resulting in an uneven application of the dye. Various surfactant mixtures are used in this area and additional benefits such as wetting and solubilization as well as foam control are noticed. Acetylenic glycols are very useful in this context (14). Dyeing is only one of several steps where foaming can make fiber processing difficult. Antifoam may be required when any size or finish is applied to a textile material. One example is the pretreatment step in the processing of cotton. The fabric is exposed to strongly alkaline sodium hydroxide and anionic surfactant solution. Phosphate ester antifoams are much used in this application. Textile operations are also notorious for their wastewater foaming problems.

Fertilizers. The fertilizer industry for many years has used tall oil fatty acids for the production of phosphoric acid by the digestion of phosphate-containing rocks with sulfuric acid. Carbon dioxide is liberated and presents a difficult, highly acidic foaming problem. Formulated products are now used, many of which continue to contain tall oil fatty acids, but which also contain emulsifiers and wetting agents such as dioctyl sodium sulfosuccinate, which greatly increase their effectiveness. Partially wetted gypsum particles contribute to the foam stabilization, and the modification of the gypsum wettability using these wetting agents makes more effective.

Food and Beverages. Antifoam applications in the food and beverage industry include uses in both the preparation and processing of foodstuffs and in

the cleaning and disinfecting of containers. Poly(alkylene oxide)-based antifoams have played an important role in satisfying the foam control demands of this industry (78). The sugar beet industry is a prolific user of antifoams (79). This is now a fully mechanized automated procedure. The sugar is extracted with hot water, treated with limewater and carbon dioxide, filtered, and the filtrate is subjected to evaporation. Foaming occurs during many of these steps. Another food processing area with considerable foam problems is the production of chips, fries, mashed potatoes, and potato starch. Proteins, starch, and other natural products in potatoes cause troublesome foams in wash baths. Beers and wines are also produced with the aid of antifoams. They permit more efficient use of vats and containers and permit more controllable bottling procedures. The growth in returnable bottles and the widespread use of automated mechanical cleaning equipment has increased the use of antifoams in this industry. They can be used directly or incorporated in low foaming cleaning agents. It is important to note that foams occurring in food processing are generally stabilized by surface-active macromolecules, such as proteins or starch, instead of the more usual small-molecule surfactants, and this is reflected in the composition of antifoam products for these applications.

Leather. Almost every stage in leather processing, from the initial rawhide preparation through tanning and dyeing and other finishing treatments has the potential for causing foaming. Many of the preparations used in these steps contain wetting agents and other surfactants or are applied in the form of emulsions or dispersions. The trend, as with many other antifoam applications, is to formulate the antifoam into the treatment product rather than deal with numerous optimized antifoams at each of the several processing steps.

Adhesives and Sealants. Most industrial adhesives contain surface-active components and additives, and air entrainment during their mechanical application can significantly reduce joint strength. Antifoams are usually formulated into adhesives to protect users against such difficulties. Additional benefits such as improved uniformity of products, increased throughput, and reduced labor costs can also result from the use of antifoams during adhesive application. The footwear and nonwoven fabric industries are extensive users of antifoams in this way.

Chemical Processing. Agitation, distillation, and pressure differences are commonplace in many chemical processes. These are conducive to foam formation, and even when the plant design minimizes these problems, it is still often necessary to employ antifoams. A review of this field (80) lists numerous problems encountered with unwanted foam in chemical processes: increased cost of coping with safety hazards from slippery floors, corrosive residues, or flammable liquids; interfering with process instruments, pumps, and so on; slowing the drainage of liquids from products being dried; product rejection due to incompletely filled containers; reducing capacity in vats; premature failure of bearings and other mechanical devices because of loss of lubrication; separating and segregating critical process ingredients; and perceived negative environmental impact on the discharge by the community.

Medical/Pharmaceuticals. Silicone antifoams (also known as simethicones) have been used in pharmaceuticals since the 1950s (81). The earliest and most important application is their use to combat intestinal gas. Because of

their chemical inertness and physiologically neutral behavior, silicone antifoams are admitted as antifatulents for cattle and humans. They are found in different dosage forms such as tablets, oral suspensions, and emulsions. Numerous publications have demonstrated their effectiveness against abdominal foams.

The list of applications described here is certainly not meant to be exhaustive, and one could cite many other areas where antifoams are used, among which are flotation, refrigeration, hydraulic fluids, and desalination.

Testing Methods

The ultimate test of a antifoam is an actual field trial, and occasionally this is the only testing carried out. More usually, some laboratory-scale evaluation of several different products is conducted before a recommendation is made for a suitable, economical antifoam for a specific application. Although suppliers have their own standard foaming surfactants, it is usual to work with the potential customer's foaming medium. Often, this work is done at the plant site to obtain fresh foaming liquors. Establishing that a given antifoam is effective in a particular application is only part of the testing required. The absence of any adverse effect on the final product and the manufacturing and use environments must also be determined. In addition, to be marketable, the antifoam must be cost-effective and convenient and easy to handle for the customer. A useful account of the practical selection of antifoams has been given in Reference 80.

There are many laboratory methods for testing of the relative merits of one antifoam against another. This diversity of test methods is reflected in American Society of Testing and Materials (ASTM) recommendations (82). It is a simple matter to measure foam height as a function of time to compare the performance of various foam surfactants and antifoams. Unfortunately, this simplicity has led to a wide variety of methods and conditions used with no standard procedure that would make the measurement of foaminess a characteristic of a solution as its surface tension or viscosity. In practice, a wide variety of simpler methods are used that generally use one of the five main categories:

Shaking Methods. Agitation is the easiest way of producing foam, but the results are very dependent on the details of the shaking procedure (container shape and size, shaking speed, and amplitude). Foam height, foam collapse time, or, for more viscous fluids, specific gravity changes are usually measured. A shake test method is described in ASTM D3601-88 (revised in 2007).

Pneumatic Methods. Gas introduction is controlled by injection through capillary tubes, sintered glass spargers, diffuser stones, and the like. The method is often referred to as "Bikerman test," "sparge test," or "bubbling method." Foam heights or volumes are monitored after gas injection or while the gas continues to produce bubbles (dynamic conditions). Pneumatic methods are recommended for lubricating oils (ASTM D892-89) and engine coolants (ASTM D1881-86), but they are also used with aqueous surfactant systems.

Pour Methods. The liquid is poured or drained from one vessel into another. This approach is used to assess foams produced from dissolved gases in the liquid and has also become a standard in the detergent industry (the Ross-Miles test). It is described in ASTM D1173-07 (revised in 2007).

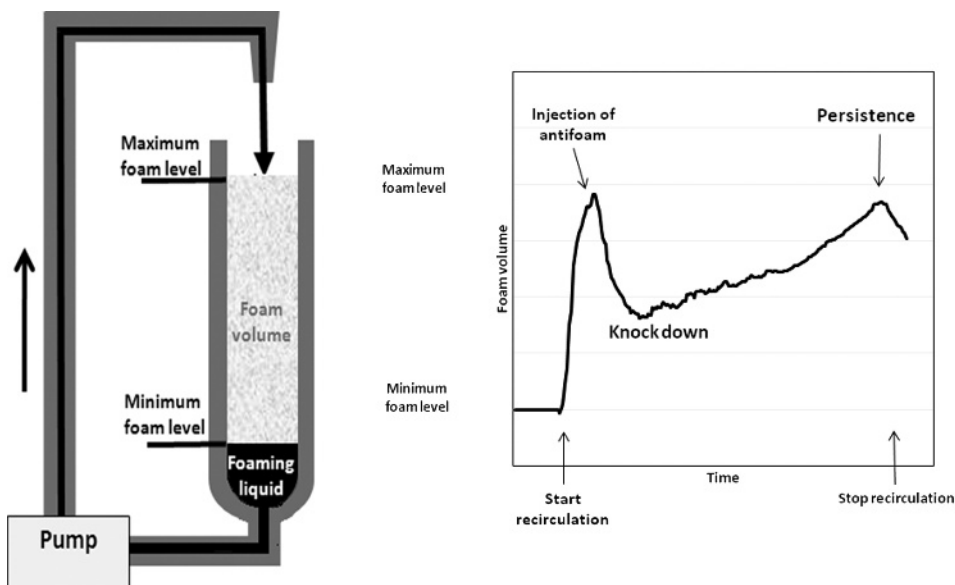


Fig. 5. Schematic representation of the recirculation method and the recorded foam profile. The graph shows an example of foam profile; after the start of the recirculation, the system reaches a given level of foam at which the antifoam is injected. The foam collapses down to a minimum level, which is the knockdown. The recirculation is maintained for a period until the foam reaches a maximum level, which is the persistence related to the antifoam durability. Good antifoam has short knockdown and long persistence.

Recirculation Methods. These dynamic methods are probably the most satisfactory for antifoam evaluation (15,71). The foaming solution is usually recirculated through a vertical cylinder where foam volumes or heights can be measured as a function of time (Fig. 5). In such a device, a steady state can be achieved with a given foaming system and antifoam measured at selected concentrations. The test enables various important antifoam characteristics to be measured such as the knockdown time, the time taken to collapse a preformed foam, the knockdown, which is the minimum foam level of foam collapse, and the persistence or hold-down time, the time taken for the foam to recover to some agreed “maximum” level at the top of the foam cell column. This method is commonly used in the pulp and paper industry for brownstock washing filtrates (black liquors) or white waters. Automated equipments have been developed in recent years.

Stirring and Blending Methods. Like shaking methods, stirring and blending methods are very dependent on procedural and equipment details, but they are simple to use and are widely employed for comparative purposes, for example, in coatings and paints. An example is given in ASTM D3519- 88 (revised in 2007).

For some applications, it is impossible to use a model laboratory test; testing is then done directly using the actual equipment. This is the case with laundry washing machines, where foam can be assessed visually through the window (front-loading machines) or by opening the lid (top-loaders), and with automatic dishwashers, which can be equipped with sensors to detect foam levels (73).

Health and Safety Factors

Antifoams are usually added at low bulk concentrations ranging from a few to a thousand parts per million of the foaming medium. Often the health risk posed by such additives is negligible as compared with that of the material being defoamed. Such is the case in the defoaming of asphalt and phosphoric acid. Sometimes a specific antifoam type/foaming medium combination presents a particular problem, and so the supplier should always be involved in antifoam selection. Examples are the increase in flammability of polyester textiles with free PDMS (76), and the possibility that mineral oil antifoams may contain precursors that form dioxins in bleached pulp after chlorination (83). Health and safety concerns arise primarily in applications in the food and drug industries. Antifoams can be incorporated directly into these products, as in the production of sugar from sugar beets or in the defoaming of fats for frying potato products, and indirectly, as in the manufacturing of paper- or plastic-packaging materials. US government regulations regarding the use of additives such as antifoams in food and drugs are listed in the Code of Federal Regulations (CFR). Title 21 contains the rules established by the Food and Drug Administration (FDA); title 40 covers those that are the concern of the EPA. For example, part 173.340 of title 21 deals with antifoams that may be safely used in processing foods, whereas part 180.1001 of title 40 lists those materials exempted from the requirement of tolerance levels in pesticide chemicals, including antifoams used therein. Other parts of title 21 that cover antifoam uses include 176.200 on coatings and 176.210 on the manufacture of paper and paperboard. One antifoam is also used as an active drug ingredient—the antifatulent silicone named simethicone. Such a use is regulated by the FDA under part 332 of title 21. Regulations are subject to change, and the CFR is revised at least once each calendar year. It is also kept up –to date in the individual issues of the *Federal Register*, a daily government publication. Although the intent may be the same, the regulatory practices differ in other countries and a multitude of regulations exist worldwide.

In Europe, the legal requirements for food contact are harmonized: Materials and articles intended to come into contact with food are subject to the Framework Regulation (EC) number 1935/2004. When there are no specific measures in this regulation, which is the case for paper, board, and silicones, the general requirements apply. For the interpretation of materials that are not yet regulated, national measures are still permitted. The German Recommendations (BfR) stipulate very extensive specific measures, which are used as a standard in several industries, in particular paper manufacturing: Recommendation XXXVI describes the regulations for paper and board for food contact, and recommendation XV deals with silicones. These recommendations are only valid for Germany but are widely acknowledged internationally. They contain positive lists of toxicologically evaluated materials, which are regularly reviewed by the BfR commission.

Under the auspices of the Joint Expert Committee on Food Additives of the FAO–WHO, efforts are being made to establish international guidelines. However, despite the changing regulatory climate, the differences in practice between countries, and a wide range of differences in antifoam components, the best advice for those interested in health and safety aspects of antifoams is to contact

the producers directly. Their skill and experience are the best advisers for the appropriate use of the antifoam.

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ANTIOXIDANTS

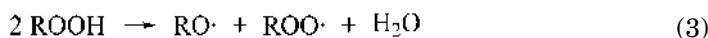
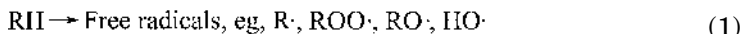
Introduction

Antioxidants are used to retard the reaction of organic materials, such as synthetic polymers, with atmospheric oxygen. Such reaction can cause degradation of the mechanical, aesthetic, and electrical properties of polymers; loss of flavor and development of rancidity in foods; and an increase in the viscosity, acidity, and formation of insolubles in lubricants. The need for antioxidants depends upon the chemical composition of the substrate and the conditions of exposure. Relatively high concentrations of antioxidants are used to stabilize polymers such as natural rubber and polyunsaturated oils. Saturated polymers have greater oxidative stability and require relatively low concentrations of stabilizers. Specialized antioxidants which have been commercialized meet the needs of the industry by extending the useful lives of the many substrates produced under anticipated conditions of exposure. In 2000, approximately 227,000 t (500 million pounds) of antioxidants were sold in polymer applications, with a value of \$1.3 billion (1). On average, the growth rate of antioxidants is around 4%, roughly tracking the growth of the global polymer markets (2).

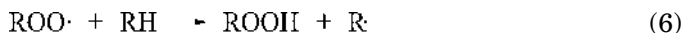
Mechanism of Uninhibited Autoxidation

The mechanism by which an organic material (RH) undergoes autoxidation involves a free-radical chain reaction is shown below (3–5):

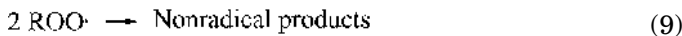
Initiation



Propagation



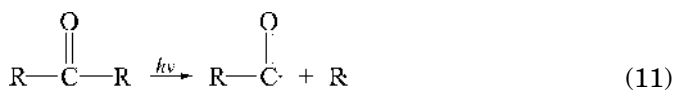
Termination



Initiation. Free-radical initiators are produced by several processes. The high temperatures and shearing stresses required for compounding, extrusion, and molding of polymeric materials can produce alkyl radicals by homolytic chain cleavage. Oxidatively sensitive substrates can react directly with oxygen, particularly at elevated temperatures, to yield radicals.

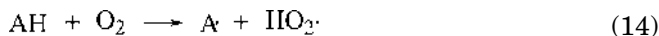
It is virtually impossible to manufacture commercial polymers that do not contain traces of hydroperoxides. The peroxide bond is relatively weak and cleaves homolytically to yield radicals (eqs. 2 and 3). Once oxidation has started, the concentration of hydroperoxides becomes appreciable. The decomposition of hydroperoxides becomes the main source of radical initiators.

The absorption of (uv) light produces radicals by cleavage of hydroperoxides and carbonyl compounds (eqs. 10–12)



Most polymer degradation caused by the absorption of uv light results from radical-initiated autoxidation.

Direct reaction of oxygen with most organic materials to produce radicals (eq. 13) is very slow at moderate temperatures. Hydrogen-donating antioxidants (AH), particularly those with low oxidation–reduction potentials, can react with oxygen (eq. 14), especially at elevated temperatures (6).



Propagation. Propagation reactions (eqs. 5 and 6) can be repeated many times before termination by conversion of an alkyl or peroxy radical to a nonradical species (7). Homolytic decomposition of hydroperoxides produced by propagation reactions increases the rate of initiation by the production of radicals.

The rate of reaction of molecular oxygen with alkyl radicals to form peroxy radicals (eq. 5) is much higher than the rate of reaction of peroxy radicals with a hydrogen atom of the substrate (eq. 6). The rate of the latter depends on the dissociation energies (Table 1) and the steric accessibility of the various carbon–hydrogen bonds; it is an important factor in determining oxidative stability (8).

Polybutadiene and polyunsaturated fats, which contain allylic hydrogen atoms, oxidize more readily than polypropylene, which contains tertiary hydrogen

Table 1. Dissociation Energies of Carbon–Hydrogen Bonds^a

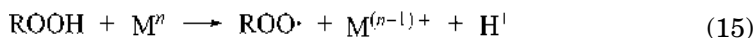
R–H	D _{R–H} , kJ/mol ^b	Bond type
CH ₂ =CHCH ₂ –H	356	Allylic
(CH ₃) ₃ C–H	381	Tertiary
(CH ₃) ₂ CH–H	395	Secondary

^aRef. 8.^bTo convert kJ to kcal, divide by 4.184.

atoms. A linear hydrocarbon such as polyethylene, which has secondary hydrogens, is the most stable of these substrates.

Autocatalysis. The oxidation rate at the start of aging is usually low and increases with time. Radicals, produced by the homolytic decomposition of hydroperoxides and peroxides (eqs. 2–4) accumulated during the propagation and termination steps, initiate new oxidative chain reactions, thereby increasing the oxidation rate.

Metal-Catalyzed Oxidation. Trace quantities of transition metal ions catalyze the decomposition of hydroperoxides to radical species and greatly accelerate the rate of oxidation. Most effective are those metal ions that undergo one-electron transfer reactions, eg, copper, iron, cobalt, and manganese ions (9). The metal catalyst is an active hydroperoxide decomposer in both its higher and its lower oxidation states. In the overall reaction, two molecules of hydroperoxide decompose to peroxy and alkoxy radicals (eq. 5).



Termination. The conversion of peroxy and alkyl radicals to nonradical species terminates the propagation reactions, thus decreasing the kinetic chain length. Termination reactions (eqs. 7 and 8) are significant when the oxygen concentration is very low, as in polymers with thick cross sections where the oxidation rate is controlled by the diffusion of oxygen, or in a closed extruder. The combination of alkyl radicals (eq. 7) leads to cross-linking, which causes an undesirable increase in melt viscosity and molecular weight.

Radical Scavengers

Hydrogen-donating antioxidants (AH), such as hindered phenols and secondary aromatic amines, inhibit oxidation by competing with the organic substrate (RH)

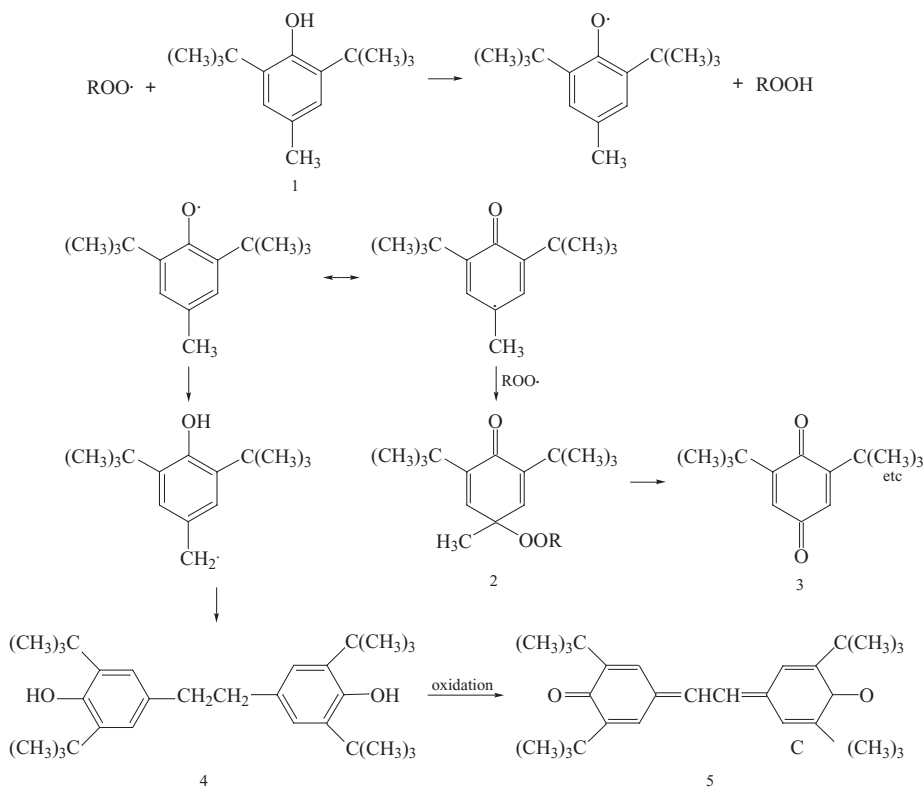
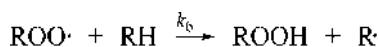
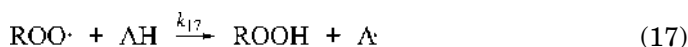


Fig. 1. Chemical transformations of 2,6-di-*tert*-butyl-*p*-cresol in an oxidizing medium (10).

for peroxy radicals. This shortens the kinetic chain length of the propagation reactions.



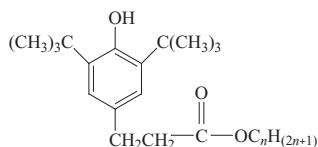
Because k_{17} is much larger than k_6 , hydrogen-donating antioxidants generally can be used at low concentrations. The usual concentrations in saturated thermoplastic polymers range from 0.01 to 0.05%, based on the weight of the polymer. Higher concentrations, ie, ca 0.5–2%, are required in substrates that are highly sensitive to oxidation, such as unsaturated elastomers and acrylonitrile-butadiene-styrene (ABS).

Hindered Phenols. Even a simple monophenolic antioxidant, such as 2,6-di-*tert*-butyl-*p*-cresol [128-37-0] (1), has a complex chemistry in an autooxidizing substrate as seen in Figure 1 (10).

Stilbenequinones such as compound 5 absorb visible light and cause some discoloration. However, upon oxidation phenolic antioxidants impart much less

Table 2. Influence of Antioxidant (6) Volatility on Effectiveness at 140°C

n^a	$t_{1/2}, h^b$	Time to failure in PP, h		Time to failure in dodecane, h
		O ₂ uptake	Airstream	
1	0.28	95	2	25
6	3.60	312	2	23
12	83.0	420	2	20
18	660.0	200	165	20

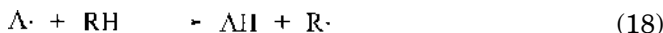
^a n in

(6)

^bAntioxidant half-life in polypropylene exposed to a nitrogen stream at 140°C.

color than aromatic amine antioxidants and are considered to be nondiscoloring and nonstaining.

The effect substitution on the phenolic ring has on activity has been the subject of several studies (11–13). Hindering the phenolic hydroxyl group with at least one bulky alkyl group in the ortho position appears necessary for high antioxidant activity. Nearly all commercial antioxidants are hindered in this manner. Steric hindrance decreases the ability of a phenoxyl radical to abstract a hydrogen atom from the substrate and thus produces an alkyl radical (14) capable of initiating oxidation (eq. 17).

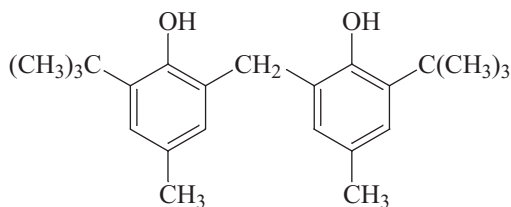


Replacing a methyl with a tertiary alkyl group in the para position usually decreases antioxidant effectiveness. The formation of antioxidants such as compound (4) by dimerization is precluded because all benzylic hydrogen atoms are replaced by methyl groups. A strong electron-withdrawing group on the aromatic ring, such as cyano or carboxy, decreases the ability of the phenol to donate its hydrogen atom to a peroxy radical of the substrate and reduces antioxidant effectiveness.

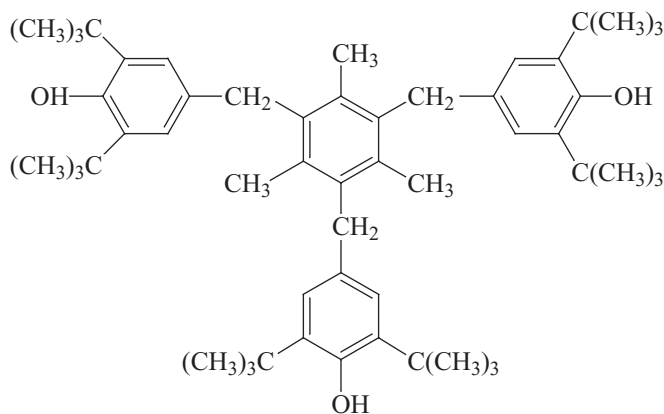
The usefulness of a hindered phenol for a specific application depends on its radical-trapping ability, its solubility in the substrate, and its volatility under test conditions. Table 2 shows the importance of volatility to stabilizer performance. Equimolar quantities of alkyl esters (6) of 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamic acid were evaluated in polypropylene at 140°C, using two different procedures (15). When tested in an airstream, only the octadecyl ester(6) (where $n = 18$) was effective in stabilizing the polymer. Under these conditions, the lower homologues were lost by volatilization. The oxygen-uptake test, carried out in a closed system that minimizes evaporative loss, showed that homologues were effective to varying degrees. The differences in effectiveness can probably be attributed to differences in the solubility of various homologues in the amorphous phase of the polypropylene. When dodecane, a

liquid in which all the compounds are soluble, was used as a substrate instead of polypropylene, the antioxidant activities were relatively close.

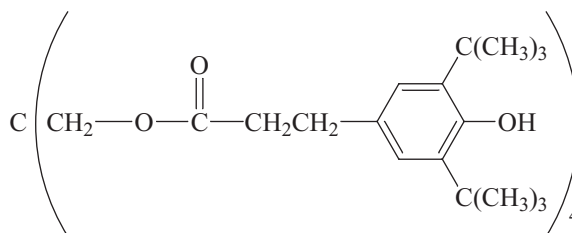
Introducing long aliphatic chains into a stabilizer molecule decreases volatility and increases solubility in hydrocarbon polymers. This improves performance; however, it also increases the equivalent weight of the active moiety. Di-, tri-, and polyphenolic antioxidants combine relatively low equivalent weights with low volatility. Commercially important di-, tri-, and polyphenolic stabilizers include 2,2'-methylenebis(6-*tert*-butyl-*p*-cresol) [85-60-9] (7), 1,3,5-trimethyl-2,4,6-tris(3'5'-di-*tert*-butyl-4-hydroxybenzyl)benzene [1709-70-2] (8), and tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane [6683-19-8] (9).



(7)



(8)



(9)

Aromatic Amines. Antioxidants derived from *p*-phenylenediamine and diphenylamine are highly effective peroxy radical scavengers. They are more

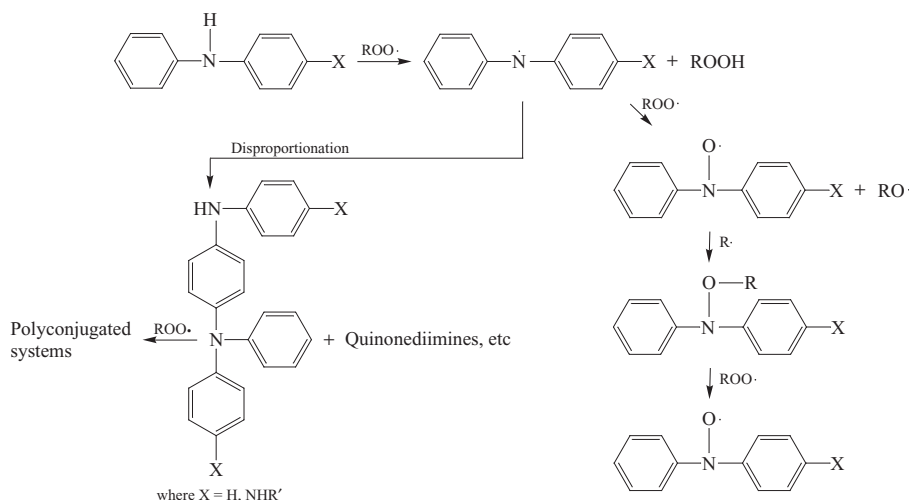
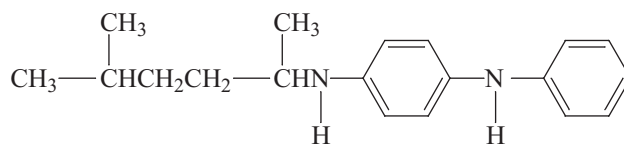


Fig. 2. Oxidation of aromatic amine antioxidants (10).

effective than phenolic antioxidants for the stabilization of easily oxidized organic materials, such as unsaturated elastomers. Because of their intense staining effect, derivatives of *p*-phenylenediamine are used primarily for elastomers containing carbon black (qv).

N,N'-Disubstituted-*p*-phenylenediamines, such as *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine [793-24-8] (10), are used in greater quantities than other classes of antioxidants. These products protect unsaturated elastomers against oxidation as well as ozone degradation (see RUBBER CHEMICALS).

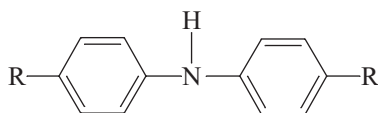


(10)

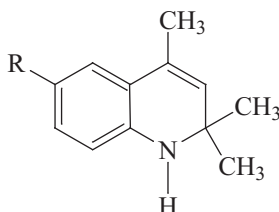
Low concentrations of alkylated paraphenylenediamines, such as *N,N'*-di-*sec*-butyl-*p*-phenylenediamine [69796-47-0], are added to gasoline to inhibit oxidation.

Figure 2 shows some of the reactions of aromatic amines that contribute to their activity as antioxidants and to their tendency to form highly colored polyconjugated systems.

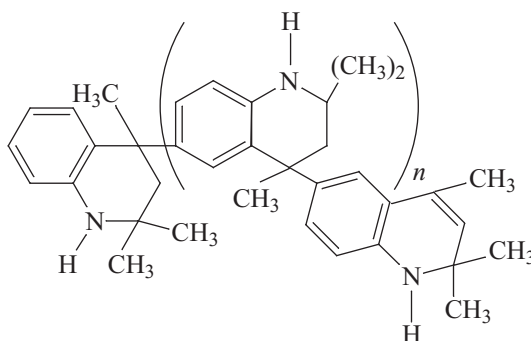
Alkylated diphenylamines 11 and derivatives of both dihydroquinoline (12) and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline [26780-96-1] (13) develop less color than the *p*-phenylenediamines and are classified as semistaining antioxidants. Derivatives of dihydroquinoline are used for the stabilization of animal feed and spices.



(11)

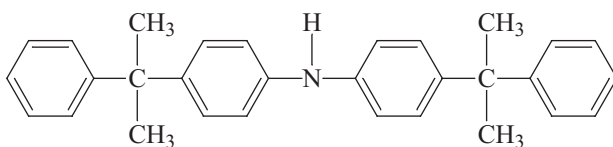


(12)

where $n = 0-6$

(13)

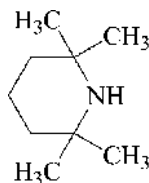
4,4'-Bis(α,α -dimethylbenzyl)diphenylamine [1008-67-1] (14) has only a slight tendency to stain and has been recommended for use in plastics as well as elastomers.



(14)

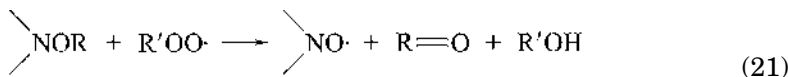
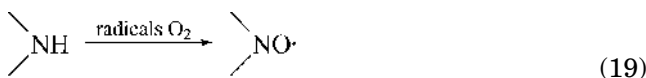
Hindered Amines. Hindered amines are extremely effective in protecting polyolefins and other polymeric materials against photodegradation. They usually are classified as light stabilizers rather than antioxidants.

Most of the commercial hindered-amine light stabilizers (HALS) are derivatives of 2,2,6,6-tetramethylpiperidine [768-66-1] (15) (16).



(15)

These stabilizers function as light-stable antioxidants to protect polymers. Their antioxidant activity is explained by the following sequence (17):



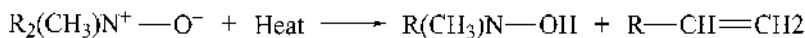
According to this mechanism, hindered-amine derivatives terminate propagating reactions (eqs. 5 and 6) by trapping both the alkyl and peroxy radicals. In effect, NO competes with O_2 , and NOR competes with RH. Since the nitroxyl radicals are not consumed in the overall reactions, they are effective at low concentrations.

Hydroxylamines. A relatively new stabilizer chemistry, commercially introduced in 1996, (18) based on the hydroxylamine functionality, can serve as a very powerful hydrogen-atom donor and free-radical scavenger (19), as illustrated in Figure 3.

This hydroxylamine chemistry is extremely powerful on an equivalent weight basis in comparison with conventional phenolic antioxidants and phosphite melt-processing stabilizers. In terms of its free-radical scavenger capability, however, it is more effective during melt-processing of the polymer, but not during long-term thermal stability (ie, below the melting point of the polymer). This is quite interesting because of the similarity between the type of free-radical scavenging chemistry that hydroxylamines and phenols are both capable of providing. However, the temperature range is different. This is discussed further below.

The only commercial hydroxylamine product used in polyolefins and other selected polymers is a product of a process based on the oxidation of bis-tallow amine [14325-92-2].

There is a similar commercially available product based on related chemistry. It is a product of a process based on the oxidation of methyl-bis-tallow amine [204933-93-7]. The oxidation product of methyl-bis-tallow amine is a trialkylamine oxide, a precursor to hydroxylamine stabilization chemistry. The trialkylamine oxide is converted to a hydroxylamine and a long-chain olefin during the initial melt compounding of the polymer by a Cope elimination reaction, as shown below.



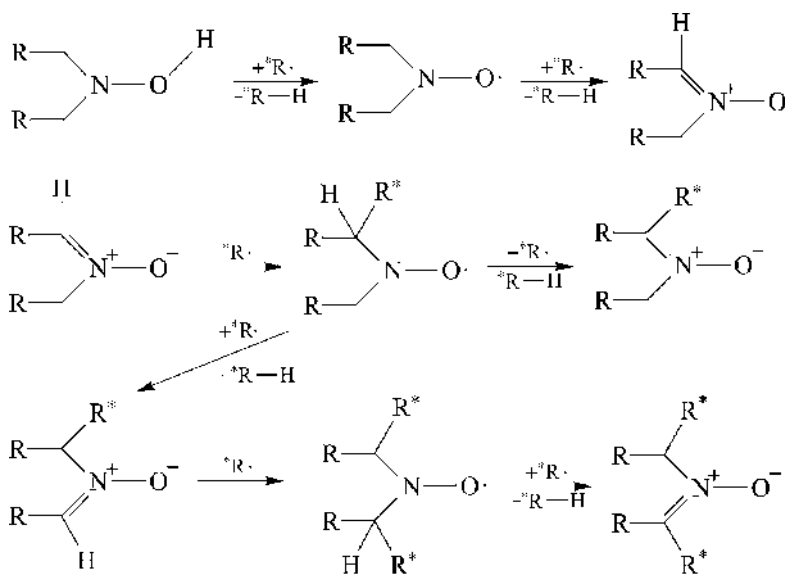


Fig. 3. Free Radical Decomposition Mechanism for Hydroxylamines. *R* = alkyl (R*), alkoxy (RO*), or peroxy (ROO*) type radicals.

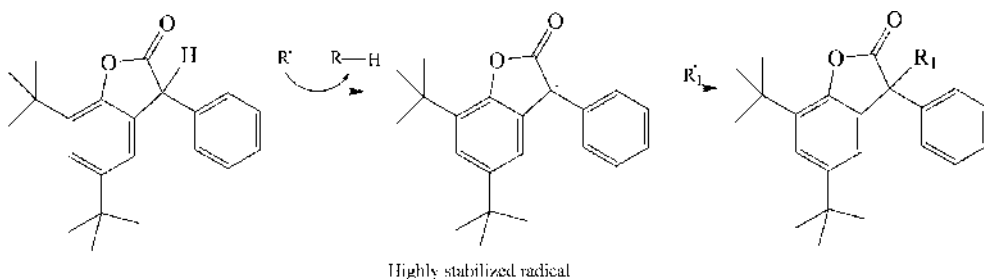


Fig. 4. Proposed Stabilization Mechanism of Arylbenzofuranones. R* = Carbon- or Oxygen-Centered Radical.

Benzofuranones. In 1997, a fundamentally new type of chemistry was introduced, which not only inhibits the autoxidation cycle, but attempts to shut it down as soon as it starts (20). The exceptional stabilizer activity of this class of benzofuranones is due to the ready formation of a stable benzofuranyl radical by donation of the weakly bonded benzylic hydrogen atom (see Fig. 4).

The resonance stabilized benzofuranyl (lactone) radicals can either reversibly dimerize or react with other free radicals. Model experiments have demonstrated that this class of chemistry behaves as a powerful hydrogen atom donor and are also effective scavengers of carbon-centered and oxygen-centered free radicals (21) (see Fig. 5).

While the sterically hindered phenols react preferentially with oxygen-centered radicals such as peroxy and alkoxy, rather than with carbon-centered radicals, benzofuranones can scavenge both types of radicals. Accordingly, a benzofuranone can be repeatedly positioned at key locations around the autoxidation

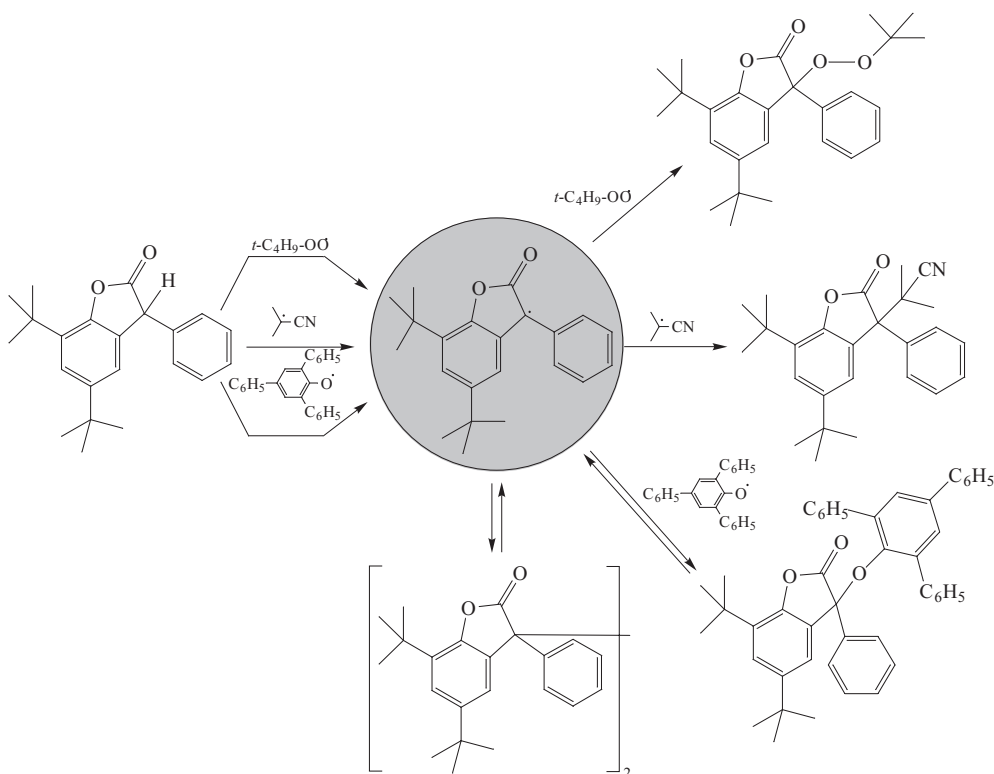


Fig. 5. Carbon-centered free-radical trapping reactions with benzofuranones.

cycle to inhibit the proliferation of free radicals. In addition, the scavenging of carbon-centered radicals is representative of a mode of stabilization that is more like “preventive maintenance,” compared with more traditional stabilizers such as phenols and phosphites, which operate in something more like a “damage control” mode.

Benzofuranones are similar to hydroxylamines in that on an equivalent weight basis, they are more powerful than conventional phenolic antioxidants or phosphite-based melt-processing stabilizers. Once again it should be noted that even though benzofuranones are capable of providing free-radical scavenging chemistry similar to phenolic antioxidants, the effective temperature domain is typically above the melting point of the polymer, eg, during melt-processing (similar to hydroxylamines). This will be discussed further below.

Peroxide Decomposers

Thermally induced homolytic decomposition of peroxides and hydroperoxides to free radicals (eqs. 2–4) increases the rate of oxidation. Decomposition to nonradical species removes hydroperoxides as potential sources of oxidation initiators.

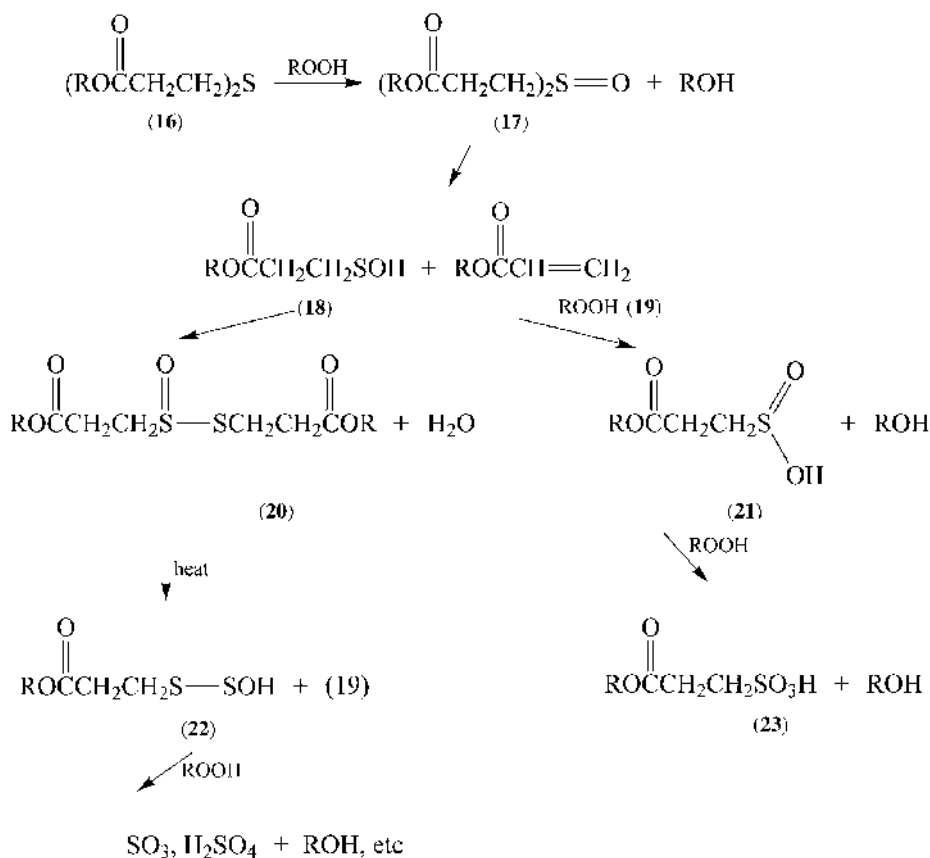


Fig. 6. Decomposition of hydroperoxides by esters of thiodipropionic acid (18).

Most peroxide decomposers are derived from divalent sulfur and trivalent phosphorus.

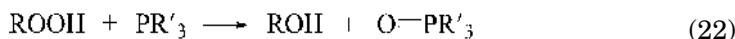
Divalent Sulfur Derivatives. A dialkyl ester of thiodipropionic acid (16) is capable of decomposing at least 20 mol of hydroperoxide (22). Some of the reactions contributing to the antioxidant activity of these compounds are shown in Figure 6 (23,24).

According to Figure 6, hydroperoxides are reduced to alcohols, and the sulfide group is oxidized to protonic and Lewis acids by a series of stoichiometric reactions. The sulfinic acid (21), sulfonic acid (23), sulfur trioxide, and sulfuric acid are capable of catalyzing the decomposition of hydroperoxides to nonradical species.

When used alone at low temperatures, dialkyl thiodipropionates are rather weak antioxidants. Synergistic mixtures with hindered phenols, however, are highly effective at elevated temperatures and are used extensively to stabilize polyolefins, ABS, impact polystyrene, and other plastics.

Esters of thiopropionic acid tend to decompose at high processing temperatures, and their odor makes them unsuitable for some food-packaging applications.

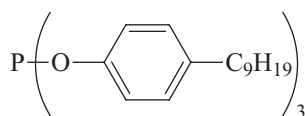
Trivalent Phosphorus Compounds. Trivalent phosphorus compounds reduce hydroperoxide to alcohols:



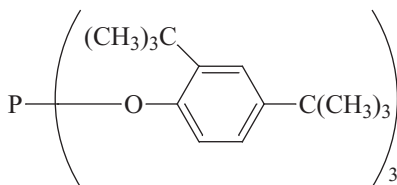
These compounds are used most frequently in combination with hindered phenols for a broad range of applications in rubber and plastics. They are also able to suppress color development caused by oxidation of the substrate and the phenolic antioxidant. Unlike phenols and secondary aromatic amines, phosphorus-based stabilizers generally do not develop colored oxidation products.

Esters of phosphorous acid derived from aliphatic alcohols and unhindered phenols, eg, tris-nonylphenylphosphite (24), hydrolyze readily and special care must be taken to minimize decomposition by exposure to water or high humidity. The phosphorous acid formed by hydrolysis is corrosive to processing equipment, particularly at high temperatures.

The hydrolysis of phosphites is retarded by the addition of a small amount of a base such as triethanolamine. A more effective approach is the use of hindered phenols for esterification. Relatively good resistance to hydrolysis is shown by two esters derived from hindered phenols: tris(2,4-di-*tert*-butylphenyl)phosphite [31570-04-4] (25) and tetrakis(2,4-di-*tert*-butylphenyl)4,4'-biphenylenediphosphonite [38613-77-3] (26). A substantial research effort over the last decade to develop hydrolytically stable phosphites while retaining the excellent hydroperoxide decomposing activity has resulted in the introduction of a number of new commercial products such as the dicumyl phosphite [154862-43-8].



(24)



(25)

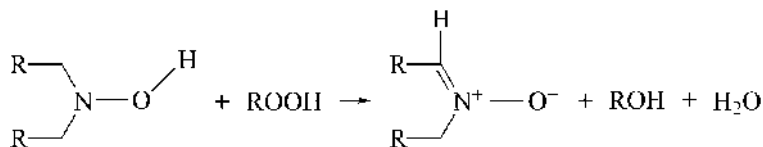
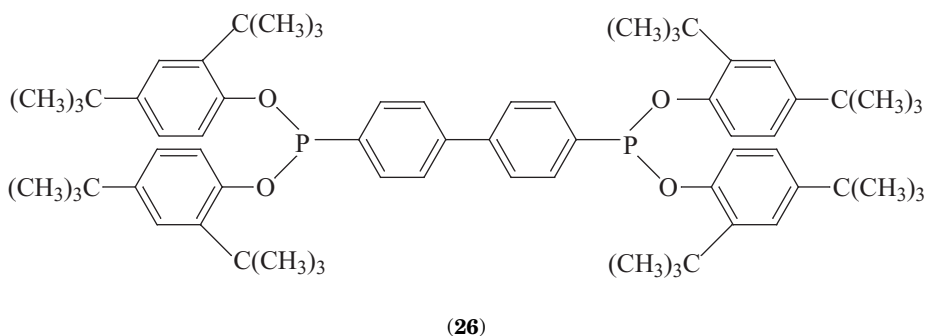
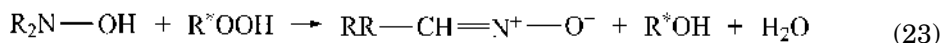


Fig. 7. Hydroperoxide Decomposition Mechanism for Hydroxylamines. R: mixture of long chain alkyl groups; C₁₆H₃₃, C₁₈H₃₇, C₂₀H₄₂, and C₂₂H₄₅.



Hydroxylamines. As mentioned above, hydroxylamines are very effective as free-radical scavengers. They are also noted for their ability to decompose hydroperoxides (25); this is shown in equation 21 and illustrated in Figure 7.



Hydroxylamines serve as a sequential source of hydrogen atoms, reducing hydroperoxides to their corresponding alcohol. In the course of this reaction, the hydroxylamine is converted to a nitron.

Metal Deactivators

The ability of metal ions to catalyze oxidation can be inhibited by metal deactivators (26). These additives chelate metal ions and increase the potential difference between their oxidized and reduced states. This decreases the ability of the metal to produce radicals from hydroperoxides by oxidation and reduction (eqs. 15 and 16). Complexation of the metal by the metal deactivator also blocks its ability to associate with a hydroperoxide, a requirement for catalysis (27).

Examples of commercial metal deactivators used in polymers are oxalyl bis(benzylidene)hydrazide [6629-10-3] (27), *N,N'*-bis-(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyl)hydrazine [32687-78-8] (28), 2,2'-oxamidobisethyl (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) [70331-94-1] (29), *N,N'*-(disalicylidene)-1,2-propanediamine [94-91-7] (30), ethylenediaminetetraacetic acid [60-00-4] (31) and its salts, and citric acid (32) (Fig. 8).

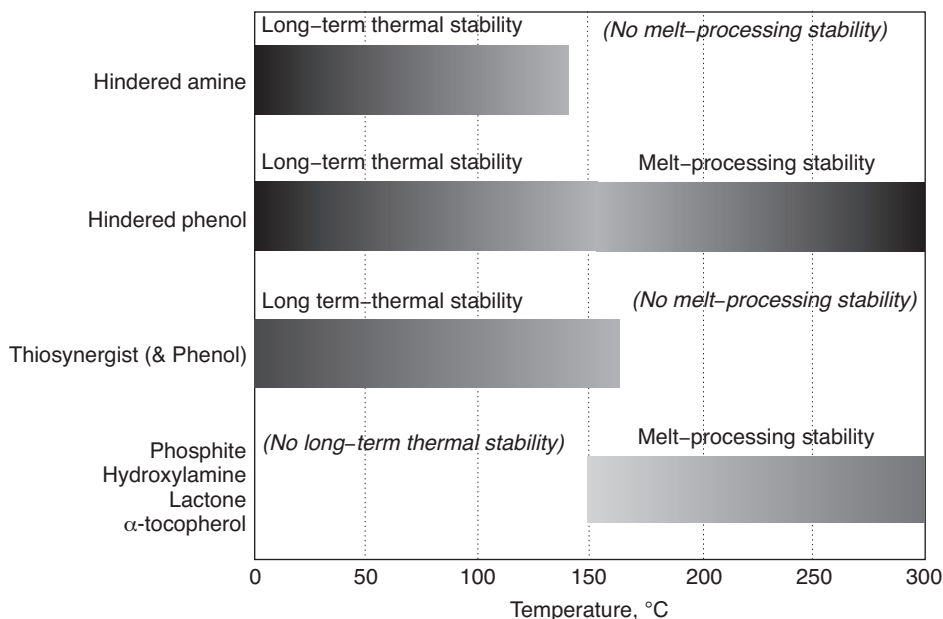


Fig. 9. General representation of effective temperature ranges for selected types of antioxidants.

antioxidant, allowing more to remain intact to help with long-term thermal stability.

One anomaly that should be pointed out is the hindered phenols based on tocopherols. Even though tocopherols, such as Vitamin E [10191-41-01], fall into the general class of hindered phenols, they behave more as melt-processing stabilizers, and less as reagents for providing long-term thermal stability, at least with regard to polymer stabilization.

Antioxidant Blends

In practical application, it is reasonable to use more than one type of antioxidant in order to meet the requirements of the application, such as melt-processing stability as well as long-term thermal stability. The most common combination of stabilizers used, particularly in polyolefins, are blends of a phenolic antioxidant and a phosphite melt-processing stabilizer. Another common combination is a blend of a phenolic antioxidant and a thioester, especially for applications that require long-term thermal stability. These common phenol-based blends have been used successfully in many different types of end-use applications. The combination of phenolic, phosphite, and lactone moieties represents an extremely efficient stabilization system since all three components provide a specific function.

For color-critical applications requiring “phenol-free” stabilization, synergistic mixtures of hindered amines (for both uv stability as well as long-term thermal stability) with a hydroxylamine or benzofuranone (for melt processing), with or

without a phosphite, can be used to avoid discoloration typically associated with the overoxidation of the phenolic antioxidant (28). The use of “phenol-free” stabilization systems is very effective in color-critical products, such as polyolefin films and fibers, as well as selected thermoplastic olefin (TPO) applications.

Synergist Mixtures of Antioxidants

A mixture of antioxidants that function by different mechanisms might be synergistic and provide a higher degree of protection than the sum of the stabilizing activities of each component. The most frequently used synergistic mixtures are combinations of radical scavengers and hydroperoxide decomposers.

Typically, blend titration experiments are performed at a set loading of additives, starting with 100% of Component A and 0% of Component B. A series of formulations are designed to shift to the other extreme with 0% Component A and 100% Component B. By measuring a series of performance parameters, the optimum ratio of A to B can be determined. This type of work is time consuming, but in the end, the optimum ratio is identified with real data. If three or more components are being assessed at the same time, statistically designed experiments are often useful in terms of sorting out the data.

Antagonistic Mixtures of Antioxidants

Mixtures of antioxidants can also work against each other. Chemistries that interfere with each other may not necessarily be obvious until the evidence is presented. For example, to ensure long-term thermal stability and good light stability, one might use a combination of a phenolic antioxidant and a divalent sulfur compound for thermal stability and a hindered amine for light stability.

Unfortunately, the oxidation products of the sulfur compound can be quite acidic and can complex the hindered amine as a salt, preventing the hindered amine from entering into its free-radical scavenging cycle. This antagonism has been generally known for quite a while (29) and has been discussed (30).

Other types of antagonistic chemistry often involve relatively strong acids or bases (either Bronstead or Lewis) that can interact with the antioxidants in such a way as to divert them into transformation chemistries that have nothing to do with polymer stabilization.

Application of Antioxidants in Polymers

Nearly all polymeric materials require the addition of antioxidants to retain physical properties and to ensure an adequate service life. The selection of an antioxidant system is dependent upon the polymer and the anticipated end use.

Polyolefins. Low concentrations of stabilizers (<0.01%) are often added immediately to polyethylene and polypropylene after synthesis and prior to isolation so as to retard oxidation of the polymer before they are exposed to sources of oxygen or air (see ETHYLENE POLYMERS; PROPYLENE POLYMERS). Higher

Table 3. Synergism between a Hindered Phenol and a Thiosynergist^a

Additive, %		Induction period, days
Radical scavenger ^b	Hydroperoxide decomposer ^c	
0.0	0.3	4
0.1	0.0	16
0.1 ^d	0.3 ^d	45

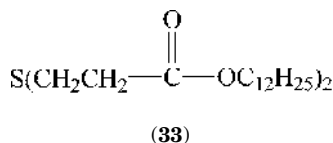
^aRef. 21.^bTetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane.^cDilauryl thiodipropionate.^dMixture.

concentrations are added downstream during the conversion of the reactor product to a pelletized form. The antioxidant components and concentrations are selected by the manufacturer to yield general-purpose grades, or can be optimized to meet a specific end-use application.

In downstream applications, these polymers can be subjected to temperatures as high as 300°C, during cast film extrusion and thin-wall injection molding. In these type of demanding applications, processing stabilizers are used to decrease both the change in viscosity (molecular weight) of the polymer melt and the development of color. A phosphite, such as tris(2,4-di-*tert*-butylphenyl)phosphite (25) or bis(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite [26741-53-7], in combination with a phenolic antioxidant such as octadecyl 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate (6), may be used. Concentrations usually range from 0.01 to 0.5% depending on the polymer and the severity of the processing conditions. For long-term exposure, a persistent antioxidant such as tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane (9), at a concentration of 0.1–0.5%, may be added to the base stabilization package.

A sulfur-containing synergistic mixture can be used to obtain an extended service life at a decreased cost.

The synergistic effect of a hydroperoxide decomposer, eg, dilauryl thiodipropionate [123-28-4] (33), and a radical scavenger, eg, compound 9, in protecting polypropylene during an oxygen-uptake test at 140°C is shown in Table 3.



The sum of the individual activities of these antioxidants was 20 days, whereas a mixture of the two stabilizers protected the polymer for 45 days (31).

Oligomeric-HALS are effective thermal antioxidants for polypropylene. Thus 0.1% of *N,N'*-bis(2,2,6,6-tetramethyl-4-piperadiny)-1,6-hexanediamine polymer, with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-2-pentaneamine [70624-18-9] (34) (Fig. 10 & Table 4), protects polypropylene multifilaments against oxidation when exposed at 120°C in a forced-air oven for 47 days (32). The simple hindered phenol 3,5-di-*tert*-butyl-4-hydroxytoluene [128-37-0] (0.1%) affords protection for only 14 days.

Table 4. Commonly Used Antioxidants^a by Class

Chemical name	CAS registry no.	Suggested substrates ^b	Suppliers
<i>Monophenols</i>			
α -Tocopherol	[10191-41-01]	PO, PUR	Ciba SC, BASF
2,6-Di- <i>tert</i> -butyl-4-methylphenol	[128-37-0]	PA, PES, PO, POM, PUR, PVC, RU, PS	Great Lakes, Merisol, PMC, Crompton
Octadecyl-3,5-di- <i>tert</i> -butyl-4-hydroxycinnamate	[2082-79-3]	CE, PA, PO, PUR, PVC, PS	Ciba SC, Crompton, Great Lakes, GE Specialty
Isooctyl-3,5-di- <i>tert</i> -butyl-4-hydroxycinnamate	[126-43-61-0]	PUR	Ciba SC, Crompton
<i>Bisphenols</i>			
2,2'-Methylenebis(4-methyl-6- <i>tert</i> -butylphenol)	[119-47-1]	CE, PA, POM, PUR, PVC, RU, PS	Cytec, RT Vanderbilt, Great Lakes, Ferro
2,2'-Methylenebis(4-ethyl-6- <i>tert</i> -butylphenol)	[88-24-4]	PA, PO, PVC	Cytec
4,4'-butylidenebis(6- <i>tert</i> -butyl-3-methylphenol)	[85-60-9]	CE, EVA, PA, PES, PO, PVC, RU, PS	Flexsys
<i>N,N'</i> -Hexamethylene bis(3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamide)	[23128-74-7]	PA, PES, PA, RU	Ciba SC, Great Lakes
1,6-Hexamethylenebis(3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamate)	[35074-77-2]	CE, PES, PO, POM, PUR, PVC, PS	Ciba SC
Benzenepropanoic acid, 3-(1,1-dimethylethyl)-4-hydroxy-5-methyl-, 2,4,8,10-tetraoxaspiro[5.5]undecane- 3,9-diylbis(2,2-dimethyl-2,1-ethanediyl) ester ^c	[90498-90-1]		Sumitomo
Triethyleneglycol bis(3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamate)	[36443-68-2]	PA, POM, PVC, PS	Ciba SC, Great Lakes
Calcium bis[<i>O</i> -ethyl(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl)]-phosphonate	[65140-91-2]	PO, RU	Ciba SC
<i>Polyphenols</i>			
1,3,5-Trimethyl-2,4,6-tris(3',5'-di- <i>tert</i> -butyl-4'-hydroxybenzyl)-benzene	[1709-7-2]	CE, PA, PES, PO, POM, PVC, RU, PS	Albemarle, Ciba SC, Great Lakes, Sigma 3V
3:1 Condensate of 3-methyl-6- <i>tert</i> -butylphenol with crotonaldehyde	[1843-03-4]	CE, PA, PES, PO, POM, PUR, PVC, RU, PS	ICI Americas

(Continued)

Table 4. (Continued)

Chemical name	CAS registry no.	Suggested substrates ^b	Suppliers
Tetrakis[methylene(3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamate)methane	[6683-19-8]	CE, PA, PES, PO, POM, PVC, PS	Ciba SC, Great Lakes, Crompton, GE Specialty Chem
1,3,5-Tris(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl) isocyanurate	[27676-62-6]	CE, PA, PES, PO, POM, PVC, PS	Ciba SC, RT Vanderbilt, Great Lakes Chem, Sigma 3V
3,5-Di- <i>tert</i> -butyl-4-hydroxy-hydrocinnamic triester with 1,3,5-Tris(2-hydroxyethyl)-s-triazine-2,4,6-(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)trione	[34137-09-2]	CE, PA, PO, PUR, PVC, RU, PS	Ciba SC, RT Vanderbilt
1,3,5-Tris(4- <i>tert</i> -butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1 <i>H</i> , 3 <i>H</i> ,5 <i>H</i>)trione	[40601-76-1]	CE, PA, PES, PO, POM, PUR, PVC, RU, PS	Cytotec, Ciba SC, Great Lakes Chem
Bis[3,3-bis(4-hydroxy- <i>tert</i> -butylphenyl)butanoic acid], Glycol ester	[32509-66-3]	CE, PA, PES, PO, POM, PVC, PS	Clariant
Butylated reaction product of <i>p</i> -cresol and dicyclopentadiene	[31851-03-3]	CE, PA, PES, PO, POM, PVC, RU, PS	Goodyear
<i>Phenolics with dual functionality</i>			
4,4'-Thiobis(6- <i>tert</i> -butyl-3-methylphenol)	[96-69-5]	PA, PES, PO, PVC, RU, PS	Flexsys, Sumitomo
4,4'-Thiobis(2-methyl-6-butylphenol) ^c	[96-66-2]	PO, RU	Albemarle
Thiodiethylene bis(3,5-di- <i>tert</i> -butyl-4-hydroxycinnamate)	[41484-35-9]	CE, PA, PO, PUR, PVC, RU, PS	Ciba SC, Great Lakes
4,6-Bis(octylthiomethyl)- <i>o</i> -cresol	[110553-27-0]	RU, PS	Ciba SC
Reaction product of nonylphenol, dodecanethiol, and formaldehyde	[188793-84-2]	RU, PS	Goodyear
2,4-Bis(<i>n</i> -octylthio-6-(4-hydroxy-3,5-di- <i>tert</i> -butylanilino)-1,3,5-triazine	[991-84-4]	RU, PS	Ciba SC
2-(1,1-dimethylethyl)-6-[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]methyl-4-methylphenylacrylate	[61167-58-6]	PS	Sumitomo, Ciba SC

<i>Metal deactivators</i>				
<i>N,N'</i> -Bis(3,5-di- <i>tert</i> -butyl-4-hydroxyhydrocinnamoyl)hydrazine	[32687-78-8]	PA, PO, RU	Ciba SC, Great Lakes	
2,2'-Oxamidobisethyl(3,5-di- <i>tert</i> -butyl-4-hydrocinnamate)	[70331-94-1]	PA, PO, RU	Crompton	
Oxalic acid, bis(benzylidenehydrazide) ^c	[6629-10-3]	PA, PO, RU	Eastman	
<i>Arylamines</i>				
4,4'-Bis(dimethylbenzyl)-diphenylamine	[10081-67-1]	RU, PO, PS, PUR	Crompton	
<i>N</i> -Phenyl- α -naphthylamine	[90-30-2]	PA, PES, PO, RU	Bayer, Flexsys, RT Vanderbilt	
<i>N</i> -Phenyl- <i>N'</i> -isopropyl- <i>p</i> -phenylenediamine	[101-72-4]	RU	Bayer, Flexsys, RT Vanderbilt, Crompton	
Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline ^c	[26780-96-1]	RU	Flexsys, RT Vanderbilt, Crompton	
Octylated diphenylamine	[68411-46-1]	RU, PUR	Ciba SC, Crompton, Great Lakes, RT Vanderbilt	
<i>Thioethers</i>				
Didodecyl-3,3'-thiodipropionate	[123-28-4]	PA, PO, RU	Cytec, Crompton, Evans Chemetic	
Distearyl-3,3'-thiodipropionate	[693-36-7]	PA, PO, RU	Cytec, Crompton, Evans Chemetic	
Pentaerythritol tetrakis(3-dodecylthio)propionate	[29598-76-3]	PA, PO	Crompton	
<i>S,S'</i> -Distearyl disulfide	[2500-88-1]	PA, PO, RU	Clariant	
<i>Phosphites / phosphonites</i>				
Tris nonylphenylphosphite	[26523-78-4]	CE, PES, PO, PUR, PVC, RU, PS	Crompton, GE Specialty, Dover	
Tris(2,4-di- <i>tert</i> -butylphenyl)phosphite	[31570-04-4]	CE, PES, PO, PUR, PS	Ciba SC, GE Specialty, Great Lakes, Crompton	
Distearyl pentaerythritoldisphosphite	[3806-34-6]	CE, PES, PO, PUR, PS, RU	GE Specialty	

(Continued)

Table 4. (Continued)

Chemical name	CAS registry no.	Suggested substrates ^b	Suppliers
Bis(2,4-di- <i>tert</i> -butylphenyl)pentaerythritol diphosphate	[26741-53-7]	CE, PES, PO, PUR, PS, RU	GE Specialty, Ciba SC, Great Lakes
2,4,6-Tri- <i>tert</i> -butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite	[161717-32-4]	PO, PS	GE Specialty
Bis(2,4-dicumylphenyl)pentaerythritol diphosphate	[154862-43-8]	CE, PES, PO, PUR, PS, RU	Dover
Tetrakis(2,4-di- <i>tert</i> -butylphenyl)-4,4'-biphenylene diphosphonite	[119345-01-6]	CE, PES, PO, PUR, PS, RU	Clariant, Ciba SC, Great Lakes
<i> Hindered amines</i>			
Poly[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl][(2,2,6,6-piperidinyl)imino]-4-piperidinyl]imino]	[71878-19-8]	PO, EVA	Ciba SC
Poly[6-[1-morpholinol-1,3,5-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]	[82451-48-7]	PO, EVA	Cyttec
Butanedioic acid, dimethyl ester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine, ethanol	[65447-77-0]	PO, EVA	Ciba SC
7-Oxa-3,20-diazadispiro[5.1.11.2]heneicosan-21-one, 2,2,4,4-tetramethyl-, hydrochloride, reaction products with epichlorohydrin, hydrolyzed, polymerized	[202483-55-4]	PO, EVA	Clariant

1,3-Propanediamine, <i>N,N''</i> -1,2-ethanediyldis-, polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with <i>N</i> -butyl-2,2,6,6-tetramethyl-4-piperidinamine	[136504-96-6]	PO, EVA	Sigma 3V
1,3,5-Triazine-2,4,6-triamine, <i>N,N'</i> -1,2-ethane-diyl-bis[(4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-3,1-propanediyl)]bis(<i>N',N'</i> -dibutyl- <i>N',N'</i> -bis(1,2,2,6,6-pentamethyl-4-piperidinyl) siloxanes and silicones, methyl-hydrogen, reaction products with	[106990-43-6]	PO, EVA	Ciba SC
2,2,6,6-tetramethyl-4-(2-propenyloxy)piperidine <i>Processing stabilizers</i>	[182635-99-0]	PO, EVA	Great Lakes
2(3 <i>H</i>)-Benzofuranone, 5,7-bis(1,1-dimethylethyl)-3-hydroxy, reaction products with <i>o</i> -xylene	[181314-48-7]	PO, PUR	Ciba SC
1-Octadecanamine, <i>N</i> -hydroxy- <i>N</i> -octadecyl	[123250-74-8]	PO, RU	Ciba SC
Di (rape oil)alkyl- <i>N</i> -methylaniline oxide	[204933-93-7]	PO, RU	GE Specialty

^aFDA regulated unless otherwise indicated. Regulated by the U.S. Food and Drug Administration as an indirect food additive under Title 21 of the U.S. Code of Federal Regulations (21 CFR), Part 175 (Adhesives and Coatings) and/or Part 177 (Polymers).

^bCE: cellulostics; EVA: ethylene-vinyl acetate copolymers; PA: polyamides; PES: polyesters; PO: polyolefins; POM: polyoxymethylenes; PUR: polyurethanes, polyols; RU: rubber; PS: polystyrenes; PVC: poly(vinyl chloride).

^cNot FDA regulated.

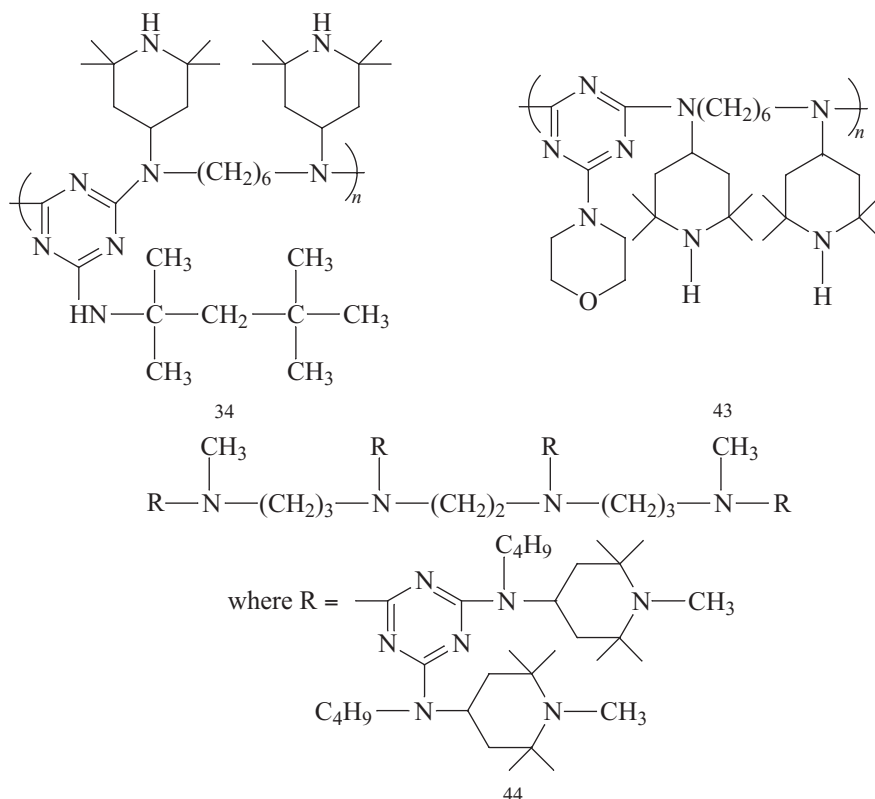


Fig. 10. Hindered 1,6-hexanediamine antioxidants.

The stabilization of polyolefins used to insulate copper conductors requires the use of a long-term antioxidant plus a copper deactivator. Both compounds 28 and 29 are bifunctional antioxidants that have built-in metal deactivators. Compound 27 is an effective copper deactivator as part of an additive package that includes an antioxidant.

Polyamides. Because of their excellent mechanical properties at high temperatures, polyamides, particularly mineral and glass-filled grades, are finding increased usage in demanding applications such as automotive (under-the-hood) applications (see POLYAMIDES, PLASTIC). Only a few publications dealing with stabilization of polyamides are found in the literature (33). The aliphatic polyamides differ in their structure, PA 6,6, PA 6, PA 4,6, PA 11, and PA 12 being the most common types. The oxidative stability of the various types is dependent on the density of the amorphous phase and the degree of crystallinity because these two factors control oxygen migration into the polymer matrix (34). Aromatic polyamides are rather insensitive to oxidative degradation.

The traditional stabilization system for aliphatic polyamides are copper salts. Typical systems are based on low levels of copper (<50 ppm) and iodide or bromide salts (35). The mechanism of stabilization is not well understood but may be due to hydroperoxide decomposition initiated by metal ions (36). These

systems are effective in polyamides whereas in other polymers, such as polyolefins, small amounts of oxidized copper can often act as prodegradants. Good dispersion of the copper is critical to good performance. Since copper salts are water soluble, they can be leached from the polymer in certain applications (eg aqueous dye baths), leading to reduced efficacy and environmental issues. Aromatic amines are effective long-term stabilizers, but because of their discoloring nature, their use is limited to carbon black-filled systems. Phenolic antioxidants when added during the polycondensation reaction, contribute to improved initial color and long-term thermal stability, particularly at lower end-use temperatures. The relative merits of the various stabilization systems are shown in the following table:

Antioxidant system	Advantages	Disadvantages
Copper/halogen salts	Best performance at elevated temperatures ($>150^{\circ}\text{C}$) Very low levels required	Discoloration Leaching in aqueous environment Must be well dispersed
Aromatic amines	Good long-term thermal stabilizer performance	Discoloration
Phenolics	Best performance at lower temperatures when copper salts cannot be used Good initial and long-term color performance	Needs high concentration Less effective at high temperature conditions such as under-the-hood

Styrenics. Unmodified styrenics such as crystal polystyrene are relatively stable, and under most end-use conditions it is not necessary to add antioxidants (see STYRENE POLYMERS). Low levels (0.1%) of a hindered phenolic antioxidant are added to protect the polymer during repeated processing of scrap. Styrene-acrylonitrile (SAN) copolymers discolor during processing above 220°C (see ACRYLONITRILE POLYMERS). While this is primarily a nonoxidative process related to the acrylonitrile comonomer, the color can be suppressed to some extent through the addition of a combination of a phenolic antioxidant and a phosphite (37). High impact polystyrene (HIPS) is more susceptible to oxidative degradation because of the presence of an unsaturated butadiene rubber phase. Antioxidants can be added either during the manufacturing process to protect the rubber phase during polymerization and monomer stripping or postpolymerization. Color and impact properties are typically better if the antioxidant is added during polymerization, but care must be taken to avoid adverse effects on the kinetics through interaction with the peroxide catalysts. This is particularly problematic if phosphites are added. Acrylonitrile–butadiene–styrene (ABS) is a graft copolymer produced primarily in an emulsion process followed by a compounding step in which the high rubber content polymer is blended with SAN in various ratios to achieve the desired end-use properties. Antioxidants are required during the coagulation and drying steps to protect the high rubber content particles. The best performance is achieved through the use of a combination of hindered

phenol (0.25%) and thioester synergist (0.5%) (38). The stability of the finished ABS is directly related to the butadiene content (39).

Polyesters. Poly(ethylene terephthalate), PET, requires little to no antioxidant during thermal processing. In some cases, phosphites are added to improve the color of regrind. During polycondensation, pentavalent phosphorus compounds such as triphenylphosphate or trimethylphosphate may be added. These additives form complexes with the transesterification catalyst residues (manganese, tin, zinc), yielding a polymer with reduced hydroxyl end groups. This affords better hydrolytic stability during end use and reduced discoloration prior to the condensation reaction (40). Poly(butylene terephthalate), PBT, because of its higher hydrocarbon content, is more susceptible to oxidative degradation than PET. The combination of a phenolic antioxidant (0.05–0.10%) and a phosphite (0.1%) is typically used to stabilize PBT (see POLYESTERS, THERMOPLASTIC).

Polycarbonate. Polycarbonate, PC, is susceptible to photo-oxidation, and antioxidants are necessary to maintain the low color and high transparency critical to its end-use applications (see POLYCARBONATES). Phosphites (0.1%) are used to minimize color development during processing. It has been shown that the inherent stability of PC is related to the level of phenolic end groups (41). These levels can increase as a result of humidity-induced hydrolysis catalyzed by acid. The phosphite chosen must be very stable to avoid the generation of catalytic amounts of phosphorus acids.

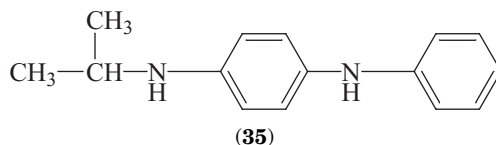
Polyacetal. Polyacetals thermally decompose by an acid-catalyzed depolymerization process starting at the chain ends (see ACETAL RESINS). The polymer structure is stabilized by end capping and introducing comonomers to interrupt the unzipping. The process is autocatalytic since the liberated formaldehyde is easily oxidized to formic acid, which is a prodegradant. Formaldehyde scavengers and phenolic antioxidants are typically used in polyacetal formulations (42).

Polyurethanes. The oxidative stability of polyurethanes (PURs) is highly dependent on the chemical nature of both the polyol component and the isocyanate. Thus, PUR derived from a polyester polyol is typically more stable than one derived from a polyether polyol (see POLYURETHANES). The methylene group adjacent to the ether linkage in polyether polyols is easily oxidized to hydroperoxides during storage. If not inhibited, decomposition of these built-up hydroperoxides can occur catastrophically during the highly exothermic reaction of the polyol and the isocyanate. Blends of a hindered phenol (0.2%) and an aromatic amine (0.1%) are typically used as storage stabilizers in polyether systems providing PUR foams with excellent color. Similar systems are used in polyester polyols, but at lower use levels (43).

Elastomers. Polyunsaturated elastomers are sensitive to oxidation. Stabilizers are added to the elastomers prior to vulcanization to protect the rubber during drying and storage. Nonstaining antioxidants such as butylated hydroxytoluene (1), 2,4-bis(octylthiomethyl)-6-methylphenol [110553-27-0], 4,4'-bis(α,α -dimethylbenzyl)diphenylamine (14), or a phosphite such as tris(nonyl-phenyl)phosphite (24) may be used in concentrations ranging from 0.01 to 0.5%.

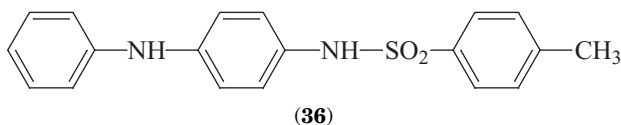
Staining antioxidants such as *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine [101-72-4] (35) are preferred for the manufacture of tires. These potent antioxidants also have antiozonant activity and retard stress cracking of the vulcanized rubber. Carbon black, used in tires for reinforcement, hides the color developed by

the antioxidant. According to use requirements, up to 3% of an amine antioxidant having antiozonant activity is added prior to vulcanization.

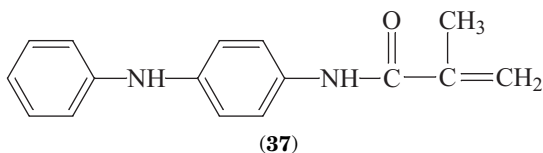


When staining tendencies of the substituted paraphenylene diamines cannot be tolerated, semistaining amine antioxidants are used to provide some protection to the elastomers. The semistaining antioxidants include polymerized compounds 13 and compound 14. These compounds, however, provide no protection against ozone.

Antioxidants resistant to extraction by lubricants and gasoline are preferred for the stabilization of elastomers used in automotive applications such as gaskets and tubing. Aromatic amine antioxidants such as *N*-phenyl-*N'*-(*p*-toluenesulfonyl)-*p*-phenylenediamine [100-93-6] (36), with low solubility in hydrocarbons, are extracted slowly from elastomers and are used for these applications.

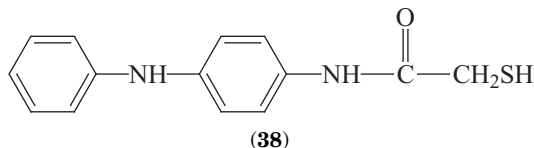


Binding the antioxidant chemically to the elastomer chain by copolymerization or grafting is a better solution to this problem. The addition of *N*-(4-anilinophenyl)methacrylamide [22325-96-8] (37) to a polymerization recipe for nitrile butadiene rubber (NBR) produces a polymer with a built-in antioxidant resistant to extraction (44).



Raw NBR containing 1.5% of the built-in antioxidant retained 92% of its original resistance to oxidation after exhaustive extraction with methanol. NBR containing a conventional aromatic amine antioxidant (octylated diphenylamine) retained only 4% of its original oxidative stability after similar extraction.

It is also possible to graft an aromatic amine antioxidant bearing a sulfhydryl group on to the backbone of an elastomer.



When 4-(mercaptoacetamido)diphenylamine [60766-26-9] (38) is added to EPDM rubber and mixed in a torque rheometer for 15 min at 150°C, 87% of it

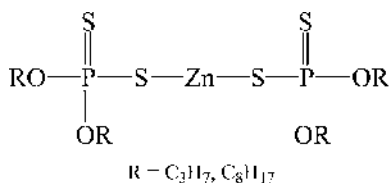
chemically binds to the elastomer (45). The mechanical and thermal stress placed on the polymer during mixing ruptures the polymer chain, producing free radicals that initiate the grafting process.

Poly(vinyl chloride). While reasonably stable with respect to oxidative degradation, PVC is very susceptible to thermal degradation. Protection of PVC from thermal degradation leading primarily to dehydrohalogenation reactions is out of the scope of this article. Some additives, used primarily as HCl scavengers, also have antioxidant properties. Aralkylphosphites, in particular, are used as components of thermal stabilizing mixtures which also exhibit antioxidant properties, leading to improved resin color.

Fuels and Lubricants. Gasoline and jet-engine fuels contain unsaturated compounds that oxidize on storage, darken, and form gums and deposits. Radical scavengers such as 2,4-dimethyl-6-*tert*-butylphenol [1879-09-0], 2,6-di-*tert*-butyl-*p*-cresol (1), 2,6-di-*tert*-butylphenol [128-39-2], and alkylated paraphenylene diamines are used in concentrations of about 5–10 ppm as stabilizers.

The catalytic activity of copper as an oxidant in fuels and lubricants can be inhibited by the use of a metal deactivator such as *N,N'*-disalicylidene-1,2-diaminopropane (30) at a concentration of 5–10 ppm.

Lubricants for gasoline engines are required to withstand harsh conditions. The thin films of lubricants' coating on piston walls are exposed to heat, oxygen, oxides of nitrogen, and shearing stress. Relatively high concentrations of primary antioxidants and synergists are used to stabilize lubricating oils. Up to 1% of a mixture of hindered phenols, of the type used for gasoline, and secondary aromatic amines, such as alkylated diphenylamine and alkylated phenyl- α -naphthylamine, are used as the primary antioxidants. About 1% of a synergist, zinc dialkyldithiophosphonate, is added as a peroxide decomposer. Zinc dialkyldithiophosphates (39) are cost-effective multifunctional additives. They interrupt oxidative chains by trapping radicals by electron donation, decompose peroxides, and serve as a corrosion and wear inhibitors.



(39)

Both zinc and phosphorus deactivate the catalysts used to control emissions and governmental regulations limit their concentrations to below 0.1%.

Test Methods

Polymers. There are a variety of test methods available for monitoring the oxidative stability in the polymer as it is exposed to different types of

stresses. These changes can be physical or aesthetic. Physical transformations of the polymer might involve changes in molecular weight, molecular weight distribution, or crystallinity. Aesthetic transformations of the polymer might involve changes such as discoloration or changes in the surface appearance due to microscopic cracks which affect gloss.

These changes can be measured using simple testing equipment and procedures described in ASTM methods (eg, tensile strength, impact resistance, color development, oxidative induction time, oven aging).

Estimation of oxidative stability under conditions of use is more difficult to measure. To decrease the time required for oxidative failure, specimens are exposed at temperatures higher than those anticipated in use. Oven aging the polymer at temperatures below the melting point of the polymer is a method for assessing the long-term thermal stability of a given substrate. A range of test temperatures can be used to create an Arrhenius plot as test temperature ($^{\circ}\text{C}$ or K) vs time to failure (eg, embrittlement, or 50% retention of tensile strength or elongation). If the apparent activation energy remains constant, a plot of the logarithm of failure time against the reciprocal of the absolute temperature results in a straight line. Extrapolation to temperature of use provides an estimate of failure time.

Because of different reactions and the raw materials used, the apparent activation energy of the overall process can deviate considerably from linearity, and an extrapolation can lead to serious errors in estimating failure time (46).

Representative measures of aesthetic properties would include color development, loss of gloss, increase in haze, chalking, loss of surface smoothness, exudation and/or blooming of additives or low molecular weight polymer, and staining.

To assess the retention of physical or aesthetic properties, it is important to understand that increasing surface area-to-volume ratio increases susceptibility to oxidation as does the rate of loss of the antioxidant by volatilization (47).

In the past, oxygen-uptake measurements at elevated temperatures were used to determine oxidation resistance. Today, other types of testing, such as oxidative induction time (OIT), by differential scanning calorimetry or chemiluminescence, are used.

For oxygen-uptake experiments, the time required to absorb a specified volume of oxygen is an indication of failure when the change in the rate of oxygen absorption is not sufficient to permit an accurate measurement of the induction period. However, the amount of oxygen absorbed and the loss of desired properties must be correlated. This type of test is not reliable for estimating service life under conditions in which the polymer is exposed to air movement.

Oxidative induction time or oxidative induction temperature experiments are used to assess the relative oxidative stability of the polymer. The experiments are typically conducted under severe testing conditions, typically at elevated temperatures (significantly above the melting point of the polymer) using oxygen as the oxidant. It should be noted that this method is not useful for predicting long-term thermal stability; however, these methods can be useful for quickly assessing the relative potency of different types of stabilizer systems (48).

For chemiluminescence experiments, the procedure is similar to the aforementioned OIT experiments, in that the time to catastrophic oxidation of the polymer is measured; in this case, below the melting point of the polymer. During this catastrophic oxidation, there are certain chemistries that take place which result in chemiluminescence. The amount of light that is given off during this process is measured by a charge-coupled device. This method, developed over the last decade, can provide useful information about the oxidative stability of the polymer in much shorter time period than conventional oven aging, but under more realistic oxidative environment in comparison with oxidative induction time (49).

Lubricants. A sequence of tests has been devised to evaluate antioxidants for use in automotive crankcase lubricants. The Indiana Stirring Oxidation Test (ISOT) JISK2514 is an example of a laboratory screening test. The oil is stirred at 165.5°C in the presence of air. Copper and iron strips are used as metal catalysts. The development of sludge, viscosity, and acidity are determined periodically. Failure time is determined when the development of acidity requires 0.4 mg KOH/g for neutralization. Formulated lubricants are then evaluated for performance in engines (see Oldsmobile Sequence III D) (50). Candidate lubricants containing the antioxidants are tested in fleets of automobiles for thousands of miles. As described above for polymers, modified oxygen uptake tests can also be used with lubricants to measure oxidative stability (51).

The effectiveness of antioxidants as preservatives for fats and oils is evaluated by determining the rate of peroxide development using the active oxygen method (52). The development of a rancid odor is used to evaluate the stability of food items (Schaal oven stability test) (53).

Ancillary Properties

In reality, there is more to antioxidants than providing stability to the polymer by quenching free radicals and decomposing hydroperoxides. Other key issues besides rates of reactivity and efficiency include performance parameters such as volatility, compatibility, color stability, physical form, taste or odor, regulatory issues associated with food contact applications, and polymer performance vs cost (54).

Volatility. Most additives are melt compounded into the polymer after the polymerization stage. The melt compounding and downstream conversion (into shaped articles) processing steps represent significant heat histories. Storage of the product can also be quite warm in certain climates. It is important that the antioxidant, as well as its transformation products that may also provide stability, does not volatilize from the polymer. Many commercial antioxidants have been designed with higher molecular weights to address this issue.

Compatibility. Antioxidants should be soluble in the polymeric matrix. If they are not soluble, they should at least migrate or diffuse slowly. If the solubility limit of the antioxidant in the polymer is exceeded, exudation will occur. Exudation or blooming involves the migration of the additive out of the polymer matrix onto the surface as a very thin film. Blooming of the antioxidant can

diminish surface gloss, create stickiness, eliminate blocking (cling) of film surfaces to one another and negatively affect printability.

Color Stability. It is important that antioxidants do not provide unwanted color because of the transformation chemistries associated with preventing oxidation. Some antioxidants are prone to forming color by their very nature, while other antioxidants discolor only when they have been overoxidized. Pigments can be used to mask the subtle changes in the base color of the polymer.

Physical Form. Because of hazards associated with dusting, many antioxidants are now being offered commercially in dust-free forms, such as granules or pellets. Liquid or molten antioxidants are another interesting alternative, as long as they are compatible in the polymer matrix. Still, some polymer manufacturers need the additives as fine powders in order to achieve good premixing with their reactor product before melt compounding into the traditional pellet form.

Taste and Odor. For applications that involve food contact, home or personal use, taste and odor are key issues. The human nose is very sensitive, more so than some analytical instruments, able to detect some compounds at the parts per billion (ppb) level.

Health and Safety Factors

Safety is assessed by subjecting the antioxidant to a series of animal toxicity tests, eg, oral, inhalation, eye, and skin tests. Mutagenicity tests are also carried out to determine possible or potential carcinogenicity. Granulated and liquid forms of antioxidants are receiving greater acceptance to minimize the inhalation of dust and to improve flow characteristics.

A number of antioxidants are regulated by the U.S. Food and Drug Administration (FDA) as indirect additives for polymers used in food contact applications (primarily food packaging) under Title 21 of the U.S. Code of Federal Regulations (21CFR), Part 175 (Adhesives and Coatings) and/or Part 177 (Polymers). Acceptance is determined by subchronic or chronic toxicity in more than one animal species and by the concentration expected in the diet, based on the amount of the additive extracted from the polymer by solvents that simulate food in their extractive effects. Materials are regulated by the FDA for use in plastics contacted by food stuffs to ensure a minimum risk to the consumer. Broad FDA regulation is increasingly a requirement for the successful introduction of a new antioxidant.

Cost Effectiveness

The point in using an antioxidant is to choose the appropriate type and level to adequately stabilize the polymer for a particular end-use application.

For example, if the material is a nondurable good, such as bags and food wrap, the type and concentration of antioxidant is chosen to minimize unnecessary costs associated with stabilizing the polymer. The antioxidant should be able to provide stabilization for the initial melt compounding and processing into the

finished article. It is important to consider that scrap from the melt compounding needs to be recycled, and unexpected shutdowns and start-ups may occur.

On the other hand, if the material is a durable good, such as geomembranes, insulation for wire and cable, or gas and water transmission pipes, the type and concentration of the phenolic antioxidant is chosen to meet the long service-life criteria. The costs associated with this type or level of antioxidant is worth the additional value of the final product.

Commercial Antioxidants. Table 4 includes the main classes of antioxidants sold in the United States and the supplier's suggested applications. Some of these are mixtures rather than single components. This is especially true of alkylated amines and alkylated phenols. The extent of alkylation and the olefins used for alkylation can vary among manufacturers. Table 4 is not a complete listing of available antioxidants in the United States.

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ATOM TRANSFER RADICAL POLYMERIZATION

Introduction

The development of living polymerization (1,2) enabled the production of polymers with precisely controlled molecular weight, narrow molecular weight distribution, and well-defined architecture and composition. For the most recent compilation of controlled/living polymerization techniques, see references (3,4). There are a number of advantages of controlled/living radical polymerization (CRP) (5–10) as compared to ionic polymerization, such as applicability to a wide range of monomers and solvents, tolerance to impurities and functional groups, and ease of experimental set-up. The most widely used CRP techniques include atom transfer radical polymerization (ATRP) (11–14), nitroxide-mediated polymerization (NMP) (15–17), organometallic-mediated radical polymerization (OMRP), (18–20), and degenerative transfer polymerization (21–25). In each case, control is maintained via fast dynamic equilibrium between dormant species and propagating chains (26,27).

Fundamentals of ATRP

The dynamic equilibrium that mediates control during ATRP is established between a low oxidation-state transition metal complex (Mt^nL_m) and its higher oxidation-state complex ($X-Mt^{n+1}L_m$). The mechanism involves reversible reaction of Mt^nL_m with an alkyl halide initiator RX by a one-electron redox process with concurrent halogen abstraction from the dormant species. This occurs via inner sphere electron transfer (28) and generates $X-Mt^{n+1}L_m$ and an organic radical $R^\bullet$, with a rate constant of activation k_{act} . The radical can add to vinyl monomer

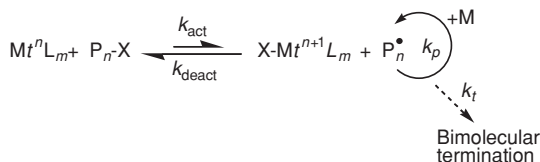


Fig. 1. Mechanism of transition metal complex-mediated ATRP.

with a rate constant of propagation k_p , terminate by coupling or disproportionation (k_t), or be reversibly deactivated by $X-Mt^{n+1}L_m$ (k_{deact}) (Fig. 1). The termination of a small amount ($\sim 5\%$) of growing polymer chains at the initial stage of polymerization prevents halogen abstraction from oxidized metal complexes that suppress further termination reactions via the persistent radical effect (29,30). The ATRP equilibrium ($K_{ATRP} = k_{act}/k_{deact}$) is, thus, heavily shifted towards dormant species, and the polymerization is characterized by uniform growth of polymer chains. A broad body of evidence has confirmed the presence of intermediate radical species in this process. This support includes an abundance of similarities between conventional free-radical polymerization and ATRP, such as the lack of effect of protic solvents, radical scavengers, and transfer agents (31), the atacticity of polymers prepared by ATRP (32–34), similar reactivity ratios in copolymerization (35–39), similar rates of racemization, exchange, and trapping reactions (40,41), and indistinguishable ^{13}C kinetic isotope effects (42); concomitant formation of higher oxidation state metal species during the polymerization (43); and direct electron spin resonance observation of radicals (44).

The rate of polymerization in ATRP is proportional to initiator concentration and the ratio of activator to deactivator concentrations, according to eq. 1.

$$R_p = -d[M]/dt = k_p [M][P^\bullet] = k_p [M]K_{ATRP}[RX]([Mt^n/L]/[Mt^{n+1}X/L]) \quad (1)$$

It is noteworthy that polymerization rate does not depend on the absolute amount of catalyst in the system, which suggests that catalyst concentration can be decreased without affecting R_p , as long as the ratio of activator to deactivator concentrations remains constant. However, the synthesis of polymers with low polydispersity requires sufficient concentration of deactivator (eq. 2) in order to reduce the number of monomer units added during each activation step and equalize probability of growth of all chains.

$$PDI = \frac{M_w}{M_n} = 1 + \frac{1}{DP_n} + \left(\frac{[RX]_0 k_p}{k_{deact}[Mt^{n+1}X/L]} \right) \left(\frac{2}{Conv.} - 1 \right) \quad (2)$$

Components

A wide range of monomers have been successfully polymerized by ATRP, including various styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, each of which contains substituents that can stabilize propagating radicals. The polymerization rate of each monomer is determined by its unique values of k_p and

K_{ATRP} , the latter of which can be adjusted by modification of the catalytic complex. Optimal ATRP conditions, including catalyst type and concentration, solvent, and temperature, must be selected for each monomer in order to obtain a sufficiently high polymerization rate while maintaining a low concentration of radicals and, thus, a controlled polymerization. The successful ATRP of acidic monomers, vinyl acetate, and dienes remains a challenge, for a variety of reasons. Acidic monomers poison the ATRP catalyst by coordination to the metal and protonation of the N-based ligand; poly(meth)acrylic acids are typically prepared by polymerization of a protected monomer, such as trimethylsilyl methacrylate or *tert*-butyl methacrylate, followed by deprotection (45). The controlled polymerization of vinyl acetate is limited by a low value of K_{ATRP} , which is due to the high carbon-halogen bond strength exhibited by this monomer (46,47). Solving these challenges requires a thorough understanding of the rules for rational catalyst selection (see section 3).

A variety of commercially available alkyl halides can be employed as initiators for ATRP. A typical initiator is comprised of a transferable halogen that is activated by α -carbonyl, phenyl, vinyl, or cyano substituents. If initiation is fast and quantitative, the relative concentrations of monomer and initiator determine the number of growing chains and therefore the degree of polymerization (DP) or molecular weight of the polymer (eq. 3).

$$\text{DP} = [M]_0 / [\text{initiator}]_0 \times \text{conversion} \quad (3)$$

The transition metal complex that mediates ATRP is typically Cu-based, but a multitude of other metals have been demonstrated to successfully control the process, such as Ti (48), Mo (49–51), Re (52), Fe (53–56), Ru (12,57), Os (58), Rh (59), Co (60), Ni (61,62), and Pd (63). The characteristics that a transition metal center must possess in order to be an efficient catalyst include at least two accessible oxidation states separated by one electron, affinity towards a halogen, and an expandable coordination sphere. The complexing ligand serves to solubilize the transition metal and adjust the catalyst redox potential in order to ensure an appropriate equilibrium between dormant and propagating species. Typically employed nitrogen-based ligands include derivatives of 2,2'-bipyridine (bpy) (11,64), pyridine imine (65,66), diethylenetriamine (DETA) (67), tris[2-aminoethyl]amine (TREN) (68), and tetraazacyclotetradecane (CYCLAM) (69), among others (70,71). Phosphorous-based ligands are used in ATRP catalyzed by complexes of Re (52), Ru (12,57), Fe (53,54), Rh (59,72), Ni (62,73), and Pd (63), but not Cu.

Mechanistic Considerations

Measuring K_{ATRP} . Successful polymerization of new or challenging monomers will require a thorough understanding of the factors that affect the ATRP equilibrium. The value of K_{ATRP} for any particular catalyst and initiator system must be determined experimentally, which can be easily accomplished by reacting alkyl halide with transition metal activator and monitoring the increase in deactivator concentration over time. A plot of $F([\text{Cu}^{\text{II}}\text{L}_n\text{X}])$ versus time is then

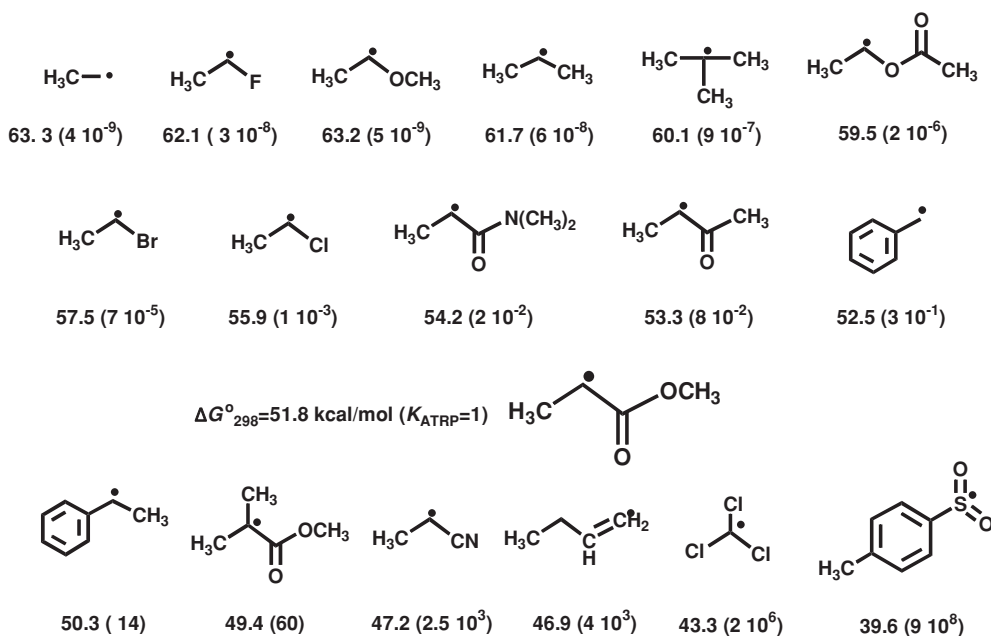


Fig. 2. Free energy change and relative K_{ATRP} values for homolytic bond cleavage of alkyl bromides at 25 °C relative to methyl 2-bromopropionate, as determined by DFT (47).

constructed, and K_{ATRP} is calculated from the slope of the linear dependence (eq. 4) (30). Typical values for various initiators and Cu(I) complexes are between $10^{-10} - 10^{-4}$ (30,74–76). A large value of K_{ATRP} is characteristic of an active catalyst (eq. 4).

$$F([\text{Cu(II)}L_nX]) \equiv \frac{[\text{Cu(I)}L_n]_0^2}{3([\text{Cu(I)}L_n]_0 - [\text{Cu(II)}L_nX])^3} - \frac{[\text{Cu(I)}L_n]_0}{([\text{Cu(I)}L_n]_0 - [\text{Cu(II)}L_nX])^2} + \frac{1}{[\text{Cu(I)}L_n]_0 - [\text{Cu(II)}L_nX]}$$

$$= 2k_t K_{\text{ATRP}}^2 t + \frac{1}{3[\text{Cu(I)}L_n]_0} \quad (4)$$

ATRP Subequilibria. In order to critically evaluate the factors that affect the ATRP equilibrium, it is convenient to express this equilibrium as the product of four reversible reactions: oxidation of the transition metal activator, or electron transfer (K_{ET}); formation of halide anion, or electron affinity (K_{EA}); bond homolysis of the alkyl halide initiator (K_{BH}); and association of halide anion with deactivator, or “halidophilicity” (K_{X}) (eq. 5, 6, 7, 8, 9) (77). Bond homolysis is the only of the four reactions that does not depend on the nature of the catalyst. Alkyl halide bond dissociation energies have been reported to correlate well with measured values of K_{ATRP} (Fig. 2) (47). For systems employing the same catalyst and conditions, the rate of polymerization can therefore be predicted from the calculated bond dissociation energies.





$$K_{ATRP} = \frac{k_{act}}{k_{deact}} = K_{BH}K_{EA}K_XK_{ET} \quad (9)$$

The concentration of deactivator present in the system and, thus, the extent of control over the polymerization, depends on the value of halidophilicity, K_X . This value is strongly solvent dependent, and is significantly higher in nonprotic solvents than in protic solvents where the halide anion is efficiently solvated (78). Conducting ATRP in aqueous solvents typically leads to fast polymerization and loss of control as the majority of the halogen is dissociated from the deactivating species. This can be partially suppressed by the addition a large initial amount of $X-Mt^{z+1}L_m$ or halide salts (79).

ATRP is a redox process, and therefore catalyst activity depends on the redox potential of the transition metal/ligand complex. A linear correlation has been established between K_{ATRP} and $E_{1/2}$ values for Cu complexes with a variety of N-based ligands (80,81). Similar correlations between redox potential and ATRP catalytic activity have been demonstrated for Fe (55) and Ru (82,83) complexes. The relative activities of catalysts derived from different transition metals cannot be predicted solely by examining redox potentials due to the differences in halidophilicity of each metal center.

Rational Catalyst Selection.

Predicting Catalytic Activity. In order to obtain a sufficiently fast polymerization while maintaining control, a catalyst must be selected that exhibits high activity and stability. The rules for rational selection of ATRP catalysts have been thoroughly described (84,85) and is briefly in this article. Although these rules have been developed using Cu-based ATRP, they are applicable to all transition metals that catalyze this process.

The activity of an ATRP catalyst is related to its reducing power, which in turn depends on the relative stabilities of the Cu(I) and Cu(II) oxidation states (quantified by the stability constants $\beta(I)$ and $\beta(II)$, see eq. 10). A ligand that strongly stabilizes the Cu(II) state will generate a corresponding Cu(I) complex with high activity. In addition, stabilization of both oxidation states (ie, large values of $\beta(II)$ and $\beta(I)$) will yield a catalyst that is significantly less susceptible to ligand substitution reactions with monomer, polymer, or solvent, even at low catalyst concentration. Therefore, knowledge of the readily measurable stability

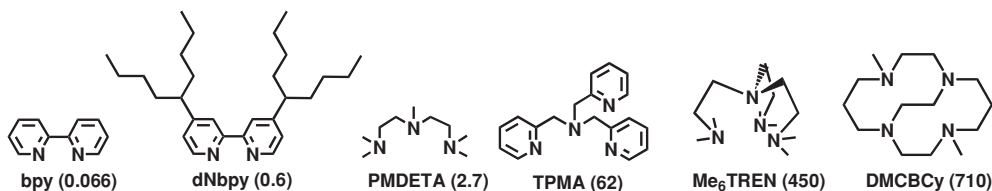


Fig. 3. Rate constants of activation ($\text{M}^{-1}\text{s}^{-1}$) for nitrogen-based ligands with ethyl 2-bromoisobutyrate and CuBr in acetonitrile at 35 °C.(89).

constants of each oxidation state allows for prediction of the activity and stability of a catalytic complex. The most active Cu-based ATRP catalyst known to date is the complex with 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (dimethyl cross-bridged cyclam, DMCBCy) (76), which is also exceptionally stable.

$$E \approx E^0 + \frac{RT}{F} \ln \frac{[\text{Cu(II)}]_{\text{tot}}}{[\text{Cu(I)}]_{\text{tot}}} - \frac{RT}{F} \ln \frac{\beta(\text{II})}{\beta(\text{I})} \quad (10)$$

Although values of K_{ATRP} for Cu complexes can be predicted using stability constants and redox potentials, knowledge of K_{ATRP} is not sufficient to determine whether a polymerization will be controlled. Fast activation and deactivation (with $k_{\text{act}} \ll k_{\text{deact}}$) are required to obtain polymers with predetermined molecular weight and narrow molecular weight distribution. The rate constant k_{act} can be determined by spectroscopically or chromatographically monitoring the consumption of alkyl halide upon activation by a Cu(I) complex, which generates radicals that are trapped by an excess of scavenging agents such as nitroxides (86). The value of k_{deact} can be measured by a type of clock reaction in which radicals are simultaneously trapped by a nitroxide and transition metal deactivator (87). It can also be estimated from initial molecular weight and polydispersity index values (88), as well as measured values of K_{ATRP} and k_{act} (41).

The rate of activation in Cu-based ATRP has been shown to strongly depend on the structure of the complexing nitrogen-based ligand. The values of k_{act} span more than six orders of magnitude and generally obey several trends, with activity depending on: linking unit between nitrogen atoms ($\text{C4} \ll \text{C3} < \text{C2}$) and/or coordination angle; ligand topology (cyclic $\sim$ linear $<$ branched); nature of the ligand (aryl amine $<$ aryl imine $<$ alkyl imine $<$ alkyl amine $\sim$ pyridine); and steric bulk around the metal (Fig. 3) (89). A seemingly minor change in ligand structure can have a pronounced effect on catalytic activity; for example, the Cu(I) complex of DMCBCy is ~ 1000 more active than that of Me₄Cyclam. A similar correlation between ligand structure and k_{deact} has not been observed, although it has been proposed that the ease of structural reorganization of the Cu(II) complex upon halogen abstraction should be a determining factor in the observed rate of deactivation (90).

In addition to rational selection of the catalyst, consideration must be given to employing the most appropriate initiator for a particular polymerization. As mentioned earlier, fast and quantitative initiation is necessary to obtain

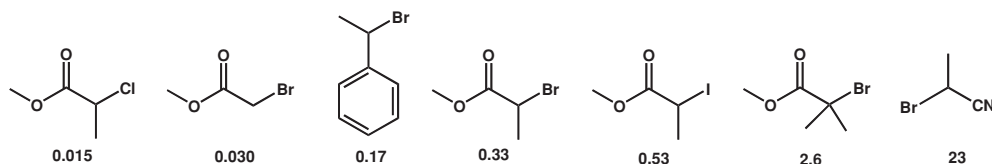


Fig. 4. Values of k_{act} (in $\text{M}^{-1} \text{s}^{-1}$) for various initiators with CuX/PMDETA in acetonitrile at 35 °C (91).

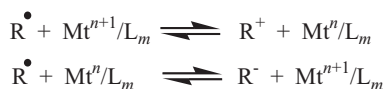
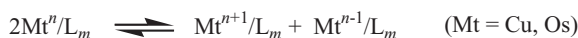
polymers of predetermined molecular weight. An initiator that is characterized by sufficiently fast activation must be selected according to the following rules: activity depends on the degree of substitution (primary < secondary < tertiary), transferable group (Cl < Br < I), and radical stabilizing group ($-\text{Ph} \sim -\text{C}(\text{O})\text{OR} \ll -\text{CN}$) (Fig. 4).

Avoiding and Exploiting Side Reactions. Choosing the appropriate catalyst for a particular ATRP system requires consideration of the side reactions that may take place during polymerization (Fig. 5). These reactions have been thoroughly discussed (10,85), and are briefly outlined in this article. Outer sphere electron transfer involves the catalytic reduction of propagating radicals to carbanions or oxidation to carbocations (28). For example, the former can occur when a highly active (ie. reducing) catalyst is employed in the polymerization of an electrophilic monomer, such as acrylonitrile (92–95). Coordination of vinyl monomer to the catalyst (96,97) does not significantly affect polymerization under normal conditions, but may become an issue at low catalyst concentration. Conducting ATRP in protic media can be accompanied by several side reactions (79,98,99), including loss of deactivator via solvation of halide anion (as discussed earlier) and disproportionation of the metal center. The latter reaction can be avoided by choice of a ligand that sufficiently stabilizes the Cu(I) oxidation state relative to the Cu(II) state in protic media.

Finally, it should be noted that certain “side reactions” can be exploited as efficient techniques for materials synthesis and the investigation of new catalysts. These include atom transfer radical coupling (a manipulation of bimolecular termination) as a route to telechelic polystyrene, (100,101) β -H abstraction from growing polymer chains for the generation of oligomers (49,102), and the formation of organometallic species that may be able to simultaneously mediate ATRP and OMRP (18,49,103).

Initiation Systems.

Normal/Reverse/Simultaneous Reverse and Normal ATRP. Normal ATRP consists of an alkyl halide initiator and transition metal catalyst initially in its lower oxidation state. Although this technique is easily applicable in an academic setting, the oxidative instability of the catalyst and relatively large amounts typically employed may pose difficulties on an industrial scale. Reverse ATRP was developed in order to circumvent oxidation problems. This method utilizes a conventional radical initiator (such as AIBN) to generate propagating radicals that are reversibly deactivated by a higher oxidation state metal, in order to generate the ATRP activator *in situ* (104–106).

Outer Sphere Electron Transfer**Monomer Coordination****Halide Dissociation****Disproportionation****Formation of Organometallic Species** **β -H Abstraction****Fig. 5.** Possible side reactions during ATRP.

Although reverse ATRP provides a convenient alternative to handling air-sensitive catalysts, it cannot be used in chain extension reactions for the preparation of block copolymers because the radical source does not contain a transferable atom. Simultaneous reverse and normal initiation (SR&NI) is conducted in the presence of an alkyl halide initiator, and AIBN is used to generate the ATRP activator from its higher oxidation state complex (107). In this way, handling problems can be avoided while the ability to prepare block copolymers is maintained. This technique has been utilized in bulk and miniemulsion (108,109).

Activators Generated by Electron Transfer (AGET). Due to the presence of a radical source that can initiate new chains, SR&NI is limited in its ability to prepare clean block copolymers. AGET ATRP circumvents this difficulty by generation of the lower oxidation state activator via reducing agents that cannot produce new radicals. A variety of reducing agents can be used for this process, including zero valent Cu, (110,111) tin^(II) 2-ethylhexanoate, (112) ascorbic acid, (113,114) and triethylamine (115). This technique is particularly applicable to aqueous and miniemulsion systems (116–118).

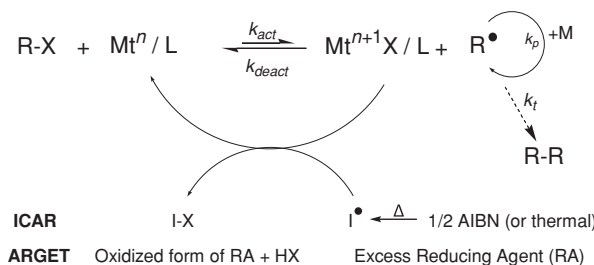


Fig. 6. Mechanism of ICAR and ARGET ATRP.

Decreasing Catalyst Concentration by New Initiation Processes (ICAR and ARGET). As described earlier, the total catalyst concentration in ATRP can be reduced without affecting polymerization rate because R_p depends on the ratio of activator to deactivator concentrations. However, the amount of catalyst cannot be decreased indefinitely in normal ATRP due to unavoidable radical termination reactions that occur at the initial stages of polymerization. If catalyst concentration is less than the concentration of terminated chains, all of the activator will eventually be present as a persistent radical and the reaction will stop at low conversion. A new initiation process known as initiators for continuous activator regeneration (ICAR) allows ATRP to be conducted in the presence of ppm amounts of catalyst. The technique works by the continuous generation of radicals by decomposition of a conventional radical initiator (such as AIBN), which reduces Cu that is present as a persistent radical to the corresponding lower oxidation state activator (Fig. 6) (119). In the polymerization of styrene, thermal initiation generates a sufficient amount of radicals without the need for an additional radical source. Polymerization rate during ICAR ATRP depends on the concentration of the radical source, and not on the nature of the catalyst.

A dramatic reduction in catalyst concentration can also be achieved using an excess of reducing agent instead of a radical source (Fig. 6). This technique, which is known as activators regenerated by electron transfer (ARGET) (120), has been utilized to prepare homopolymers and clean block copolymers in the presence of < 50 ppm of Cu catalyst (121). The reducing agents employed in this process include hydrazine, phenol, glucose, ascorbic acid, Sn(II) species, and Cu(0). Careful consideration must be given to choice of catalyst for this process (119), since a number of side reactions that can occur during ATRP (such as halide dissociation and monomer coordination) are exacerbated during polymerization in the presence of low catalyst concentration (85). However, it is noteworthy that a diminished concentration of catalyst can reduce the occurrence of certain side reactions, such as outer sphere electron transfer and β -H elimination. This has recently allowed the preparation of high molecular weight poly(styrene-*co*-acrylonitrile) (122) and polyacrylonitrile (95) by ATRP.

Conducting ATRP

ATRP can be conducted in bulk, solution, or a variety of heterogeneous media, (123) including miniemulsion (113,124–126), microemulsion (127),

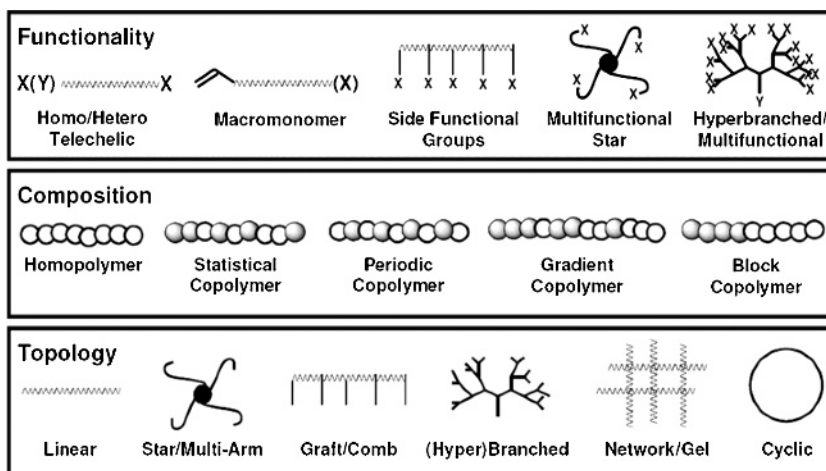


Fig. 7. Illustration of polymers with controlled functionality, composition, and topology.

emulsion (128), suspension (129–132), dispersion (133), and inverse miniemulsion (118,134,135). The choice of polymerization media depends primarily on solubility considerations. A solvent is necessary in certain instances, such as during polymerization of acrylonitrile (the formed polymer is not soluble in its monomer) or room temperature polymerization of methyl methacrylate (the system will vitrify at high conversion). It should be noted that the chosen solvent should be suitable not only for monomer and obtained polymer, but also for the catalytic complex.

Judiciously selected additives can enhance the capabilities of ATRP. Lewis acid complexing agents have been shown to increase polymerization rate and in some cases decrease molecular weight distribution (136,137). They can also increase the extent of syndiotacticity and isotacticity in a polymer (138,139). Reducing agents, such as tin(II) octanoate (119), ascorbic acid (114), and Cu(0) (114), can reduce handling difficulties and allow ATRP to be conducted in the presence of significantly lower amounts of catalyst.

Materials

ATRP has been used to prepare polymers with various functionalities, compositions, and topologies (Fig. 7) (140). Highlights from each of these categories are discussed in the following sections.

Functionality. The presence of functional groups within a polymer are important in fine-tuning many properties, such as solubility, polarity, biocompatibility, melting/glass transition temperatures, elasticity, tensile strength, crystallinity, electrical conductivity, etc. Functionality can be incorporated within a polymer via modified monomers, initiators, or chain ends (Fig. 7). The use of a functional monomer will have the greatest effect over bulk properties, while chain end functionality can lead to materials good for blend compatibilization.

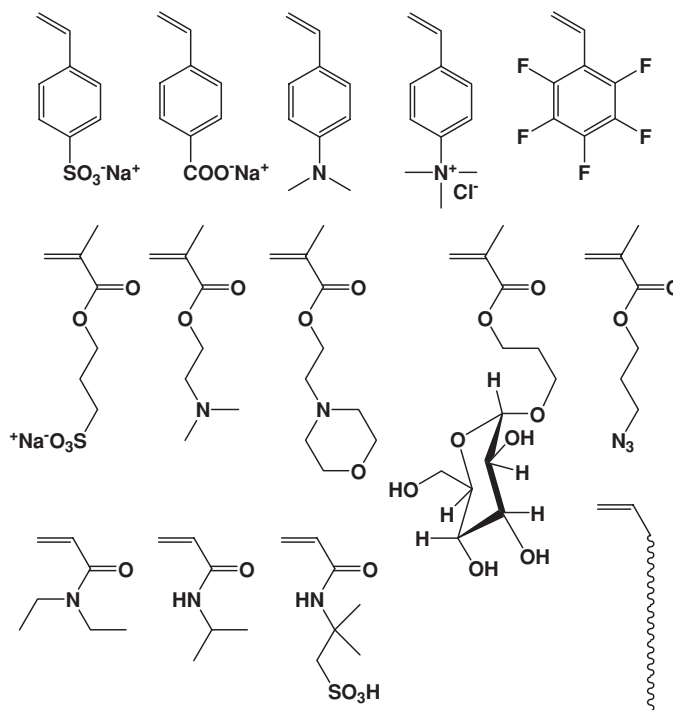


Fig. 8. Various classes of functional monomers.

ATRP is tolerant to several types of functional groups, although certain groups may interfere with the ATRP mechanism (eg, acidic groups). These can be easily incorporated through post polymerization modification, as discussed earlier.

Functional monomers. The various monomers polymerizable by ATRP include styrene derivatives, (meth)acrylates, (meth)acrylamides, and acrylonitrile. These monomers can be modified accordingly in order to incorporate more sophisticated functional groups (Fig. 8). Other classes of functional monomers include macromonomers (which consist of a polymer chain with a polymerizable group at its terminus), monomers containing an ATRP initiator (leading to hyperbranched polymers), and monomers displaying two or more polymerizable groups (leading to a cross-linked network).

A multitude of styrene derivatives have been polymerized via ATRP, exhibiting both electron-withdrawing and weakly electron-donating substituents on the aromatic ring (141). The presence of electron withdrawing groups (such as sulfonates, carbonyls, and halogens) leads to a faster polymerization, due to decreased stability of the dormant species and thus increased propagation rates. The polymerization of 4-acetoxystyrene has been demonstrated (142), and styrene derivatives containing alkyl substituents were also successfully polymerized. As mentioned earlier, acidic derivatives (such as 4-vinylbenzenesulfonic acid and 4-vinylbenzoic acid) are typically protected as a salt in order to prevent catalyst disruption (143). The ATRP of 4-vinylpyridine has also been accomplished,

although the catalytic complex was carefully selected in order to prevent side reactions with this nucleophilic and basic monomer (74).

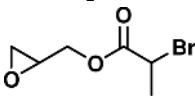
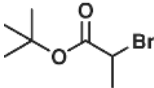
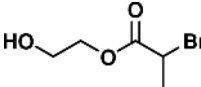
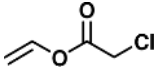
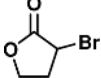
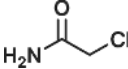
(Meth)acrylates represent the broadest range of monomers polymerizable by ATRP. Some of the many examples of functional (meth)acrylates include 2-hydroxyethyl (meth)acrylate, (79) glycidyl (meth)acrylate (144), 2-trimethylsilyloxyethyl (meth)acrylate (145–147), 2-(dimethylamino)ethyl methacrylate (148), and allyl (meth)acrylate, among others. Various bioconjugates have been prepared by attachment of sugars (149) and short sequences of nucleotides (150,151) to vinyl monomers. ATRP of several (meth)acrylamides has also been demonstrated (152–155).

Each of the functional monomers illustrated above yields polymers with unique properties. Particularly interesting properties are found in “smart” materials, which are polymers that respond to environmental changes. These materials contain functionality that contributes to thermo- (154,156), light- (157), and/or chemo-responsive behaviors (158). For example, poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) exhibits thermo-responsive behavior, and is characterized by a lower critical solution temperature (LCST) of 32 °C. Below this temperature, PDMAEMA is water-soluble while above its LCST, the polymer becomes hydrophobic and precipitates from aqueous solution. Light-responsive polymers include (meth)acrylates containing azobenzene or spiroopyran units, and will undergo a change in molecular structure upon ultraviolet irradiation (159,160). This leads to changes in dimension and polarity. There are other classes of polymers which respond to changes in pH or polarity of solvent.

Functional Initiators. Initiators can be modified in a variety of ways, provided that the functional group does not interfere with the ATRP mechanism. The use of a functional initiator allows for direct incorporation of a functional group onto a chain end, yielding a telechelic polymer. Telechelic polymers have also been synthesized using functional initiators and atom transfer radical coupling (101). Several examples of functional initiators that have been successful for the ATRP of styrene are illustrated in Table 1. Polymers prepared by ATRP are halogen-terminated and can subsequently be used as macroinitiators to form block copolymers. An initiator can also contain multiple initiating sites. Difunctional ATRP initiators have been used in the synthesis of multiblock copolymers, building from the core out (161). Other difunctional initiators can contain one ATRP site and an initiating group for another polymerization mechanism to make block copolymers through mechanistic transformation (162). Multifunctional ATRP initiators can be used to synthesize star (co)polymers and other hyperbranched materials as well.

Chain End Functionality. The halogen located at the end of a polymer prepared by ATRP can be easily displaced by numerous other functionalities (Fig. 9). Some examples include initiating sites for other polymerization mechanisms, a polymerizable double bond for the generation of a macromonomer, or precursors for “click” chemistry. Currently, the most popular click reaction is the Cu(I)-catalyzed azide-alkyne cycloaddition (164,165), which has been prolifically combined with ATRP to prepare pendant-functionalized polymers (166), end-functional polymers (167,168), multisegmented block copolymers (169), stars (170), brushes (144,171), and other architectures (172).

Table 1. Functional initiators used for the polymerization of styrene in bulk.^a

Initiator	Conv.	$M_{n,SEC}$ (g/mol)	M_w/M_n
NC-Ph-CH ₂ -Br	4-cyanobenzyl bromide	0.48	5,500 1.10
Br-Ph-CH ₂ -Br	4-bromobenzyl bromide	0.48	4,500 1.16
CH ₃ -CH(CN)-Br	2-bromopropionitrile	0.48	5,100 1.09
CN-CH ₂ -Br	bromoacetonitrile	0.48	4,500 1.10
	glycidol 2-bromopropionate	0.62	6,800 1.12
	<i>t</i> -butyl 2-bromopropionate	0.41	4,000 1.17
	hydroxyethyl 2-bromopropionate	0.48	7,500 1.10
	vinyl chloroacetate	0.94	5,800 1.12
	α -bromo butyrolactone	0.41	4,000 1.17
	2-chloroacetamide	0.12	4,000 1.51

^aAt 110 °C, with $[M]_0/[I]_0/[CuBr]_0/[dNbpy]_0 = 100/1/1/2$ (163).

Polymer Composition and Microstructure. There are several combinations in which monomers can be arranged along a linear polymer chain, which is described by the instantaneous composition (Fig. 7). A linear polymer chain consisting of one type of monomer is known as a homopolymer. When more than one monomer is polymerized, random, periodic, block, or gradient copolymers are possible, depending both on the reactivities of each monomer and the method through which they were polymerized. Different properties can be obtained from polymers that have the same ratio of monomers and molecular weights, but differing instantaneous chain composition. Precise control over the composition of a single polymer chain is possible by ATRP, because essentially all the polymer chains grow at the same rate throughout the polymerization. Control over polymeric microstructure in terms of tacticity is not as simple, and can be developed further.

Random/Gradient Copolymers. Reactivity ratio is defined as the ratio of the rate constants of homopropagation to cross-propagation. If the reactivity ratios of comonomers are similar, a polymer with a random/statistical distribution of each monomer along the chain will be obtained. If one monomer has a significantly higher reactivity ratio than the other, a gradient copolymer is formed (173).

Gradient copolymers cannot be prepared by conventional radical polymerization due to rapid monomer propagation and a very short chain lifetime. Copolymer chains rich in one comonomer are initially formed, while chains rich in the

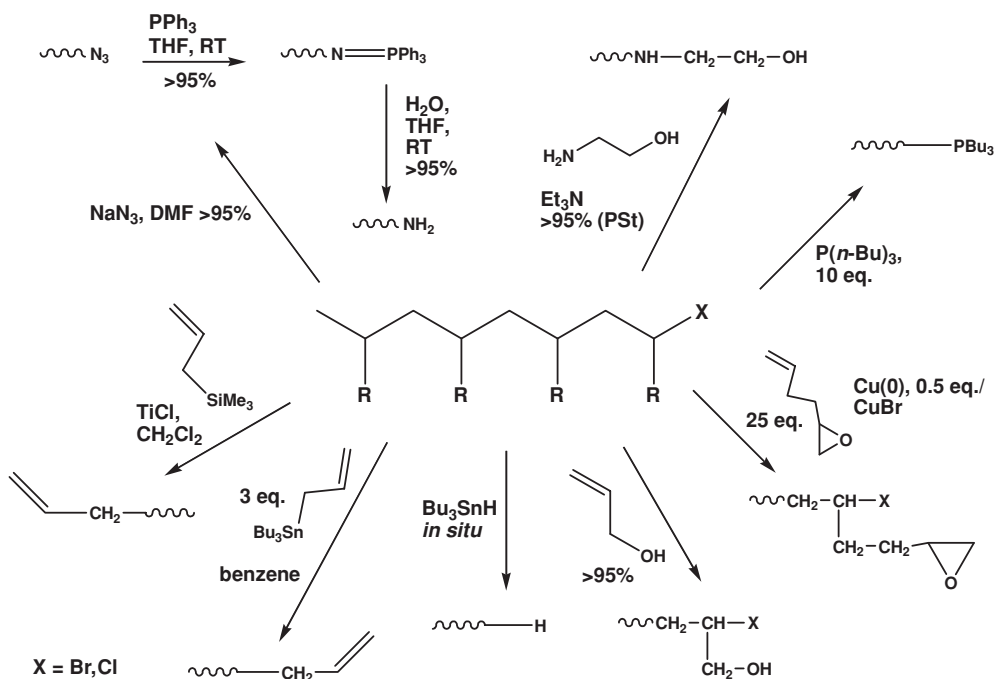


Fig. 9. Examples of post-polymerization modification of a polymer chain prepared via ATRP.

other comonomer form later in the polymerization. These materials typically exhibit poor properties and macroscopic phase separation. In ATRP, however, the gradient exists along each chain instead of between chains (174).

Gradient copolymers can be synthesized by two methods, batch or semi-batch. A batch process is used to prepare a spontaneous gradient copolymer if the reactivity ratios of the two monomers significantly differ. For comonomers with similar reactivity ratios, the semi-batch process can be used to generate a "forced" gradient by controlled addition of one comonomer to the reaction mixture throughout the reaction. Aspects of both random and block copolymers are brought together in gradient copolymers. These materials possess a broader glass transition temperature range, reduced order-disorder temperature, and can form new types of morphologies through self assembly (175). These properties can lead to several desirable applications, such as vibration- and noise-dampening materials, compatibilizers for immiscible blends, and surfactants in emulsion polymerizations (176,177).

Alternating/Periodic Copolymers. Comonomers that exhibit a tendency to polymerize in an alternating fashion form periodic, or alternating copolymers. This occurs when both monomer reactivity ratios are much less than one, indicating cross-propagation is preferred to homopropagation. The most common example is the copolymerization of styrene (an electron-donating monomer) with maleic anhydride (a strong electron acceptor) (178). Tendency to alternate can

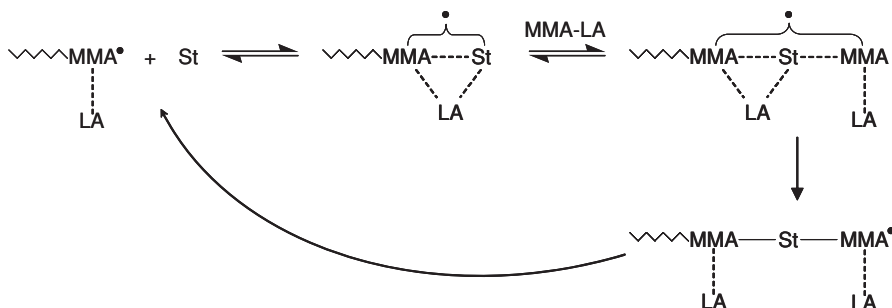


Fig. 10. Formation of poly(methyl methacrylate-*alt*-styrene) in the presence of a Lewis acid.

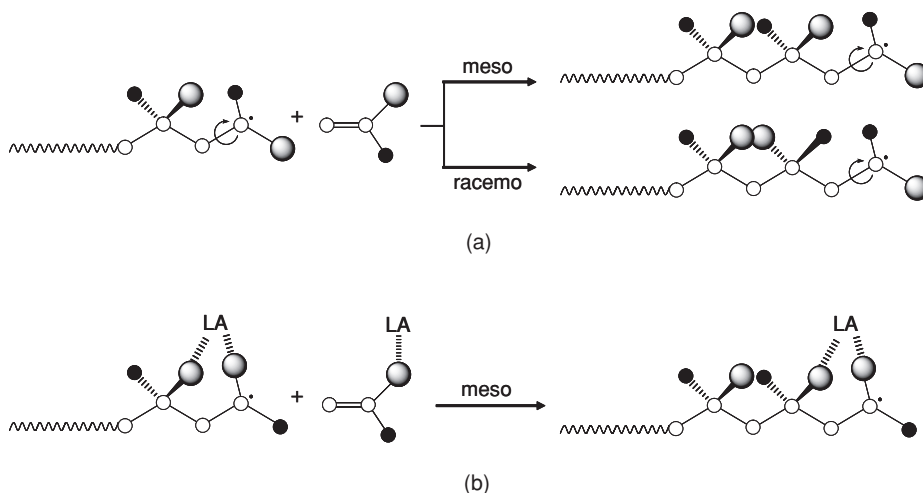


Fig. 11. Free radical propagation in the absence (a) or presence (b) of Lewis acid (LA).

also be strongly increased in the presence of additives, such as Lewis acids (Fig. 10) (179).

Block Copolymers. Block copolymers are prepared by extension of a pure macroinitiator with another monomer (180,181). The order of monomer reactivity must be obeyed during block copolymer synthesis. If the first monomer is similarly or more ATRP active than the second monomer, a clean extension occurs to form well-defined block copolymers. However, if the first monomer is less reactive, inefficient extension of the macroinitiator will result in a product exhibiting bimodal molecular weight distribution (91). A method known as halogen exchange was developed to overcome this problem in ATRP (182,183). Halogen exchange requires sufficient amount of the catalyst to be present in order for less reactive chloride-terminated chain ends to form, and therefore it cannot be employed in polymerization techniques that utilize low catalyst concentration, such as ARGET ATRP. A recent report demonstrates that efficient chain extension of a less reactive monomer with a more reactive one can be achieved during ARGET and ICAR by conducting the reaction in the presence of a small amount of styrene (184).

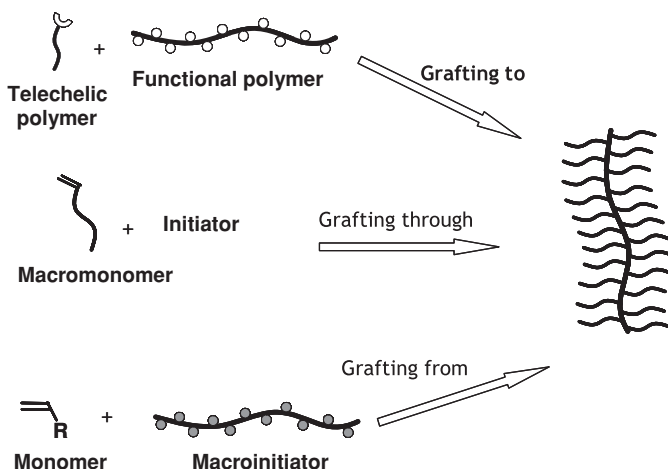


Fig. 12. Methods to obtain a polymeric brush.

An enormous variety of block copolymers have been prepared by ATRP, including diblock, triblock, and multisegmented; block copolymers by mechanistic transformation; and organic/inorganic hybrid block copolymers. Many of these materials are used commercially, for example, as thermoplastic elastomers, adhesives, and surfactants.

Control of Tacticity/Stereoblocks. Control over tacticity is difficult in a radical polymerization because the propagating center is a nearly planar sp^2 hybridized carbon, which results in poor stereoselectivity (Fig. 11a). However, the use of Lewis acids to prepare highly isotactic acrylic polymers via ATRP has been demonstrated (185–187). Lewis acids coordinate to the carbonyl group of acrylic-based monomers. If the complex is located between the last two segments of a growing polymer chain, they will be forced into a meso configuration (Fig. 11b). This produces an isotactic polymer that contains a high percentage of meso dyads. This method has also been utilized for the formation of stereoblock copolymers. A Lewis acid was added to the polymerization of *N,N*-dimethylacrylamide after a certain conversion, which yielded an atactic-*b*-isotactic polymer.

Topology. The various topologies available by ATRP include graft copolymers, star copolymers, cyclic polymers, (hyper)branched materials, and cross-linked networks (Fig. 7).

Graft/Brush Copolymers. A graft or brush copolymer consists of many polymer chains originating from a linear polymer backbone. Due to the unique structure of polymeric brushes, they can form super soft-elastomers (188,189) or can be used as templates for semiconducting or magnetic nanorods (190). The three methods to synthesize brushes are grafting from (191–196), grafting onto (166,197), and grafting through (Fig. 12) (198–204).

Grafting onto involves reaction of a pre-formed polymeric side chain with a backbone polymer. This method typically cannot be used to synthesize brushes with a high grafting density due to steric crowding of the reactive sites. In the grafting through method, macromonomers are directly polymerized to form the brush copolymer. This method is often limited in the degree of polymerization

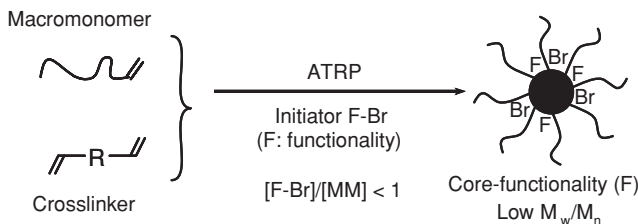


Fig. 13. Preparation of star copolymers with narrow molecular weight distribution.

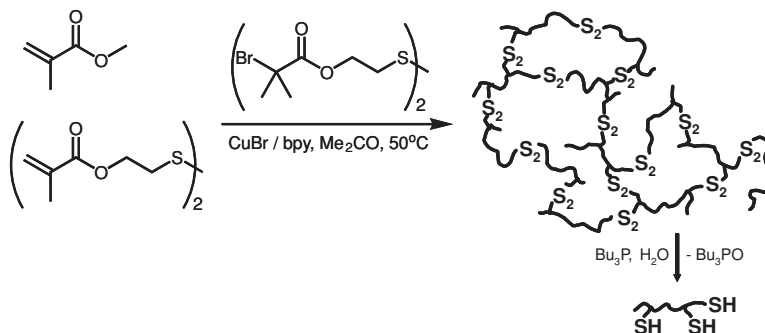


Fig. 14. Formation of a biodegradable nanogel.

that can be obtained. The most often used method is grafting from, in which monomer is grown from a linear polymer backbone that is functionalized with many ATRP initiating sites along the chain. This method allows significant control over the grafting density, which depends on how the polymer backbone is synthesized. In order to prevent brush-brush coupling, dilute solutions are required during polymerization. Coupling can also be prevented using a miniemulsion method. A variety of molecular brushes have been prepared by ATRP, including brushes with a gradient in grafting density (205), block copolymer side chains, (206), and a block copolymer backbone with different types of polymers grafted onto each block. Polymer chains can also be grafted from surfaces or particles to create a multitude of hybrid materials (207,208).

Star Copolymers. A star copolymer is a nonlinear structure with a central branch point (209). The polymer chains radiating out from this point are known as arms. It is possible for a star copolymer to have multiple arms with multiple functionalities. Star copolymers typically exhibit high molecular weights and low viscosities, and can be used as lubricants, coatings, and carriers for small molecules. There are two general methods to synthesize a star copolymer: polymerizing the arms from the core, or attaching pre-polymerized arms to the core. In the first method, organic or inorganic multifunctional cores can be used to prepare 3, 4, 6, or 8 armed stars (210–216). A hyperbranched core with many functional sites (created by the polymerization of a monomer functionalized with an ATRP initiator) was also reported to yield a star with ~ 80 arms (140). To generate stars starting from pre-formed arms, the arms can be attached to a functionalized core (for example, using click chemistry) (170,217) or cross-linked in the presence of divinyl compounds (218–220). Arms that are cross-linked and still

contain ATRP initiating groups at the core may be used for the generation of miktoarm stars, which contain arms of different functionality and different lengths (220). A recent technique using macromonomers has been developed to create stars with exceptionally low polydispersity (Scheme 13) (221,222). Polymeric brushes with a star structure have also been synthesized by grafting polymer branches from the arms of a star-shaped backbone (223).

Hyperbranched/Cross-linked Networks. The synthesis of hyperbranched and cross-linked networks with well-defined structures has been realized through ATRP and other CRP processes. Branching is often unavoidable in radical polymerizations due to radical transfer to polymer. The amount of branching can be controlled in ATRP by polymerizing monomers containing initiator functionality (224–226), or by polymerizing a dilute solution of divinyl monomer (227). Branching is regulated in each case by controlling the degree of polymerization. Cross-linked topologies can be obtained directly by polymerization of divinyl monomers, or monomers containing cross-linkable pendant functionalities which are then connected in a post-polymerization step (228). If the amount of cross-linker is high enough, a network is obtained. Reversibly degradable gels have been prepared using ATRP by utilizing disulfide bonds as the crosslinking points (228). The disulfide bond is broken under reductive conditions, and can be reformed under oxidizing conditions. Biodegradable nanogels were also prepared using disulfide linkages, which have potential as drug delivery systems (Fig. 14) (229).

Cyclic Polymers. The formation of cyclic polymers via condensation and ionic polymerization methods has been well documented. Generating cyclic polymers through a radical polymerization mechanism, however, is difficult due to the unselective reactivity of the propagating radical. Cyclization of a telechelic polymer chain synthesized via ATRP has been reported (230,231). Heterotelechelic azide- and acetylene-terminated polystyrene was cyclized using Cu(I)-catalyzed click chemistry under high dilution. This method can be extended to other functional polymers as well.

“Green” ATRP

Recent advances in catalyst design, initiation systems, and materials synthesis have expanded the potential of ATRP as an environmentally benign process (98,99). The rational selection of highly active and stable catalytic complexes and the development of ICAR and ARGET have allowed ATRP to be controlled efficiently by essentially insignificant amounts of catalyst. It has been abundantly demonstrated that ATRP is compatible with environmentally friendly reaction media, such as water (79,123,232,233) and carbon dioxide (234–236). Finally, a variety of “green” materials have been prepared by ATRP, including self-plasticized polymers (237), degradable polymers (126,238–243), materials for water purification (244), and nonionic polymeric surfactants (245).

Summary and Outlook

Since the emergence of ATRP over a decade ago, this powerful process has been enthusiastically explored in order to enhance mechanistic understanding and

prepare a wide variety of new materials. Exquisite process control can be attained by appropriate choice of initiator and transition metal catalyst, both of which can be selected from a multitude of commercially available compounds. Recent fundamental investigations into the factors that affect activation, deactivation, and the position of the ATRP equilibrium have provided the polymer synthesis community with rules for the rational selection of the most suitable catalyst for almost any ATRP system. This can potentially provide new approaches for the polymerization of currently challenging monomers, such as α -olefins and (meth)acrylic acids. The development of new initiation systems, such as ICAR and ARGET, has allowed ATRP to be successfully controlled in the presence of only 10 ppm of catalyst and can provide an avenue for facile industrial scale-up and the preparation of sensitive biomaterials. Indeed, a number of companies specializing in the production of polymers using ATRP are currently in operation. The materials that have been prepared by ATRP include functional polymers; random, gradient, and block copolymers; graft and brush copolymers; star polymers; surface-grafted materials; hyperbranched polymers; and cross-linked networks. In addition, due to their well-defined structure and composition, polymers prepared by controlled/living methods are ideal candidates for structure–property studies. Finally, ATRP has exhibited increasing potential to not only be conducted in an environmentally friendly manner, but also to provide materials that can help combat current environmental problems.

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ATOMIC FORCE MICROSCOPY

Introduction

From their early beginnings in thermoset resins to the breakthrough thermoplastics of the mid-twentieth century and the liquid crystalline materials and other high performance materials of the 1970s to the present, polymers have established key roles in all sectors of human endeavor. From transportation to construction, microelectronics, and packaging, use of polymeric materials contributes to prosperity and performance. Development of new polymers for use as stand-alone materials, polymer solutions, blends, or composites is at the core of macromolecular science. It is in this arena where the disciplinary efforts of synthesis, structure, properties, and performance hybridize into a tetrahedral coordination of interdisciplinary research and engineering. While confirmation of chemical fidelity is highly advanced, the ability for structure and property determination at submicrometer scales is lacking. Most recently, the advantages of Nanocomposites are becoming clear (1) and this trend will continue only to the extent of the ability to characterize these new materials. Moreover, processing of polymer materials is critical to device performance, and affects the microstructure of semicrystalline castings as well as the nanostructure of mechanically strained or drawn films (2). The atomic force microscope enables characterization of these materials and therefore the development of more new materials.

The microscope is an invaluable tool to the materials scientist. There are two quantities that enable microscopy: contrast and resolution. Sensitivity is not inherently an issue in microscopy: signal level is not limiting because it is now possible to count single photons and electrons. Contrast and resolution determine one's ability to see at all scales. Contrast is the ability to measure changes in signal with a detector. The detector can be your eye, a CCD camera, or an electronic amplifier. The contrast of the signal can be from intensity changes, spectral changes, phase differences, scattering of electrons or ions, transmission of tunneling electrons, or force on an atom from a probe, amongst others. Without contrast there can never be resolving power. Resolution is defined as the smallest distance between two points in a sample, that one can detect as a change in signal. There are two modes to operate a microscope. The difference between far-field detection mode and near-field detection mode is that in the former the detector is "far" away from the signal source. When the source-to-detector distance is several times the wavelength of the signal, the system displays its wave character and is therefore subject to the diffraction limit of light. This is a fundamental limit and is a result of Heisenberg's uncertainty principle (3), which is of course a result of one of the postulates of quantum mechanics. Near-field detection does not require wave propagation of the signal. Therefore, resolution is determined by the size of the probe or pinhole detecting the signal. To increase the resolving power of the microscope, the tip of the probe needs to be smaller. This is the concept that drives the maturing area of scanning probe microscopy and is what makes the scanning tunneling microscope and atomic force microscope so powerful.

Since the development of the scanning tunneling microscope (STM) in 1982 by Binnig and Rohrer (4) (Recipients of the 1986 Nobel Prize in Physics for this

discovery), the capabilities of microscopy in general have been pushed to previously unrealizable capabilities. The enhanced resolving power of the STM is attributed to the special contrast mechanism it employs. An STM operates in the near-field detection mode and is therefore not limited by diffraction as described above. In fact, only the interaction area of a local probe with the sample determines the limit of its resolution. This interaction area is actually difficult to access and strongly depends on the experimental method and the sample under study. The contrast mechanism of the STM is due to changes in the local density of electronic states at the sample. This results in a position sensitive quantum mechanical tunneling current flowing between the metal STM tip and the electrically conducting sample. Polymers, in general, are not good conductors and are therefore not typically examined with an STM. Fortunately the concepts and the technology of the STM have been applied to many other contrast mechanisms. This class of scanning probe microscope (SPM) has revolutionized surface science and has enabled a nanotechnology already yielding useful new advanced materials.

Various contrast mechanisms have been deployed toward studies of materials and polymers. In general, any physicochemical signal that can be measured by a probe or through an aperture can be developed into an SPM, where the resolution of the subsequent microscope is governed by the sample-to-probe distance dependence of the measured signal. Specifically the “P” in SPM can be replaced by “near-field optical” (5) or “capacitance” (6,7) or “magnetic force” (8) or “thermal” (9) or “acoustic” (10) or “electron spin resonance” (11) or “nuclear magnetic resonance” (12) or “thermovoltage” (13–16). Other variants are too numerous to be inclusive. The late 1980s to early 1990s can be thought of as the renaissance period of SPM inventions.

Microscopy of polymer surfaces and their high spatial resolution analysis is accomplished typically with the atomic force microscope (AFM) used in various modes of operation. The contrast mechanism of the AFM is the interatomic forces between the scanning probe and the sample’s surface. The forces are measured easily and result from the mean pairwise potential energies of the interacting atoms. Extracting the exact form of the potential energy versus tip-to-sample position is difficult with regard to the microscopic detail. However, it is generally described by a steep attractive interaction followed by a very steep repulsive interaction at closer separation. It is the shortness of range of this interaction energy that enables the near atomic resolution commonly provided by the AFM.

Analysis

Synthesis and processing are integrally important when designing for the properties and performance of a polymer system. Bulk characterization of the system is often not enough to predict, control, and maintain desired system performance when surface interactions and particle incorporation are significantly involved. The discovery, development, and optimization of new polymeric systems (eg, composites, films, or fibers) often require ensembles of analytical investigation; no one technique is enough. The cohort of surface analytical techniques is

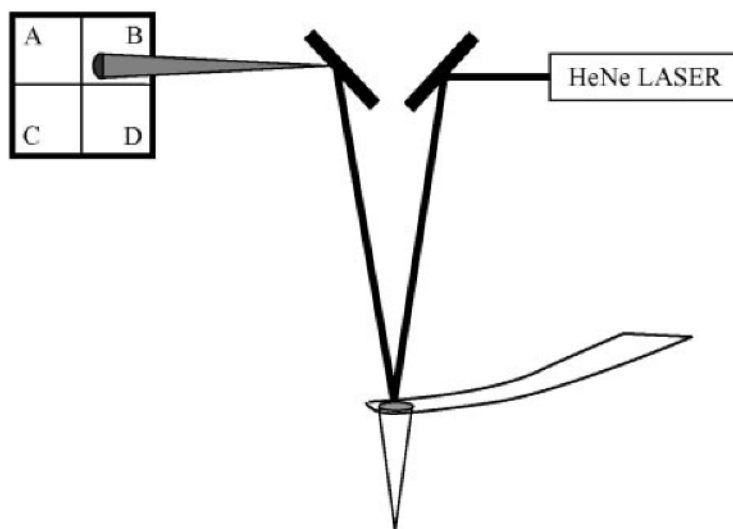


Fig. 1. Commercial AFM design.

voluminous and not appropriately reviewed here (17). It is, however, important to realize that the spatial resolution of an analysis is both technique- and sample-dependent. Atomic force microscopes are versatile analytical tools. They excel at topographic characterization of surfaces. Moreover, they can be used to probe the identity of chemical constituents at a surface and the mechanical properties of the near-surface region, both with high spatial resolution.

Imaging. Mechanical design and control of the AFM is now mature. Early in its development there were some design constraints similar to all models (7,18–24). Notably, reduction of environmental noise, sharpness of the tip-probe asperity, and sensitivity of the force transducer are the most critical design elements. By far, the most commercially successful AFM design is based on the laser-diode optical lever (24) coupled to an integrated micromachined Si or SiN cantilever and tip (25), as illustrated in Figure 1. There are several limitations to the resolving power of an AFM; noise being one of the more benign and easily removed. Since the tip is not infinitely sharp and the tip or samples are not infinitely hard (ie, they have measurable Young's moduli), the resultant micrograph will be a convolution of the chemical, physical, and topographic properties of the entire system. This is a very important point since an artifact is only realized in hindsight.

For the idealized case of hard materials, an extremely small/sharp tip and a relatively flat sample, the principal concern is tip-sample convolution artifacts (26). Typical, commercially available AFM probes have tips with radii of curvature of the order of 30 nm and with varying aspect ratios. As the topographical relief of the surface increases so must the aspect ratio of the tip. A common artifact found in samples of high relief is that the sample is actually imaging the shape of the tip instead of the converse. Since the quality of a tip varies with manufacturability and with use, overinterpretation of image structure without knowledge of tip-shape is ill-advised. A second common artifact, for the idealized sample, is observed when there is significant thermal drift, and nanometer

spatial resolution is desired. Polymers have large coefficients of thermal expansion (eg, several hundred ppm/°C). Image acquisition with the AFM is accomplished by raster scanning the probe across the sample. The scanner displaces the probe relative to the sample, one line at a time. Each line is typically scanned at a rate of many hundreds of nanometers per second in the “fast-scan” direction. After the scanner repositions the probe to the beginning of the first line, it steps down the “slow-scan” direction. This process is linear and slow. Therefore, any thermal drift will be convoluted mainly with the slow-scan direction. The effect will be to distort the image. This artifact is corrected for by subtracting out thermal drift (assuming it is constant) or by rotating the scan direction by 90°. Another common misinterpretation of AFM images occurs when periodic structure is being investigated. In general, any periodic structure that is either parallel to or perpendicular to the scanning direction should never be believed. Sinusoidal noise in any number of the system’s components will look like periodic structure perpendicular to the scan direction. Since the noise will most likely be out of phase with the scanning frequency, the image will appear to have a “crystalline” structure. Rotating the scan direction will not change the image. Also, SPM data should not be accepted as true unless it has been reproduced at several scan speeds, several scan dimensions, a couple of scan directions, and in several areas of the sample. An AFM is very powerful and can be made to generate any possible image, regardless of its validity.

There are several operating modes where the AFM can generate microscopic contrast. These various modes can help deconvolute topographic relief from chemical and mechanical surface inhomogeneity. Topographic information is most precisely obtained in “contact” mode where the AFM probe is very close to the sample and interacts with the repulsive potential energy of the surface. This is arguably the point at which the probe “touches” the sample. As long as the cantilever force transducer is significantly softer than the material being scanned over, such that excessive (force)/(contact area), that is pressure, does not perturb the sample, the AFM will accurately trace the surface. This is an idealized situation since there will always be some deformation of the polymer surface by the probe even at static, zero applied force F conditions. The perturbed contact area of radius a is described in the Johnson–Kendal–Roberts (JKR) (27) theory of adhesion mechanics as

$$a^3 = \frac{R}{K} \left[F + 3\pi R W_{\text{tip-sample}} + \sqrt{6\pi R W_{\text{tip-sample}} F + (3\pi R W_{\text{tip-sample}})^2} \right]$$

where R is the mean radius of curvature of the tip and sample, $W_{\text{tip-sample}}$ is the tip-sample surface energy, and K is the weight averaged elastic moduli (28). For typical polymer systems, this result would predict a “contact” radius of 1–2 nm even for zero applied force. This seems to preclude atomic resolution with the AFM; however, the JKR theory does break down at these small length scales. The AFM can resolve atoms on “soft” materials, but it is difficult. Nanometer scale spatial resolution is more easily obtained, and in general, the resolution is inversely proportional to a material’s elastic moduli.

While in contact mode, the user can collect both sample height and probe force information as the probe scans across the surface. In feedback mode (or

height mode), the AFM tries to maintain a constant applied force by driving together or retracting apart the tip from the sample as the probe is scanned. Ideally this would follow the topography of the sample, as the force would remain constant. This "height mode" has two advantages over the "force mode" with the feedback control turned off. Since the system is trying to keep a constant force, it is less likely to damage soft polymer surfaces having significant topographic relief. Moreover, the height mode provides a direct measure of the sample's topography. When the AFM is operated in force mode (still addressed as contact AFM), the probe-to-sample distance is not changed rapidly with varying topography. Therefore, as the tip travels over higher areas of the sample, the interatomic forces increase, resulting in the upward bending of the probe's cantilever. This mode has the advantages of allowing high scanning speeds and providing images with less noise and scanning artifacts. These come at the expense of not being able to acquire accurate and direct height measurements of the sample, and there is the possibility of more damage by the tip onto the polymer surface than when running in height mode. If only qualitative microscopy is required, force mode is the more useful technique.

An AFM cantilever is flexible in several directions (29); it can be bent up and down to measure vertical displacement of a sample and it can be torqued about its long axis because of the moment applied to the end of the scanning tip. Because of the phenomena of friction and Newton's third law, there will be a measurable force applied to the tip, which is perpendicular to the load force applied normal to the sample. While the probe is scanning, this results in the twisting of the cantilever. Modern AFMs detect the reflection of a diode-laser from the end of the cantilever onto a position sensitive four-quadrant photodetector. The laser spot deflection is illustrated in Figure 2. The total laser power on the detector is the sum of the signal from each quadrant, $T = A + B + C + D$. Changes in sample height will cause the cantilever to deflect up or down, and the signal is recorded as $\delta H = [(A + B) - (C + D)]/T$. Simultaneously the cantilever may twist because of the frictional drag on the tip as it is pulled over the sample. The torque will deflect the laser beam horizontally and the "friction" signal is recorded as $\delta f = [(A + C) - (B + D)]/T$. Since friction is related to both surface chemistry and surface roughness, the two signals may not be independent. Variations in surface composition are easily detected in force mode, whereas the topography signal may not detect any change in the surface character (30–33). Although differences in surface composition are sought with friction mode AFM, friction forces can be dominated by the near-surface yield strength of the polymer and by any adsorbed water vapor forming a meniscus at the tip-sample contact (33).

By chemically modifying the surface of the tip with self-assembled monolayers of alkanethiols, the surface free energy and therefore the frictional drag on the system can be reduced. This technique has been used to obtain superior images of biaxially oriented PET films that are typically degraded by standard contact AFM (34). Friction force studies provide another viable contrast mechanism for high spatial resolution microscopy of inhomogeneous polymer surfaces. However, it is very difficult to get absolute friction forces and thereby the coefficient of friction. Relative changes in frictional drag are measurable and aesthetic. Chemical modification of AFM tips used in friction mode defines another category of "chemical force" microscopy. Selecting the terminal group at the

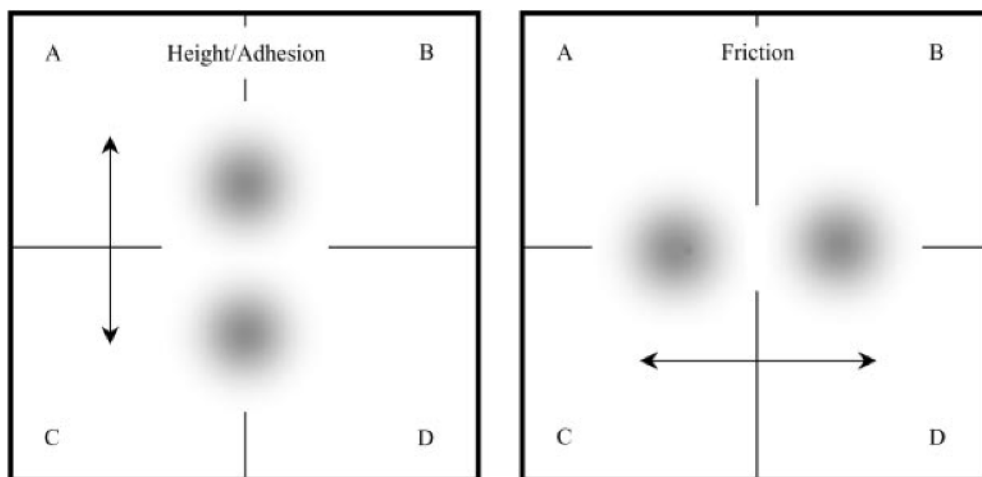


Fig. 2. Laser spot deflection.

surface of the tip (ie, making it more hydrophilic or hydrophobic) enhances the contrast of friction studies on chemically inhomogeneous surfaces (35). Even when there is no apparent change in topography, chemical force microscopy can define nanometer scale domains on polymer surfaces. Since friction is an energy dispersion phenomenon, we expect variations with surface temperature. In fact, scanning friction microscopy can be used to measure the viscoelastic properties of the near-surface region of poly(ethylene terephthalate), poly(methyl methacrylate), and polystyrene (PET, PMMA and PS, respectively) (32). As the temperature of a polymer surface increases, there are more available energy modes to dissipate the energy absorbed during the tip sliding process. These modes are intrinsic to the chemical composition near the surface.

Contact mode AFM inherently damages soft materials. This is useful when trying to study wear resistance; however, it is deleterious to image quality and surface processing studies. Alternatively, the AFM can interact with the attractive potential energy, just above the surface and therefore not “touch” the surface or be dragged across it during a scan. The attractive force microscope was developed early in the evolution of the SPM (19) explicitly to minimize sample perturbation from the scanning probe. It is difficult to maintain a stable mechanical system when the tip is being held a few nanometers away from and being attracted to the surface. Thermal fluctuations, scanning irregularities, sample inhomogeneity, and most importantly, capillarity affects from adsorbed water layers all contribute to this instability where the tip suddenly and unintentionally snaps onto the surface. To improve the attractive force mode, stiffer cantilevers were used. For contact AFM of polymer surfaces, the softest cantilever that gives reliable scanning should be used. However, for noncontact mode, system stability requires that the force constant of the cantilever be greater than the force gradient $\partial F/\partial z$ felt by the tip near the surface, which gets larger as tip-sample separation z decreases. Moreover, lateral resolution decreases rapidly with increasing separation. For these and other mechanical design criterion, very high force

constant ($k > 100$ N/m) cantilevers should be used. The trade-off in using stiff levers is that they do not deflect enough to detect the already small tip-surface forces (Recall Hook's law for a spring, $F = kz$). Various techniques were deployed to increase the sensitivity of the stiffer systems. Of these ac detection schemes, the most sensitive was heterodyne interferometry (8,23).

AC detection techniques in AFM are similar in that they all oscillate the cantilever by driving the damped spring system with a sinusoidal input. The amplitude of oscillation of the free "undamped" probe A_0 is frequency dependent and reaches a maximum at its resonance frequency $\omega_0 = \sqrt{k/\mu}$ where μ is the effective mass of the probe. When the cantilever is very far from the surface, the undamped tip oscillation lags behind the sinusoidal driving signal by 90° . As the probe is brought closer to the surface, the attractive van der Waals forces pull down on the tip during the approach phase of the oscillation. This drag damps out the amplitude of oscillation by changing the effective mass of the cantilever, thereby moving the system off resonance with the driving frequency. Since the amplitude change is very sensitive to the average tip-sample separation, it can then be used to generate sample contrast and be deployed as a feedback mechanism to track sample topography. The principal disadvantage of this technique is the loss in lateral resolution because of the more gentle slope of the potential energy versus distance curve at these necessarily larger separations.

A significant advance in the development of "noncontact" AFM is a new "tapping mode" AFM (TMAFM) (36,37). The required equipment for TMAFM is similar to that for attractive force AFM; however, the amplitude of oscillation A_0 is set to be much larger (typically >20 nm vs <5 nm for attractive force mode). Because of the larger amplitude, there is more energy stored in the cantilever as it accelerates away from the surface, thereby reducing the sticking instability discussed above. TMAFM actually intermittently "touches" the sample and the repulsive portion of the interatomic potential therefore affecting its motion, whereas non-contact AFM involves only the attractive portion (38,39). As the oscillating tip is brought closer to the sample and starts to tap the surface, the system undergoes a transition from attractive mode to tapping mode and the "damped" oscillation amplitude decreases linearly and sensitively with average tip-surface separation. Again, this decrease in amplitude is used as a set point for feedback control of the probe. Interatomic potential functions rise very steeply in the repulsive regime. Since the TMAFM tip contacts the surface at each oscillation ($>10,000$ samples per second), the lateral resolution found in contact mode AFM is regained or surpassed (40). As with contact mode, TMAFM can also operate in liquids (40,41) although interpretation of the images is less clear because of the mechanical response of the fluid. To reduce friction-induced surface damage from contact mode AFM, samples and probes are typically immersed in a liquid, which reduces the attractive capillarity force loading the tip onto the sample. With TMAFM the tip contacts the sample for a very small percentage of the time and the repulsive forces at contact are still as small, or smaller, than those found in contact AFM. Since the tip is most likely not contacting the surface when the probe is scanned laterally, there will be no frictional drag, effectively eliminating friction-induced damage. TMAFM has solved many of the damage and scanning artifact issues present in AFM imaging of soft materials (eg, polymers, monolayers, and biological materials). Tapping mode is far superior to other AFM modes for imaging

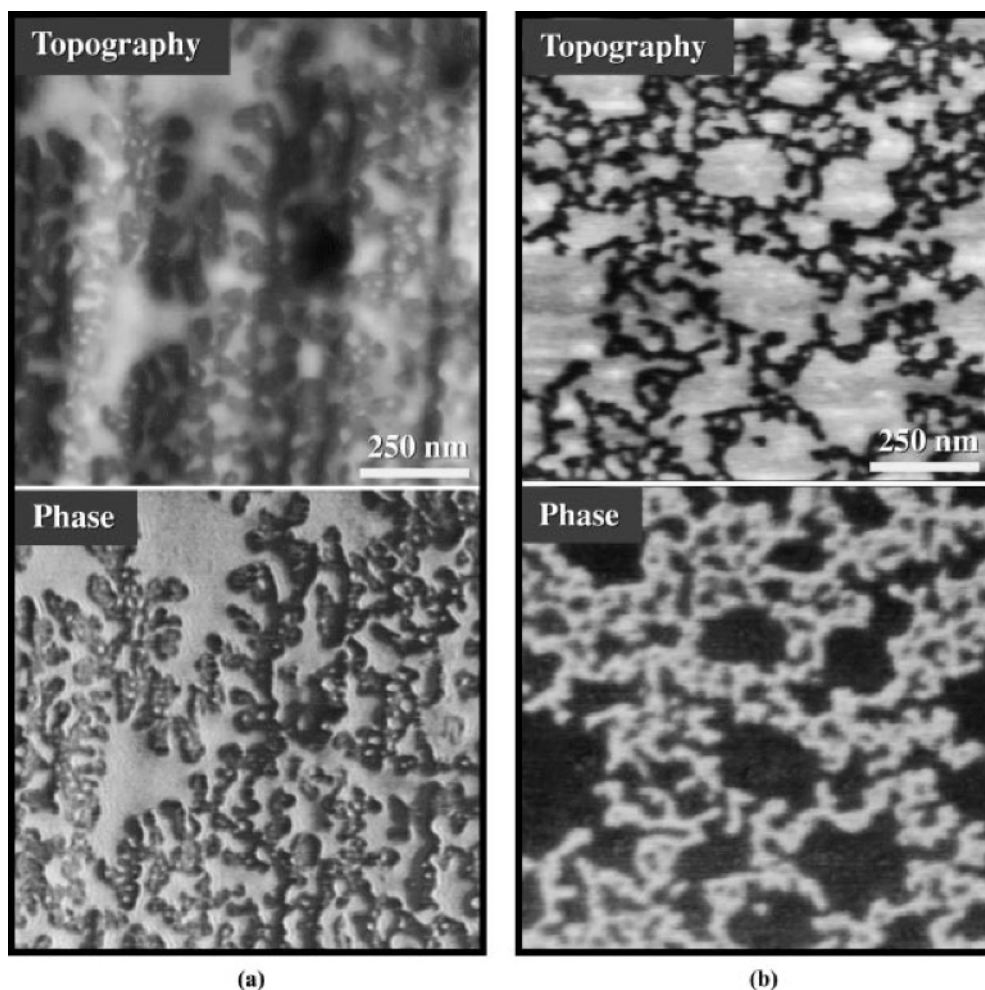


Fig. 3. Examples of TMAFM. Reprinted from Ref. 42, Copyright (1998), with permission from Excerpta Media Inc.

and is currently the recommended state of the art. A good example of TMAFM is illustrated in Figure 3 where the height and phase mode images of gelatin films on polystyrene (PS) and on mica are examined (42).

Mechanical Analysis. In addition to the wonderful imaging capabilities of AFM, the tip-cantilever system can be used to extract mechanical properties of soft surfaces with the highest of spatial resolution. Since the mechanical behavior of bulk material can be dominated by the properties of the microstructure, aggregation, and domain segregation, analysis of these at length scales smaller than the surface inhomogeneity is critical for advanced materials design and characterization. Essentially, by “pushing” on the surface with the probe, one can extract a form of the Young’s modulus (compliance), degree of plastic deformation, scratch and wear resistance, and the tribology of the viscoelastic nature of polymer surfaces. There are three ways to extract a relative Young’s modulus E . The most

accurate, easy to interpret but time-consuming method to get E (or something that looks like compliance) is with force–distance curves (FCs). As illustrated in Figure 4, the force on the cantilever is measured as a function tip–sample distance for a polystyrene/poly(vinyl methyl ether) (PS/PVME) blend (31). Initially, the tip is far from the surface and is driven toward the sample. In general this is a relative displacement; either the tip or sample is moved (typically the sample is moved, not the tip). As the tip experiences the attractive forces near the surface (mainly because of capillarity if the sample is exposed to air) it is deflected downward, toward the surface. To get accurate mechanical properties, each AFM probe must be calibrated to determine its force constant (they vary greatly from designed specification) and the radius of curvature R of the tip. With knowledge of k , cantilever deflections are converted to actual forces. As the tip is driven further toward the sample the resultant force gradient exceeds the value of k ; therefore, the system becomes mechanically unstable and snap to contact the surface. Once in contact with the surface and interacting with repulsive forces, further driving of the tip toward the sample results in both the upward deflection of the cantilever, p , and the downward elastic deformation of the sample, s , where the total displacement is $z = p + s$. To extract Young's modulus of soft samples (significantly softer than the AFM tip material), FC contact data are fit to $F(z) = k[z - F(h)^{2/3}(D^2/R)^{1/3}]$, where $D = 3(1 - \nu^2)/(4E)$ and ν is Poisson's ratio (43). In general, the elastic modulus is proportional to the magnitude of the slope of the FC contact data. For soft materials there is typically an hysteresis observed during the retraction of the tip from the sample. This hysteresis is more pronounced for softer materials because of the longer relaxation time of compliant polymer films. As the tip is retracted further, still it does not release itself from the surface at the same distance where it snapped into contact initially. Adhesive interactions hold the tip onto the surface until the cantilever-induced force exceeds the adhesive force, which is related to the surface energies, the contact area, and surface roughness, and it subsequently snaps away back to its original undamped state. The difference between the force at the snap to contact point and the adhesive force has been shown to correlate with observed frictional forces (31). This is naively counterintuitive since adhesive interactions are parallel with load direction, and friction is measured perpendicular to the load; they should be uncoupled. Obviously friction on soft materials deforms the surface and the tip pulls on the material as the surface yields.

Although FCs are useful and they can be quantitative, they are time-consuming, especially if one is mapping out the surface at each pixel ($>10,000$ FCs). A faster, and more convenient to visualize, method to obtain rheological information is with “force modulation” microscopy (fmm). This is a contact mode AFM experiment where the sample's height is modulated by a sinusoidal signal. This is similar to TMAFM except that the sample is driven while the tip remains in contact and that the oscillation frequency for fmm is an order of magnitude lower. As the tip is scanned laterally, both its height and its oscillation amplitude are recorded, where more compliant materials will absorb more energy, damping out the tip's oscillation (44,45). It can also be useful to measure the dynamic mechanical (DMA) properties of the near-surface region (see DYNAMICMECHANICAL PROPERTIES). Polymers are typically characterized by DMA to yield frequency-dependent behavior. This technique is coupled to an AFM by sweeping

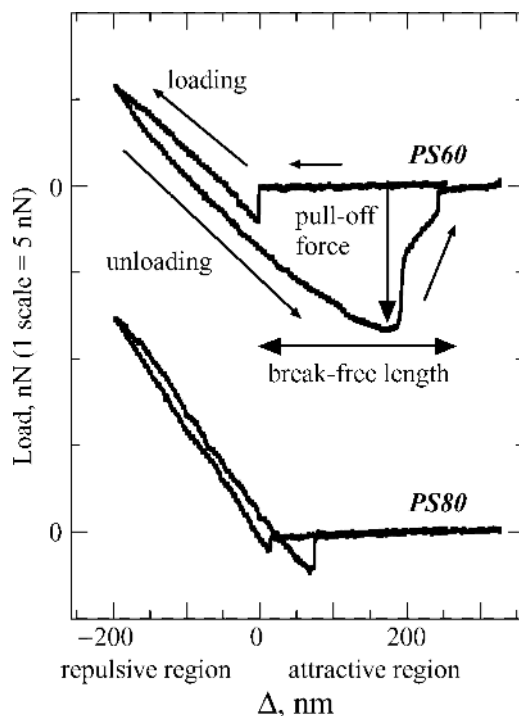


Fig. 4. Force–distance curve for a polymer blend. Reprinted from Ref. 31, Copyright (2000), with permission from AIP.

the oscillation frequency of the fmm experiment. By disabling the slow-scan direction and incrementing the oscillation frequency after each fast-scan line, an fmm amplitude versus position and frequency map is generated (44).

Since fmm is a contact mode technique it subjects the sample's surface to possibly destructive lateral forces as the tip scans. A less destructive alternative is to operate in the tapping-mode regime (46). Changes in mechanical properties near the surface will alter both the tip's amplitude of oscillation in TMAFM and also the phase shift between the probe and the oscillating signal driving its vibration. This phase angle, ϕ , is sensitive to the oscillation frequency driving the probe and will lead or lag by $\pm 90^\circ$ on either side of the resonant frequency of the free cantilever. For a given frequency and driving amplitude the phase shift will increase or decrease as the compliance of the material changes. Currently this technique is limited to qualitative imaging. Since there is a reversal in contrast as experimental parameters of the tapping tip change, it is difficult to quantify these observations. However, because of the ease at which the phase images are acquired and the nondestructive nature of TMAFM, this technique is now prevalent and found on all modern AFM instrumentation (47). A clear demonstration of the qualitative advantage provided by phase imaging is shown in Figure 5, which compares the height (right) and phase (left) images of a doped polyaniline/cellulose acetate blend (48).

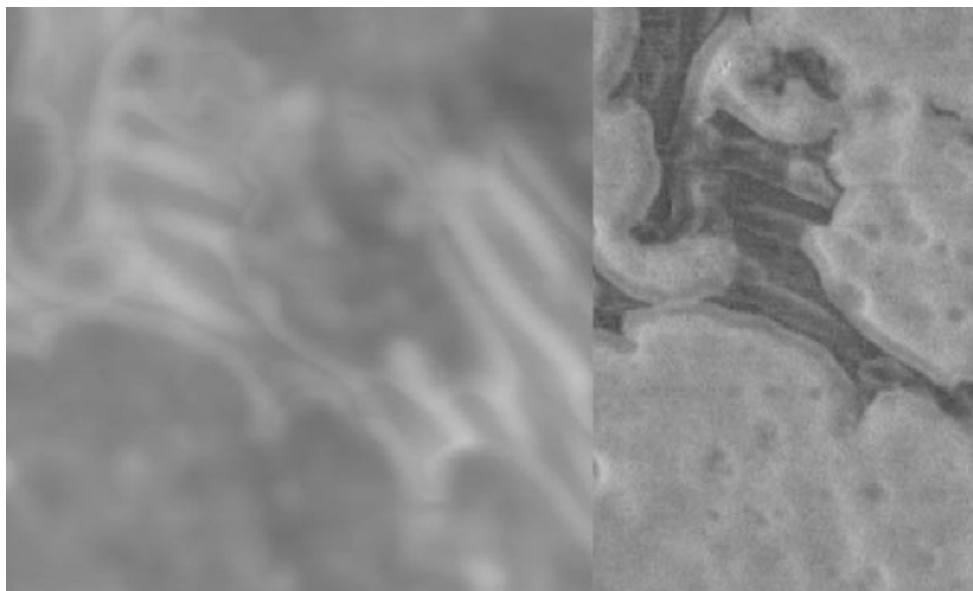


Fig. 5. Example of phase imaging for a polymer blend. Reprinted from Ref. 48, Copyright (1999), with permission from AIP.

Much effort has been directed toward minimizing damage on the surface because of the scanning probes. This implies that it is quite easy to use the AFM for studies of indentation and wear as illustrated in Figure 6 where a nano-scratch into a poly(ether ether ketone)(PEEK) matrix shows its relative poor wear resistance as compared to graphite (49). Using the stiff cantilevers required for TMAFM, while in contact mode, softer polymer surfaces and their resultant composite systems can be plastically deformed and scratched. Indentation studies (ie, Vickers Hardness testing) are obtained by simply pushing harder than usual during an FC. With the stiffer probe pushing on the elastically deforming sample, it will eventually reach the polymer's yield strength. At this point the sample will plastically deform, leaving a tip-shaped indentation as the probe is pulled away from the sample (50). After the indentation is formed, the same AFM tip is used to scan over the new topography of the surface. Typical results exhibit a tip-shaped pit surrounded by pushed-up material. Since the elastic modulus of a standard tip is several hundred times larger than that for typical soft polymers, it can be assumed that most of the deformation is confined to the sample and that the shape of the tip is not deleteriously affected. Young's moduli and the materials tensile yield stress are extracted by modeling the contact and deformation geometry using Hertzian mechanics. The principles of nanotribology have been extensively reviewed elsewhere (51). More interesting still is the AFM's ability to measure wear resistance with nanometers resolution. The contact area of the tip dragging across the sample, typically 10–100 nm, limits the spatial resolution of wear resistance studies. Using appropriate software, the AFM probe is directed across the surface to scratch out a pattern. Wear resistance versus scratch speed and tool pressure can be very useful when designing polymer blends and/or

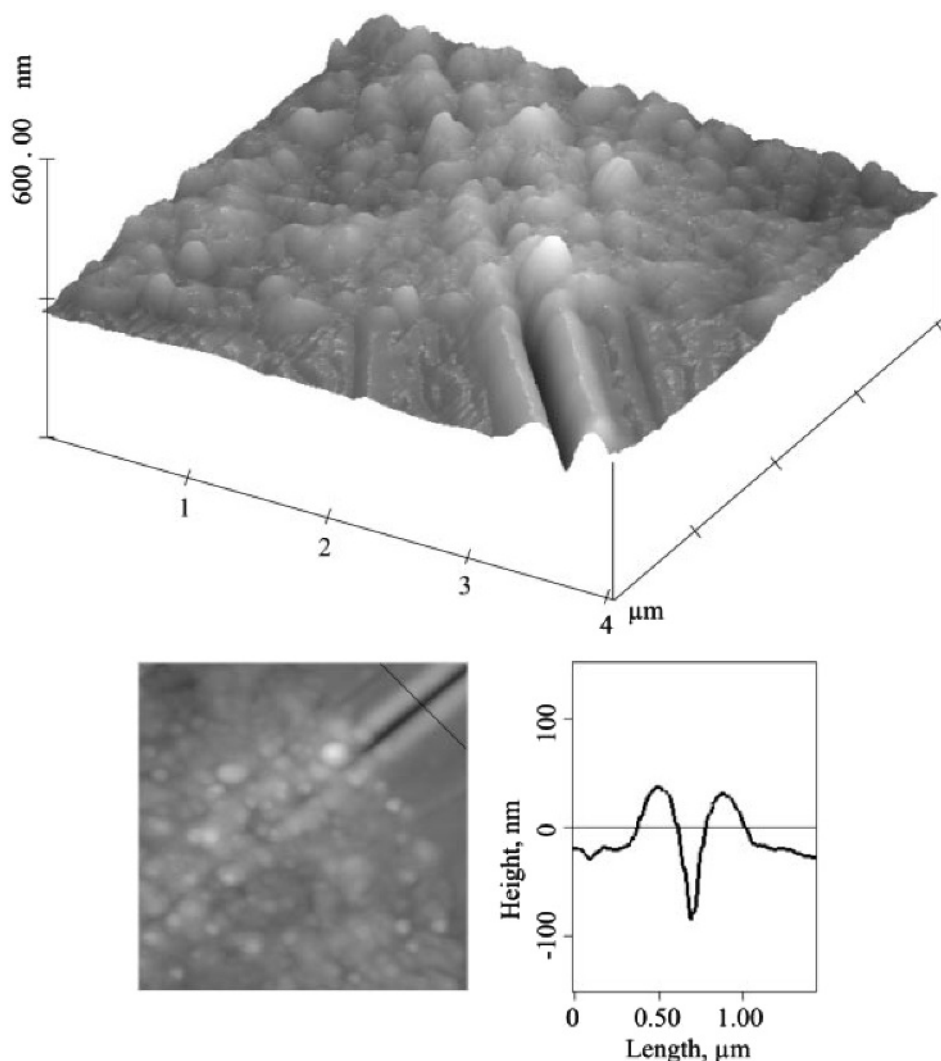


Fig. 6. Nanoscratching of a PEEK matrix sample. Reprinted from Ref. 49 (Fig. 3), Copyright (1999), with kind permission from Kluwer Academic Publishers.

composites where low compliance and low adhesion are materials trade-offs and need to be optimized (49). This method has also been considered for pattern transfer applications. By scratching through thin, soft layers of a protective coating with the AFM tip, a desired pattern can be lithographically transferred to the underlying substrate. Although direct write techniques are unacceptably inefficient, they do show promise for some limited ultrahigh resolution applications (52).

Developing Techniques. During the unloading segment of an FC on soft polymers, the tip pulls off of the surface and typically snaps back to its free position. Occasionally, however, the tip retracts in several steps, or sometimes

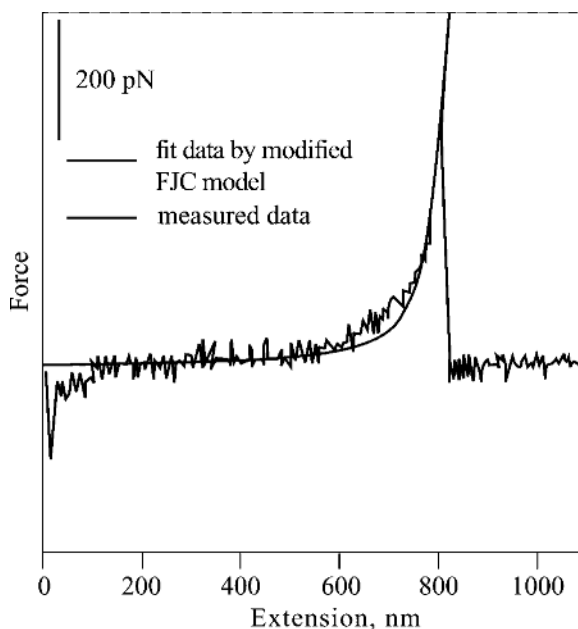


Fig. 7. A single-molecule force–distance curve for PVA. Reprinted from Ref. 54, Copyright © 1998, John Wiley & Sons, Inc.

pulls away such that the force versus distance curve is only mildly sloped. These observations are a result of polymer chain interaction with the tip (53). Material adsorbs to the AFM tip during the compression and requires time to untangle itself from the chains on the substrate during pull-off (31). This phenomenon has shed light on another outstanding capability of the AFM: its ability to perform single-molecule force studies. By properly functionalization of an AFM tip and appropriate surface preparation, individual long-chain molecules can be manipulated and extended, again revolutionizing polymer mechanics and dynamics. Studies have yielded single-molecule force versus extension curves of poly(vinyl alcohol) (PVA) (54), polysaccharides (55,56), poly(acrylic acid) (57), and biological polymers as well (58). A typical single-molecule FC is shown in Figure 7, where a single PVA chain is extended by an AFM probe, and these data are modeled well by a freely jointed chain up to the force that causes bond rupture (54). Common to many of these studies is an apparent conformational change of the polymer strand as it is extended, followed by conversion to a significantly stiffer “crystalline” strand and then finally by bond scission. As the dimensions of nanostructured polymeric materials are reduced, single-molecule mechanics should directly correlate with these processed devices. It can be expected that the promise of chemistry’s molecular fidelity finally enables true structure–function relationships for condensed materials in the near future.

In addition to imaging and mechanical analysis, researchers are now pursuing thermal analysis microscopy of polymer surfaces. Although this area is developing rapidly and has been well reviewed (59), only the state-of-the art available on commercial systems will be presented here. At the heart of scanning thermal

microscopy (sthm) is the heat transfer process at the tip-sample “contact.” Variations in heat transfer result in appropriate signal contrast where lateral resolution is limited by variations in thermal conductivity. Although thermal noise is quite low and signal sensitivity high, it is doubtful that the sthm will ever attain subnanometer resolution. Resolution of thermal contrast of approximately 100 nm is now common. There are several modes of operation, but typically a thermocouple or thermister is integrated into an AFM probe where the tip of the temperature transducer is also the scanning tip. The system operates in contact mode and either the sample or the tip is heated. AC detection of an oscillating temperature increases signal sensitivity. This is most easily achieved by modulating the output power of a laser incident on the system. If the spectral absorption of the sample is spatially inhomogeneous, this too can be measured by scanning the wavelength of the light source at each, or some, of the scanning positions on the surface (60,61).

A more useful probe for sthm is the resistive wire (62). Instead of heating the sample and measuring the temperature with the tip, the tip itself is heated and its temperature is measured, via changes in its electrical resistance. Changes in local thermal conductivity of the sample will result in changes of the tip's temperature for a constant power through the wire. Dissipation of heat at the tip-sample “contact” and through inhomogeneous samples is convoluted, making quantitative measurements poorly understood. Thermal inhomogeneity in a polymer film can be laterally across and or longitudinally through the sample. Since the thermal diffusion length of a typical polymer is of the order of a micron, nanoscale calorimetry will approach a fundamental limit. However, micron-resolved thermal conductivity of domains in a poly(vinyl chloride)/polybutadiene (PVC/PBD) polymer blend have been clearly demonstrated in the literature (63). This type of microscopy can be more relevant on composites where fine tuning of thermal and mechanical properties is desired.

In addition to thermal conductivity, modifications of the sthm can yield thermal capacity or more specifically differential scanning calorimetry (dsc). Instead of heating the resistive wire with a constant power, its temperature is modulated with an ac current. The resultant amplitude and phase shift of the wire's temperature is measured with a lock-in-amplifier. Simultaneously, the temperature of the tip and sample are ramped up slowly so as to measure the change in heat dissipation per change in temperature, dq/dT . This measure is, of course, related to the local heat capacity of the sample and is correlated with expected phase transitions of the material. Plotting the first derivative of the phase shift versus sample temperature looks very similar to the bulk DSC as shown in Figure 8 for a sample of thermally quenched PET (63). Variations of glass-transition temperatures in micrometetr-sized domains could be critical as device dimensions shrink.

Since the AFM is peerless at measuring vertical expansion, and the ac sthm can measure temperature, it should be possible to extract coefficients of thermal expansion (CTE) on thin films, which is nearly impossible with conventional thermal mechanical analysis (TMA). By modulating the sample's temperature the longitudinal composite expansion can be measured by the deflection of the sthm cantilever as the probe scans the sample (64). These capabilities are critically important when developing multilayered thin-film materials. Expansion

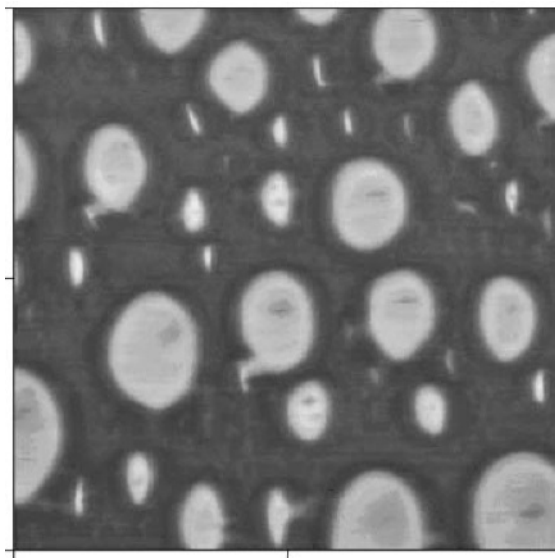


Fig. 8. A sthm scan of a PVC/PBD blend. Reprinted from Ref. 63, Copyright (1996), with permission from AIP.

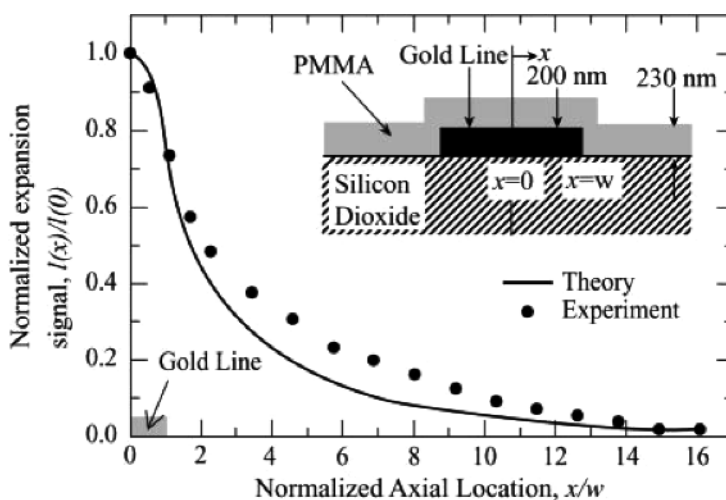


Fig. 9. A sthm scan of a multilayer device construction. Reprinted from Ref. 64, Copyright (1998), with permission from AIP.

of PMMA film insulating a gold interconnect line is measured and illustrated in Figure 9 (64). These data show that the theoretically expected expansion deviates from those observed, implying that this additional thermal fatigue could lead to premature device failure.

As mentioned above, the SPM is mostly limited to sampling the near-surface region of a polymer system. A new technique based on TMAFM has been developed to enable volume imaging with the SPM. This study tracked a series of

height and phase images of a styrene–butadiene–styrene (SBS) triblock polymer microdomain as the surface was being removed 7.5 nm at a time with a plasma etcher. These data are illustrated in Figure 10 (65).

Prior to the development of the SPM, and all its derivatives, scaling of physical properties from the macroscopic to the nanoscopic was speculative at best. “Experiments are the only means of knowledge at our disposal. The rest is poetry and imagination” (Max Plank). The AFM has opened the door of exploration into the varied complexities of advanced polymeric materials. In the following, observations on various molecular systems and the surface characteristics intrinsic to them and their processing are discussed.

Systems

LB Films. Use of Langmuir–Blodgett (LB) film techniques have been shown to be an effective method for producing thin layers of materials for thermo-mechanical evaluation. Morphological description of such samples by AFM has been used with success in a wide range of polymer systems. Individual chains of phthalocyaninepolysiloxane shish kabob molecules were deposited on metal nanoelectrodes using LB techniques (mixed with isopentyl cellulose) and then dispersed on the surface of an LB trough. The deposition surface was dipped into the dispersion to deposit the polymer mixture. The authors demonstrated that the structures of these semiconductive polymers are not disturbed by raised patterns on the electrode (66). Polystyrene/poly(ethylene oxide) (PS/PEO) diblock copolymers of differing fractional compositions were used to produce LB films. Polystyrene aggregates were observed to accumulate on the surface of the films; the features of these aggregates were directly proportional to the PS content in the starting diblock copolymer. Hence, by manipulation of the starting polymer, controlled patterning of the film surface could be accomplished without use of any lithographic methods (67) (see LANGMUIR-BLODGETT FILMS).

Changes in the environment in which polymer LB films are produced can result in significant structural changes of the deposited materials. LB films of poly(γ -benzyl-L-glutamate) produced from a number of solvents were imaged. Solvent polarity strongly influenced the self-assembly process and is manifest as thickness and height variations of individual fibers (which formed on the mica substrate), and in the lateral globular dimensions of the polymer absorbed from dilute solution. AFM allowed for the quantification of these structural differences, and was used to suggest a mechanism for self-assembly of polymer chains into fibrils (68). Varying the pH at which LB films of poly(linoleic acid) were produced resulted in major morphological changes within the deposited film. Tapping mode AFM shows spherical particles lacking any regular pattern when depositing from a subphase solution with a pH of 6.0. As the pH is increased to 6.3 and 6.6, increasing organization into a network structure was observed. At pH 6.9, much of this structure was observed to be absent; it is at this pH that a step change in chemical reactivity of the polymer film is observed as well. Therefore, this method allows for a correlation between film structure and chemical properties (69).

Morphological differences in LB films result from small compositional changes in the polymers used, and from the difference in processing between

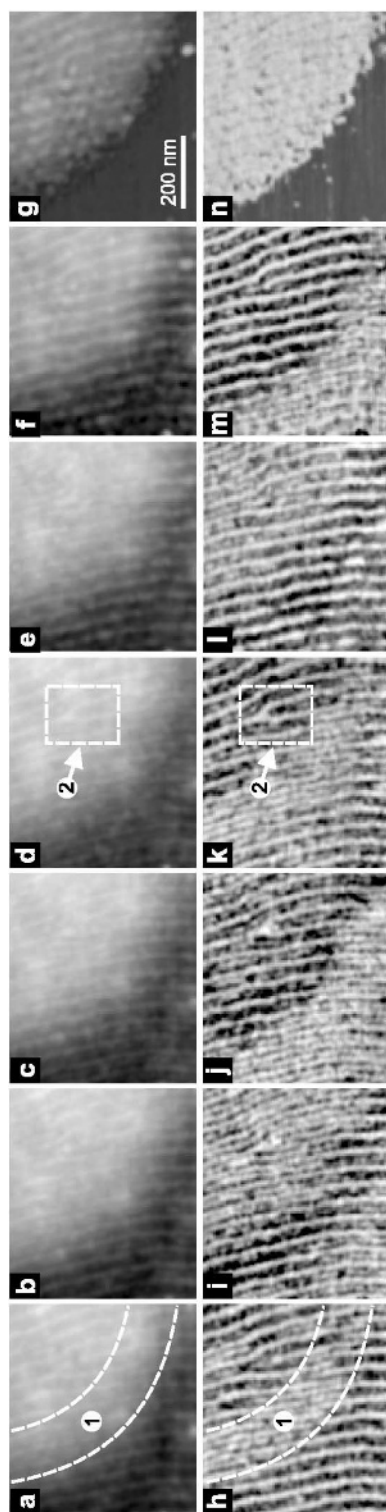


Fig. 10. TMAFM study of an SBS triblock polymer, as its surface was removed. Reprinted from Ref. 65, Copyright (2000) by the American Physical Society.

LB and freestanding thick films. Formation of LB films from salts produced from polyamic acid and a variety of alkylamines were examined by AFM. Unique morphologies were obtained, as the chemical structure of the amine was varied (70). The structure of LB films of polyaniline (PA) was shown by AFM to possess preferential orientation, but with much lower levels of porosity than which had been previously observed within freestanding films. Increases of surface roughness in LB films were observed by AFM when the ratio of low molecular weight PA to cadmium stearate in the subphase solution was increased, while domain sizes varied inversely with organic content (71). Varying the side chains of poly(*N*-alkyl acrylamides) was also demonstrated to produce major differences in morphologies in LB films. When decyl side chains were incorporated into the polymer film, these groups were observed to adopt random orientations. Increasing the chain lengths to octadecyl resulted in highly ordered two-dimensional crystals that were imaged by AFM (72).

Monolayers (Self-Assembly of Oligomers). The degree of ordering, which results from molecular self-assembly of polymer systems, is readily ascertained using AFM. Thin layers of an acetylenic phospholipid were demonstrated by AFM to self-assemble into lamellar structures when cast as thin films. UV polymerization of these films produced polymers with well-packed structures (73). Alternating layers of positively charged poly(diallyldimethylammonium chloride) and negatively charged montmorillonite clay were self-assembled onto various substrates. AFM was used to quantify the smoothing of initial surface roughness with each successful layer assembled to the surface, and to develop a representation of how clay platelets and polymer chains associate in layers (74). AFM imaging was used to determine the morphologies of nitro-containing diazoresin, as a function of deposition time, and of bilayer and multilayer assemblies of the diazoresin and poly(sodium *p*-styrene sulfonate). Flat, stable multilayer structures were demonstrated upon UV-irradiation (which resulted in replacement of the diazo group with C–C bonds between layers of polymers), and regular structures were shown to be maintained (75).

Biopolymers. Ranging from individual chains of deoxyribonucleic acid (DNA) to the “high performance” fibers produced by spiders for their use as draglines, AFM has been used to provide insights into biopolymers, much as it has for synthetic systems (see POLYNUCLEOTIDES; SILK).

Solutions of single- and double-stranded DNA (as well as several synthetic polymers) were electrosprayed onto a mica surface and imaged. Each polymer could be generated and analyzed in globular or fibrillar forms, depending on conditions of the electrospray processing of the solutions. Increasing polymer concentration in the water solutions led to formation of the globular structures. Changes in electrode potential used in the electrospraying was shown to also play a role in the morphology of the biopolymer (76).

Both stretched and unstretched silk threads from the Black Widow spider were imaged. Two types of fibers were observed within the threads (thicker, 300 nm in diameter, oriented parallel to the thread axis; thinner, 10–100 nm fibrils oriented across the thread axis). With increasing strain, mean fiber and fibril diameters were found to decrease and fibrils aligned themselves more closely with the thread axis. The authors were able to relate these structural features to models of secondary and tertiary structure and organization in spider silk (77).

Thermosets. Structure determination in thermoset polymer systems can at times be problematic because of their relative insolubilities and large molecular weights. Direct observation of structural details by AFM has been advantageous for such systems, describing both inherent material properties as well as the impact of processing steps on final structure properties.

The role of processing of thermosets in determining ultimate polymer structure is well studied using AFM. The morphological structures of fibers and films produced from segmented Polyimides were shown to match closely those predicted by molecular modeling (Fig. 11). In these systems, two-dimensional arrays of ordered polymer chain backbones were observed. For fibers, the polymer chain backbones were found to be oriented at a definite angle with respect to the fiber machine axis, where this angle is hypothesized to be due to differential shrinkage of the core and surface of the fiber during solvent removal and heat treatment of the fibers (78). AFM imaging of carbon fibers revealed extrusion lines, as well as the presence of "dirt" inclusions. A correlation between the concentration of these particles and the strength of the fibers was observed, providing a structural basis for optimizing the fiber-making process (79).

Inherent polymer morphologies have been determined using AFM imaging. This technique was used to discover a parallel-rod structure on the surface of fluorinated polyimide films produced by vapor deposition polymerization; these structural details were not apparent by scanning electron microscopy (SEM). When spin-cast films of the same polymer were imaged, a rough structure lacking the rod-like morphology was observed. The authors concluded that the parallel-rod morphology resulted from both polymer-polymer and polymer-substrate interactions (80). Cleaved surfaces of the polyacetylene poly(2,4-hexadiyne-1,6-diol bis(*p*-toluene sulphonate)) were imaged, revealing *bc*- and *ab*-planes consistent with the crystal structure of the polymer. An overall zig-zag morphology, with step heights corresponding to one polymer chain's width, was resolved clearly. Substituents on one side of the polymer backbone were observed to stick out diagonally from the surface, while other side chains were observed to be located underneath the substituents of a neighboring polymer chain (81). Thermoset epoxy resins modified with nanoclays were imaged using phase contrast AFM. These images showed interlayer distances that were noticeably smaller than those measured by wide-angle x-ray scattering (waxs); the authors speculate that the mechanical deformation of the clay silicate layers by the AFM tip may be the cause of this discrepancy, challenging the notion that the clays serve as rigid reinforcing layers in the composite (82).

Chemical modifications of thermoset resins have been documented, using AFM as an analytical tool. Ion beam modification of polyimide surfaces were imaged in contact mode, which showed a reduction in surface roughness with increasing irradiation, and generation of a graphitic structure in the degraded polymer (83).

Thermoplastics. The largest body of AFM structural studies to date in the area of organic polymers has probed the details of commodity thermoplastic materials. Within this work, both support and extension of knowledge gained by other techniques, such as electron microscopy, as well as new insights into the structure-property differences which result from melt processing and/or thermal treatment have been gained. Specifics of thermoplastic surfaces, important in

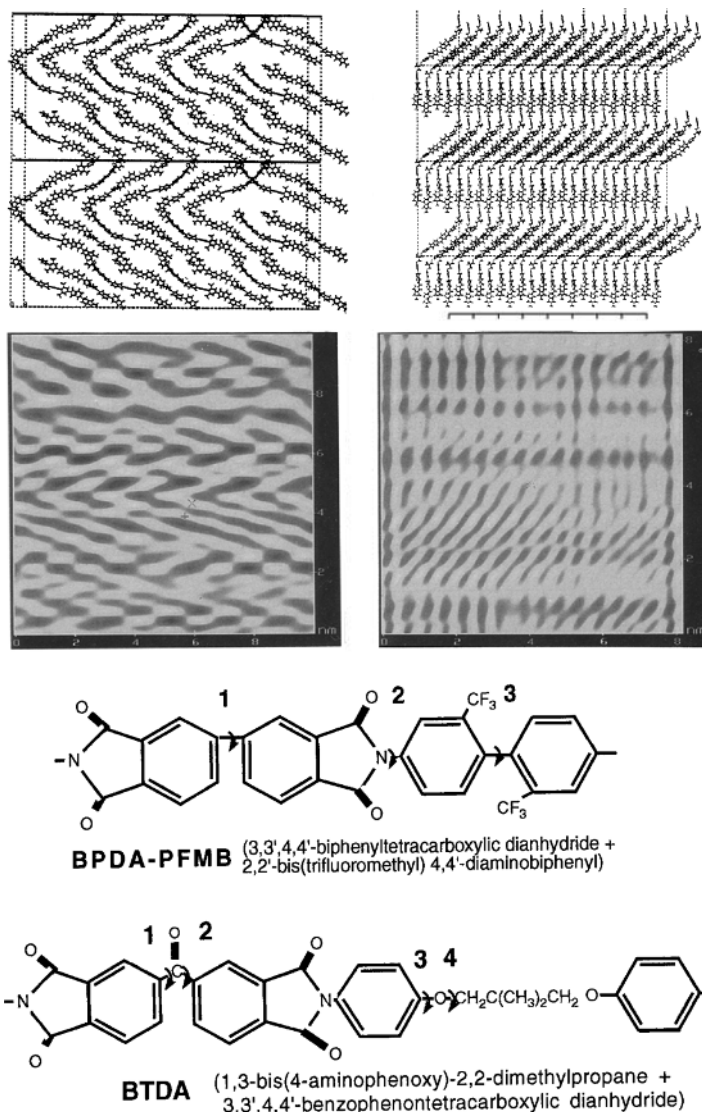


Fig. 11. Morphology of segmented polyimide structures. Reprinted from Ref. 78 (Figs. 1c, 1f, 3 and Scheme 3), Copyright (1992), with permission from Springer-Verlag.

controlling transport and adhesion phenomena, have also richly benefited from AFM studies. Structural studies of combinations of these thermoplastics is discussed later.

Polyethylene. AFM imaging of thermoplastics has been widely used to corroborate and expand knowledge obtained using other structural methods, such as x-ray crystallography and electron microscopy. Direct observation of folded chain lamellar crystals of polyethylene (PE) was provided by AFM. Spacings appropriate for the (known crystallographic) orthorhombic unit cell, and for the monoclinic unit cell that can be produced by mechanical deformation, were observed (84) as

Table 1. Morphological Differences Arising from Differential Cooling of HDPE

Imaged area	Spherulite size, μm	Band period, nm
Cooled edge	2–3	400–500
Intermediate	4–5	800–900
Middle	6–8	1000–1100
Intermediate	8.5–10.5	1200–1400
Uncooled edge	10–13	1600–2000

were boundaries between regions of differently oriented folded chains (85) (see Ethylene Polymers, HDPE).

Cold extruded PE was imaged at scales ranging from $700 \text{ nm} \times 700 \text{ nm}$ down to atomic scale resolution. Fibrillar morphology was observed for uniaxially oriented materials, with microfibrils in the 20–90 nm range, aligned with the extrusion axis. Individual polymer chains and extended chains were also observed (86).

Extruded high density polyethylene (HDPE) pipe was cooled on the outside with water, while the internal surface was allowed to cool in ambient air. As a result of this cooling gradient during fabrication, a range of crystal structures could be anticipated. AFM imaging of sections across the pipe confirmed major morphological differences that arose from the differential cooling. At all locations, spherulitic structures were observed, but spherulite size, band period, and lamellae thickness increased within the pipe from the cooled to uncooled sides (Table 1) (87).

Polypropylene and Polystyrene. As with PE, AFM has yielded important structural details for the different grades of polypropylene (PP) and Polystyrene (PS). Syndiotactic polystyrene (sPS) was imaged (Fig. 12), showing a spherulitic structure consistent with prior SEM work. The radially arranged fibrils in the spherulites were shown to consist of small lamellar crystals. The observed spherulites were also twisted. Epitaxial crystallization of sPP on *p*-terphenyl created a laminar structure, such that the lamellae stand on end, with an average thickness of 20 nm (88). Similar structural details have been observed for syndiotactic polypropylene (sPP) (89).

Uniaxially oriented isotactic polypropylene (iPP) was imaged using AFM, showing microfibrils and macromolecules. Fibrils with an average diameter of 150 nm were observed. Individual polymer chains with 1.17 nm chain–chain distance were seen. The authors propose that the (110) crystal plane was being resolved with this work (90). Other workers, who were able to clearly resolve right- and left-handed helices (Fig. 13) with pendant methyl groups visible, accomplished atomic scale resolution of iPP (91).

The metastable β -phase of iPP was imaged in another study, where epitaxial crystallization was found to result in a biaxial orientation that could not be achieved mechanically because of the $\beta \rightarrow \alpha$ transition that occurs during orientation. A lateral periodicity of 1.9 nm was found in the (110) face, corresponding to the distance between three chains, and is indicative of the frustrated

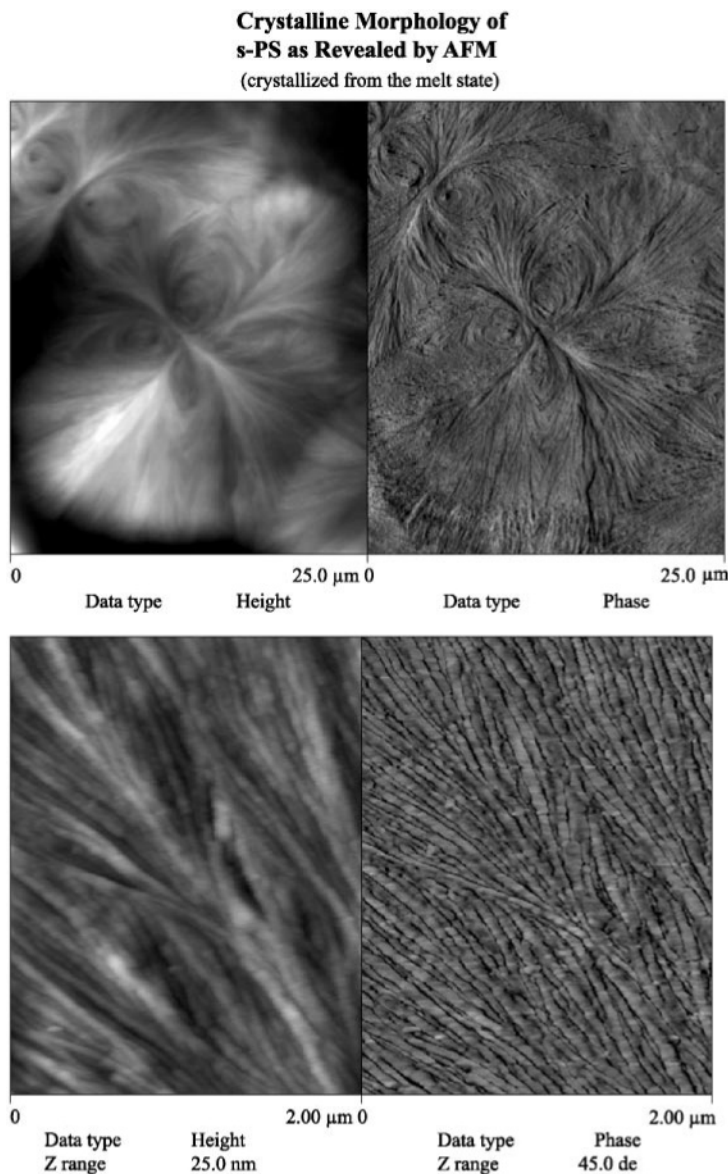


Fig. 12. Structural details of sPS. From Ref. 89, courtesy of Prof. S. Nazarenko.

packing of the β -phase of iPP. Variability in the image suggested the possibility of two distinct frustrated phases existing in the samples (92).

The effects of processing conditions on polymer structure have been demonstrated clearly using AFM images of PP. Polypropylene fibers spun using three different processes, gravity spinning, melt spinning, and melt blowing, were imaged by AFM, and the structures resulting from each of these different processing methods compared. The surface of gravity-spun PP was found to be entirely

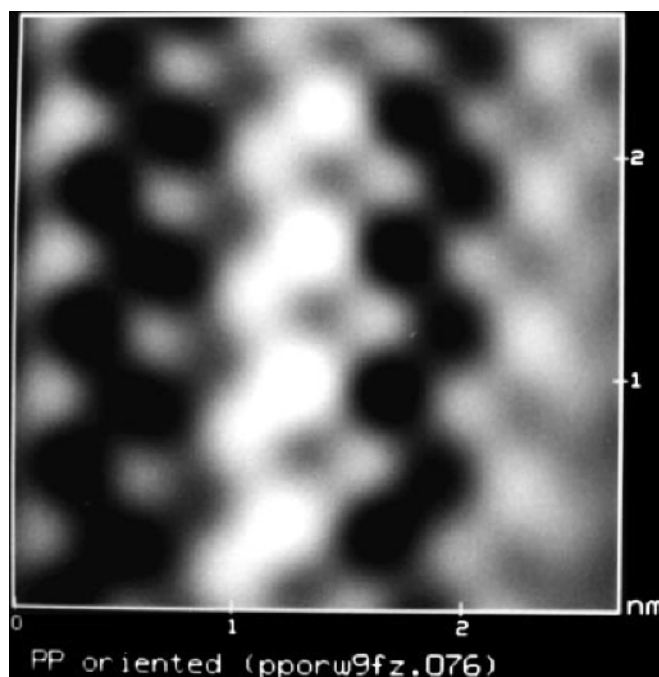


Fig. 13. Detailed structure of iPP. Reprinted from Ref. 91, Copyright (1994), with permission from Elsevier.

covered with spherulites consisting of polycrystalline aggregates formed from a radiating array. Each branch of the spherulites were composed of lamellae and are connected by regions of amorphous material, consistent with general lack of orientation along the fiber axis. Similar structures were observed for melt-blown PP fibers. Analysis of images showed that spherulite diameter versus fiber diameter for melt-blown and gravity-spun fibers are correlated, which is very useful for developing polymer processors. The intercept of this correlation line is related to the amount of amorphous material in the polymer, and the slope to the number of spherulites that can fit along the circumference of the fiber. For the melt-spun fibers, no spherulites were observed. Spherulites generally grow on nonmoving surfaces since the transfer of stress to the growing threadline leads instead to the also well-known shish kabob structure in this case, consistent with polymers crystallized under strain (93).

Thermoplastic Polyesters. The effect of substrate structure upon applied polymer layer morphology was well illustrated with a thermoplastic polyester. Poly(ethylene terephthalate) films were formed on the surface of oriented poly(tetrafluoroethylene) (PTFE) and on silicon surfaces. The PTFE surface was characterized by ridges 0.1–0.2 μm wide, running parallel to the PTFE draw direction. The silicon wafer showed regular, two-dimensional roughness features. When PET film was overlaid on these two surfaces, its morphology was surface-induced. PET applied directly to the silicon wafer exhibited random, two-dimensional roughness, whereas the PET applied

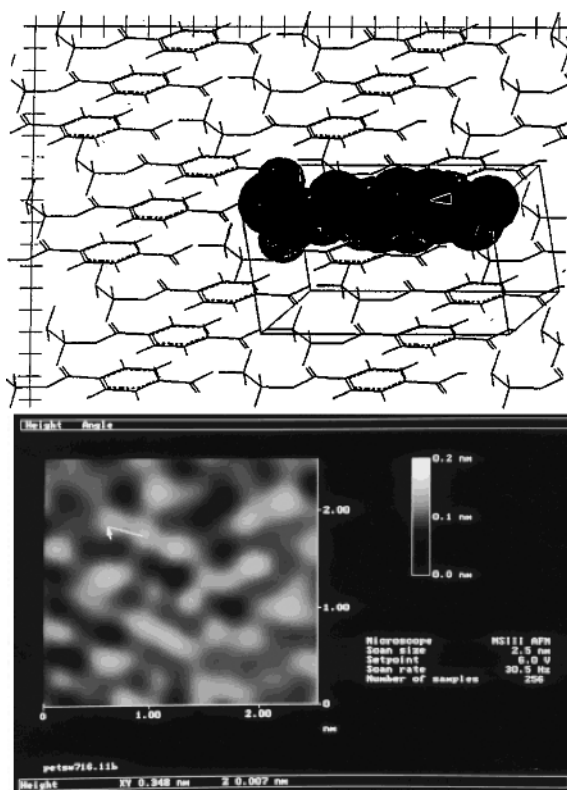


Fig. 14. Proposed atomic scale resolution in AFM of PET. From Ref. 95, Copyright © (1997). Reprinted by permission of John Wiley & Sons, Inc.

to the oriented PTFE surface aligned itself in parallel ribbons approximating the PTFE structure (94).

Specific chemical structures have been reported when near atomic scale resolution is obtained. When PET surfaces were imaged down to the nanometer scale, triads of roughly circular structures, 0.29 nm in diameter, corresponding to the expected size of terephthalate phenyl groups were observed (Fig. 14). The authors propose that the structures may indeed be terephthalate phenyl groups in the polymer (95).

Insights into the chemical properties of polyesters have also been obtained using AFM imaging as a tool. The diffusion/deposition of oligomers to the surface of PET copolyesters was demonstrated by imaging hard nodules on the polyester surfaces as a function of copolymer composition. The frequency of these hard nodules observed by AFM correlated with the levels of oligomer that could be solvent-extracted from the copolymers (96).

Other Thermoplastics. Polyoxymethylene (POM) was imaged by AFM, revealing oriented polymer chains parallel with the machine axis of sample extrusion (Fig. 15). Atomic scale resolution of the chains demonstrated the helical nature of the polymer chains. Long-range correlation between polymer chains was observed as well (97). Imaging of extended chain crystals of POM closely

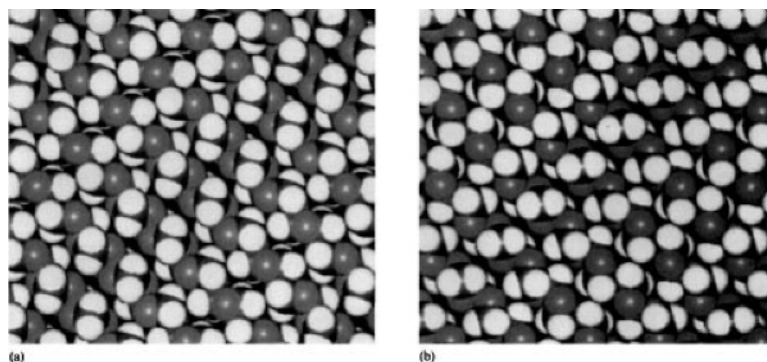


Fig. 15. Extended chain crystals of POM, showing polymer chain orientation with respect to the crystal. Reprinted from Ref. 98, Copyright (1994), with permission from Elsevier.

matched molecular models for this material, allowing for the molecular packing and order in the extended chain crystal to be well understood. The authors were able to describe the polymer chain orientations with respect to the crystal (98).

Poly(tetrafluoroethylene) was imaged after a mechanical deposition method. Parallel rows of approximately 0.5 nm spacing were resolved (99). The PTFE imaging demonstrated that because of its softness, the majority of observations with this material often are due to artifacts, rather than actual polymer structure. Operating in tapping mode, AFM images of PTFE revealed structures comparable to those obtained with SEM. The results of this work showed that PTFE is capable of supporting large forces on the millisecond time scale, but is subject to creep at longer time frames (100).

Ultrahigh molecular weight polyethylene (UHMWPE) tapes were imaged under water to minimize operating repulsive forces and contact area between probe and sample. Highly regular fibular structures were obtained. Periodic contrast variations along the stretching axis were found on drawn tapes only under stronger operation forces, suggestive that these variations are a function of surface hardness, rather than of surface topology (101). Gel-drawn UHMWPE films showed bundles of microfibrils between 4 and 7 μm in diameter, depending upon the elongation, microfibrils between 0.2 and 1.2 μm in diameter, depending upon draw ratios employed, nanofibrils which form the microfibrils, and regular chain patterns on the molecular scale which correspond to the crystalline packing of the polymer chains at the surface of the nanofibrils (102).

While normally amorphous, and generally featureless on a micron scale, crystallization of polycarbonate was solvent-induced with butyl acetate, generating a disc-like spherulitic structure of ca 10 μm in diameter surrounded by an amorphous matrix. Within the spherulite, the twisted fibrils emanating from the point of nucleation were observed in these AFM images, and is consistent with known lamellar growth mechanisms (103).

Liquid Crystalline Polymers. The high degree of stereoregularity associated with liquid crystalline polymer systems has been observed using AFM. Effects of method of sample preparation, of post-extrusion heat treatment of the

sample, and of interchain hydrogen bonding upon morphological structure have all been investigated. Lyotropic poly(*p*-phenylene terephthalamide) (PPTA) was dry-jet wet-spun from sulfuric acid into a coagulant bath, and imaged as spun, after heat treatment. The authors obtained atomic scale resolution of both forms of the fibers, observing changes in periodicity in the structures resulting from the heat treatment (104,105). Thermotropic liquid crystalline polyesters were imaged (Fig. 16), showing ribbon-like fibrils; atomic-scale details of the fibril surfaces were also obtained. In polymers capable of hydrogen bonding between chains, a greater degree of chain-to-chain cohesion, which the authors propose could result from some degree of self-assembly, was observed (106).

When macromolecular cholesteric liquid crystals were imaged, a twisting of molecular orientation, which translated into a periodic lamellar structure in the materials, was found. Good agreement between AFM and TEM (transmission electron microscopy) was obtained in determining the widths of the lamellae. When the same polymer was processed from an isotropic solution, a homogeneous and nodular structure, lacking the periodicity of the cholesteric structure, was obtained (107).

Hyperbranched Polymers and Dendrimers. The rapid growth of knowledge in the area of Hyperbranched Polymers and dendrimers has been aided by the direct observation of large-scale structure from AFM (see DENDRONIZED POLYMERS). Workers in this area have observed the nature of growth and distribution of polymeric branches as a function of both the chemical structure of the materials as well as that of surfaces on which the materials are grown. Further control of such structures, by introduction of additional, space-filling materials, has been observed by AFM, as has general structural features of these complex polymers. Hyperbranched polyacrylic acid (PAA) films were imaged and it was found that rms roughness declined as one progressed from zero to three dendrimer "generations," and then increased monotonically up through generation six when bonded to a rough gold substrate. When a smooth gold substrate was used, increasing roughness was observed starting with the first generation of hyperbranched PAA. The authors attributed this phenomenon to a sequential masking of roughness in the nonsmooth starting gold substrate through three generations. However, once a uniform surface smoothness is established, the dendrimer could then be randomly deposited on that surface, where subsequent layers would favor deposition at those sites which contain the highest chain ends to bond to, and hence, increasing roughness is developed. With the smooth substrate, the first generation would be deposited randomly, and each successive generation of hyperbranched polymer favors addition to those areas containing high concentrations of acidic polymer chain ends, thereby increasing roughness with each added generation (108). Polyimidoamine starburst dendrimers were similarly adsorbed on Au(111) surfaces. The relatively deformable fourth generation dendrimer, and the larger, more spherical and more rigid eighth generation dendrimer were tested. Directly adhered to the gold surface, the individual fourth generation dendrimers were shorter than those of the eighth generation material. Pretreating the gold surface with hexadecane thiol, which occupies surface space, led to growth of pillars of dendrimers on unoccupied surface sites, which could be imaged with AFM (109). Diaminobutane dendrimers bearing outer layers of ferrocene were imaged. Circular features were

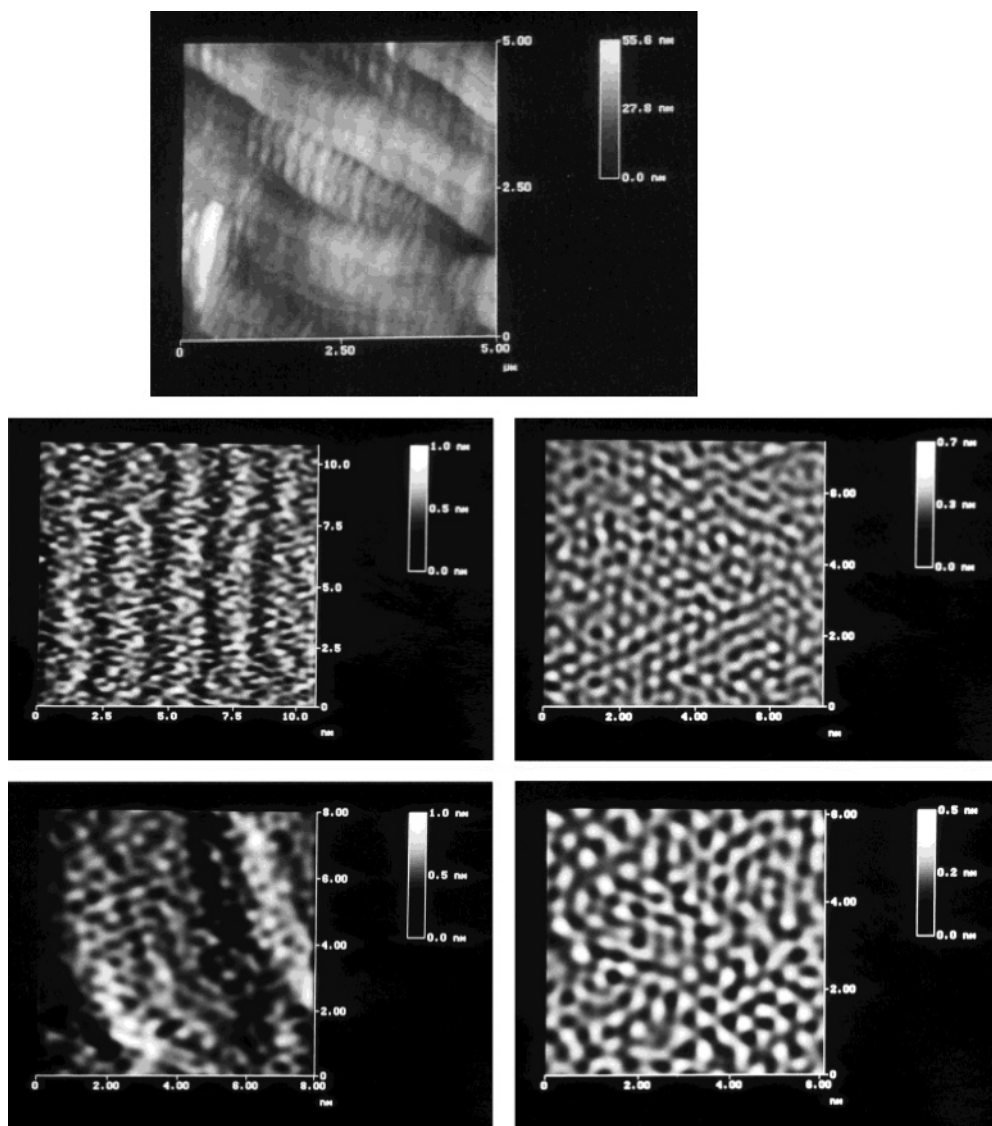


Fig. 16. An AFM of a thermotropic liquid crystalline polymer, showing details of fibrillar structure. From Ref. 106, Copyright © (1999). Reprinted by permission of John Wiley & Sons, Inc.

seen that are thought to correspond to individual dendrimer units (110). Dendronized PS was imaged with AFM, showing multilayer films made of densely packed nanorods. The cylindrical dendrimers were grouped in domains in which they are kept parallel to each other, with a periodicity of approximately 5 nm (88).

Filled Composites. Use of AFM in characterizing filled composite materials has ranged from determination of composite morphology as a function of fabrication method to examination of the morphological effects of the reinforcing

agent upon the matrix resin, and static and dynamic mechanical properties of the composites.

Poly(hydroxybenzoic acid)/copolyesterether elastomer microcomposites were imaged and it was shown that time and the solvent used to make the composite result in different morphologies. When solvents with high affinities for the elastomer were used, the resultant composite showed uniform dispersion of that material. With poor solvents, the elastomer was observed to aggregate into nonuniform aggregates (111).

Sheet molding compound thermoset materials were imaged by AFM; it was found that fiber reinforcement, as much as 1 μm under the surface, had an effect on surface morphology (112). AFM scratch tests conducted on carbon fiber-reinforced PEEK/PTFE blends demonstrated that reinforcing carbon fibers are harder and more scratch-resistant than graphite or the matrix resins (113). Styrene-butadiene rubber (SBR) vulcanizates containing carbon black were imaged under conditions of different levels of extension (0–700%). The authors found that filler particles tend to align in the force field into string-like arrays; surface cracks develop between these filler arrays, and may play an important role in crack propagation (114).

Microporous Membranes. Microporous membranes pose two separate opportunities for AFM to contribute structural knowledge of these materials. The technique is of course capable of describing the polymeric structures on scales ranging from micrometers down to tenths of nanometers, but is also able to describe the nature of the pores which modify the transport properties of membranes.

Nafion® perfluorinated sulfonic acid polymer was imaged, showing a nodular structure with 45-nm spherical domains, which in turn contained 11-nm spherical grains. Interstitial “pores” in the polymer were found to contain lower densities of polymer, but were not completely void. The authors showed that a nonuniform distribution of the grains, with wide and deep rifts, occur when the polymer is swelled with tributyl phosphate (115).

Polysulfone membranes were imaged and the microstructure and microporosity characterized. Through this work, it was determined that two different modes of phase separation existed during the formation of the membrane. Hence, the specific details of membrane processing were shown to influence morphology and final performance of the product (116). Linear and branched aromatic polyamide membranes were imaged by both AFM and field-emission SEM. The SEM work established molecular structure/morphological relationships, while the AFM was used to determine the surface roughness of the membranes. A strong correlation between molecular structure and roughness was determined, with meta-substituted molecules giving rougher, less regular structures. Correlations between this surface roughness and water permeability were determined as well, providing the authors with a molecular structure to polymer morphology to membrane performance working model (117).

Polymer Blends, IPNs, Latexes, and Block Copolymers. When two or more dissimilar materials are combined in the absence of covalent bonds, as is the case for polymer blends, interpenetrating polymer networks (IPNs) and latices, or through direct chemical bonds, as with block and Graft Copolymers, a number of important questions are raised that can be addressed by AFM. The

bulk morphology of these molecular combinations, as well as the specific chemical interactions within and between species, can provide important guidance for the design of improved materials. Variations in structural and mechanical properties of the blends and copolymer components, which result from the combining of materials or from some environmental force, which the materials are exposed to, again are important information for designers of such materials.

Blends. Blends of iPP with poly(styrene)-*block*-poly(ethylene-co-1-butene) were prepared under various conditions and imaged by AFM, where macrophase separation because of incompatibility of the components was observed (Fig. 17). The degree of phase segregation was shown to be dependent on the thermal history of the sample (118). Blends of iPP and different poly(ethylene-butene) (PEB) copolymers were imaged. The authors found that iPP and PEB containing 88% butene were miscible, and PEB containing <88% butene were partially to totally immiscible, and polybutene (100% butene) was partially miscible. So, there is a narrow window of miscibility for these blends (119).

Thin films of blended deuterated polystyrene (dPS) and poly(vinyl methyl ether) (PVME) were imaged as a function of the dPS:PVME ratio. Near the critical composition of 35% dPS, an undulating, spinodal-like structure was observed, whereas for compositions away from the critical mixture ratio, regular mounds or holes ($\phi_{\text{dPS}} < \phi_{\text{crit}}$ and $\phi_{\text{dPS}} > \phi_{\text{crit}}$, respectively) were present. These variations were assigned to surface tension effects (120). Blends of PBD, SBR, isobutylene-brominated *p*-methylstyrene, PP, PE, natural rubber, and isoprene–styrene–isoprene block rubbers were imaged (Fig. 18). Stiff, styrenic phases and rubbery core–shell phases were evident as the authors utilized force-modulated AFM to determine detailed microstructure of blends, including those with fillers such as carbon-black and silica (121).

Incompatible PS/PMMA/PVP [poly(2-vinyl pyridine)] blend films were imaged. Combining AFM and selective dissolution of the film surface, the compositional distribution of polymers was determined. The PMMA was observed to act as a compatibilizer for the more incompatible PS and PVP domains, preventing the formation of high energy interfaces. Molecular simulation for a ternary blend of polymers with distinctly different surface energies closely models the observed morphology (122). Tapping mode imaging of triblock PS–PE–PBD and iPP showed the boundary between the materials to act as a nucleating agent, where iPP lamellae grew primarily in a direction perpendicular to the interface (123). Blends of acrylonitrile–butadiene (AB) rubber and ethylene–propylene–diene (EPD) rubber were shown to be incompatible without and compatible with a compatibilizer, such as chlorinated PE. The change in phase morphology with added compatibilizer was shown clearly by AFM (124). Blends of conductive PA with plasticized cellulose acetate (CA) were imaged. The fibrillar structure of the PA in the amorphous CA matrix was evident and was correlated to electrical properties of the composite (125). Blends of poly(vinylidene difluoride) (PVDF) and PMMA or PVA were made and imaged, showing that different crystalline phases of the PVDF could be stabilized and therefore preferentially selected for use in blends with different amorphous polymers (126).

IPN. Interpenetrating networks of unsaturated polyester propylene glycol/maleic anhydride/phthalic anhydride (PG/MA/PAH) and polyurethane (PU) were imaged across a range of compositions. The AFM image of unsaturated

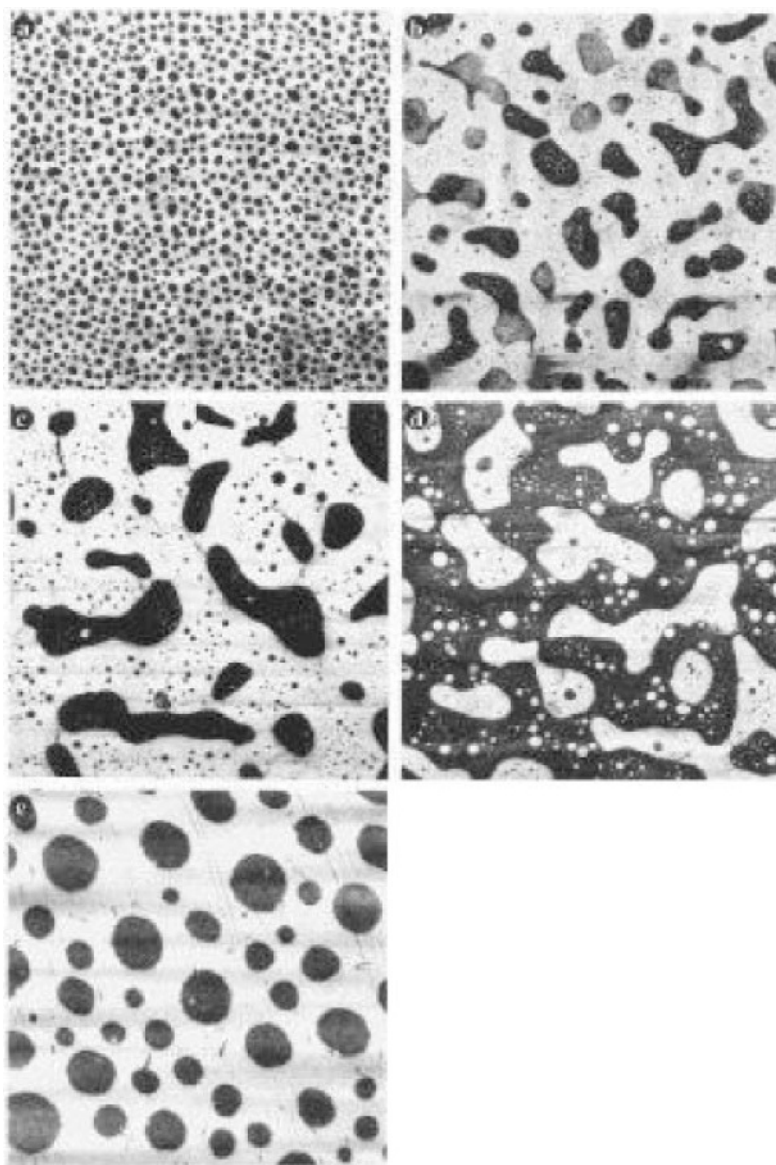


Fig. 17. Phase separation of incompatible blends of iPP and PEB, as a function of thermal history. Reprinted with permission from Ref. 118. Copyright (1998) American Chemical Society.

polyester was flat and featureless; however, with addition of 20% PU, phase separation of the polymers was observed. With increasing PU content, surface roughness and heterogeneity increased, whereas PU was preferentially dispersed on the surface of the matrix in clumps or circular plates of widely varying sizes (127).

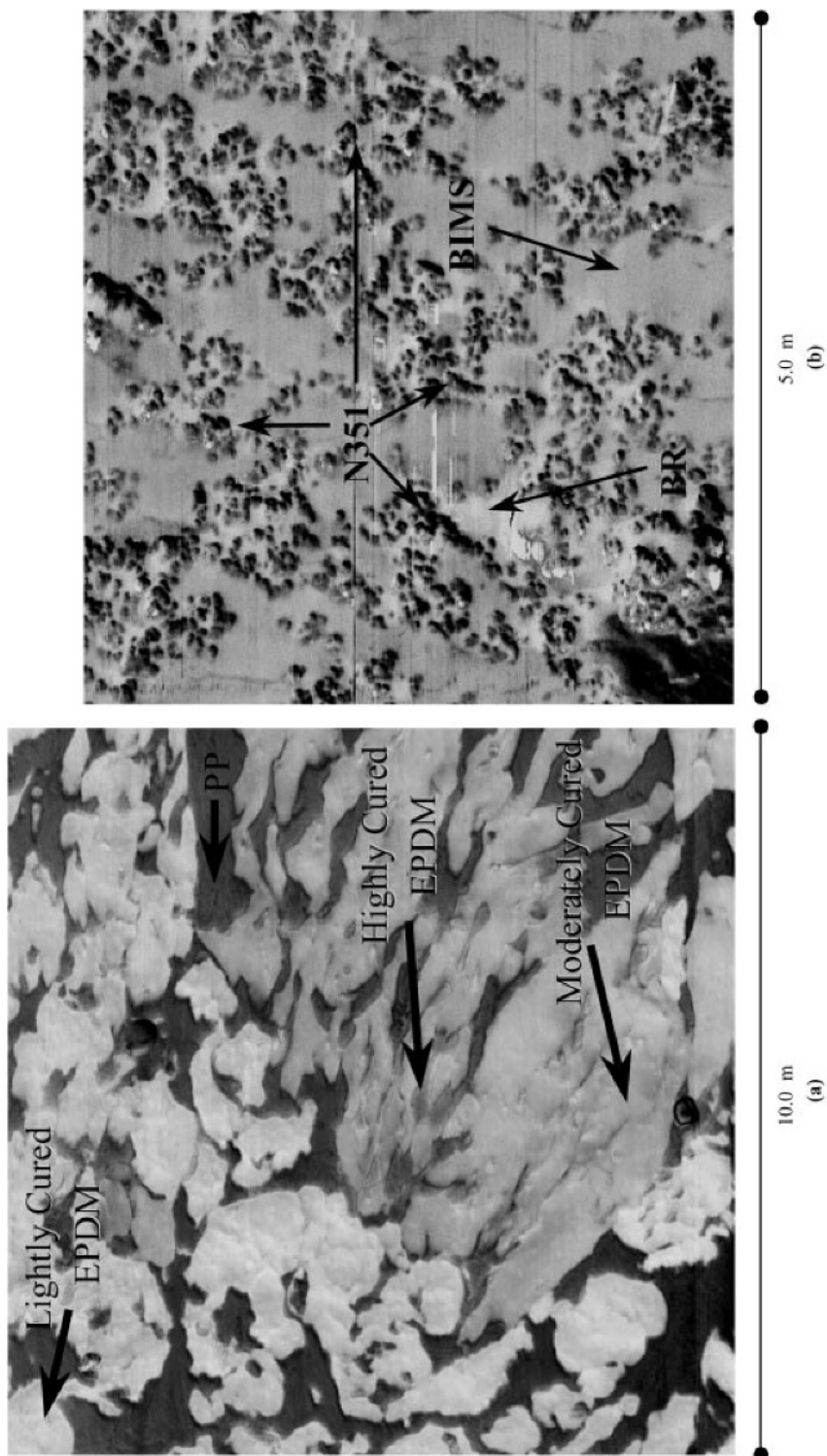


Fig. 18. Phases present in filled polymer blends. From Ref. 121, Copyright © 1997, John Wiley & Sons Limited. Reproduced with permission.

Latexes. Poly(butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) core/shell latex particles were imaged. Contact mode AFM was inappropriate because of excessive roughness and the associated artifacts typical to these types of experiments. However, in tapping mode, core/shells of varying compositions were imaged nicely. At 90/10 PBA/PMMA, the core is partially covered by PMMA and at 80/20, the PMMA microbeads are joined together into subparticles. At a 70/30 ratio, the subparticles merge into an intact shell (128). Tapping mode AFM of perfluorooctylethyl methacrylate/poly(butylmethacrylate) (PFMA/PBMA) latex blends showed that a film of PBMA was formed containing dispersed PFMA nanoparticles (65°C). Annealing to 100°C caused accumulation of PFMA at the surface of the film (129).

The morphology of rubber latex formation was followed as a function of time during the maturation of prevulcanization, and morphological features were shown to correlate with cross-link densities. Inhomogeneous latex particles cross-linked on the surface with uncross-linked cores were obtained during this process. It is proposed that these hard-shell/soft core structures coalesce to form the characteristic dimpled surface films (130).

Block Copolymers. The phase-separated diblock copolymer of PS-PMMA was imaged by AFM during annealing. Cylinders of PMMA were observed parallel to the plane of the sample film. The evolution of defects in the structure was followed as a function of annealing time, thus giving insights into mobility and structural changes (131). Phase-separated diblocks of polyparaphenylene-poly(methyl methacrylate) (PPP/PMMA) were imaged over a range of compositions. With increasing PPP concentrations, stripes or lamellae emerged within the images. The width of these stripes was interpreted to correspond to that of the PPP in the copolymer (132) (see BLOCK COPOLYMERS).

Triblock poly(styrene-*block*-ethylene/butylene-*block*-styrene) was imaged giving a repeating series of hills and valleys. The surface area fraction of the hills increased with PS content in the copolymer. The local stiffness of the hills was higher than that of the valleys, measured by force versus displacement curves generated with the AFM probe. The authors conclude that the hills are PS and the valleys are ethylene/butylene (133). Triblock PS-PBD-PMMA was imaged showing the PS/PMMA lamellae to be mainly oriented perpendicular to the observed surface. PBD-spheroids (approximately 14 nm in diameter) are separated at the lamellar PS/PMMA interfaces. The microstructure is explained on the basis of surface energies (88).

Random block copolyamide-ethers (hard-soft block elastomers) were imaged, showing that thicker films contain much larger crystals of the hard block segments than those obtained with thin films (30-nm films had crystals of approximately 7 nm × 50–100 nm; 20-μm films had crystals of about 12 nm × 200 nm). Further analysis also suggested that within the thicker films, more soft-segment is available at the surface compared to the thinner films (134).

Hybrid Organic-Inorganic Polymers. Hybrid organic-inorganic polymers, typically produced by sol-gel inorganic polymerization-derivatization of organic polymers, are materials currently under investigation for a wide range of industrial, consumer, and military applications. With regard to AFM imaging, such materials represent the combination of studies of organic polymer systems, and of inorganic polymers, most often for heterogeneous catalysts. For

these emerging hybrid materials, AFM has been shown to be able to discriminate between organic and inorganic phases, and to describe the boundary regions therein.

Nanophase-segregated morphologies of linear, sulfonated polystyrene–polyisobutylene–polystyrene triblock copolymers were demonstrated to act as templates for directing *in situ* sol–gel polymerizations of tetraethylorthosilicate (TEOS) around PS regions using domain-specific solvents and certain counterions. Suitable cations in conjunction with a solvent that swells only the PS domains allowed for hydrolyzed TEOS monomers to migrate to targeted ionic domains where sol–gel reactions occur. The morphology of these organic–inorganic hybrids consisted of rod-like, silicate-containing PS domains having inter-rod distances of tens of nanometers (Fig. 19). The rods were structured in essentially parallel arrays in micron-sized “grains” as is shown in the AFM image (135,136). Poly(methyl methacrylate)–silica hybrid materials, prepared by sol–gel chemistry, were imaged. Fracture surfaces of optically transparent hybrids were found to exhibit very low levels of roughness, suggesting that the organic and inorganic phases are not separated, whereas the translucent variants showed significant roughness (suggestive of phase separation) (137). Poly(tetramethylene oxide)–silica hybrid materials were also prepared by sol–gel chemistry. Semi-IPNs were then produced from these materials and poly(methacrylic acid). Imaging of these revealed microphase-separated polysilicate domains (138). Similar polysilicate domains have been observed with poly(vinyl pyrrolidone)–silica hybrids (139). Silicate glass fibers, used in the reinforcement of organic polymers, were imaged (1) without any treatment, (2) with organosilane coupling agent treatment only, and (3) with complete emulsion-based fiber-sizing complexes. The untreated fibers were relatively smooth. Addition of a coupling agent only resulted in a rougher surface because segments of the coupling agent were torn from the glass fiber when individual fibers were separated from one another. Treatment with the complete fiber-sizing emulsions result in largely homogeneous surfaces that were smoother than those of the starting glass fibers (140). Ladder-like polyvinylsiloxane polymers were imaged, with the highly regular, two-dimensional network structure clearly resolved by AFM. Three-dimensional nanotubular structures from these polymers, and supermolecular structures resulting from these nanotubes, were also imaged (141).

Gels. The relative softness of most gels exacerbates the problems associated with the use of a mechanical force-based probe in determining morphology and structure. Such structural details are often scarce, given the high functionality associated with many gels. Thus, both a technical challenge and a suitable reward are associated with the use of AFM with polymeric gels.

Poly(*N*-isopropylacrylamide) (PIPA) gels in water were imaged. The thickness of the gel-constrained sample geometry, cross-linking density, and osmotic pressure were all demonstrated to play a role in the observed structure. The surface microstructure, as well as the nanometer scale structure, was associated with the gel-phase transition, and there is potential, through this understanding, to control gel domain sizes. As cross-linking density was increased, the amplitude (in the AFM) due to sponge-like domains is less clear. The authors hypothesize that the cross-links create local imperfections in the swelled structure (142–144).

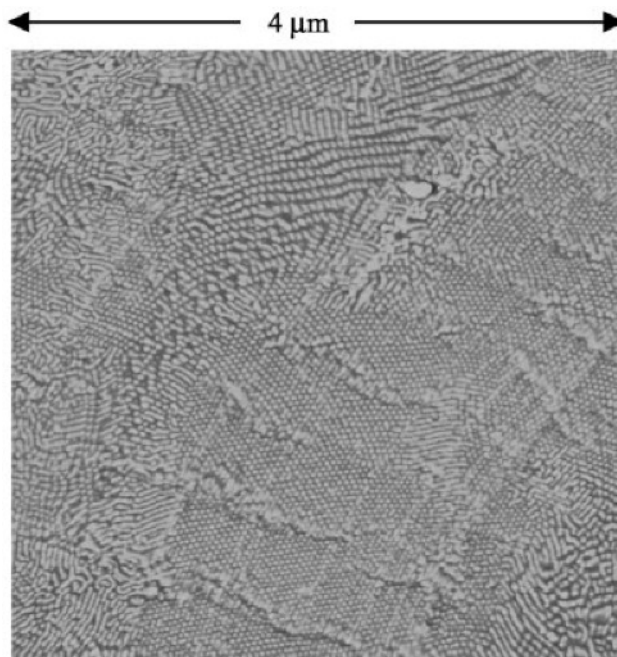


Fig. 19. Morphology of a hybrid silicate-PS molecular composite. From Ref. 135, courtesy of Prof. K. Mauritz.

Independently synthesized gel microspheres of PIPA were incorporated into PIPA matrix networks at the time of gelation. AFM imaging of these networks was used to visualize the microspheres, quantifying their degree of swelling as a function of temperature changes under constrained geometry. The authors found that this response was sensitive to the level of gel microspheres present in the macrogel; when a sufficient level of microspheres were present in the system, aggregation into three-dimensional domains of microspheres was observed (145).

Surface Characteristics

Roughness. Given that AFM is a surface topographical technique, it should not be surprising that this method can be used to quantify the roughness of polymer surfaces, giving insights into irregularities inherent in the polymer, or resultant from chemical or mechanical action on the polymer, or from heterogeneous additives.

Surface roughness of biaxially oriented PET magnetic tape with and without metal oxide particles exhibited features down to 1 nm, including some attributed to the manufacturing process (a degree of alignment of magnetic particles along the machine axis of the films that exceeds statistical behavior). Magnetic particles, $1\ \mu\text{m} \times 0.1\ \mu\text{m}$, were observed and the surface roughness was fitted to a fractal geometry. The starting PET film surface was shown to be relatively flat and featureless at this length scale. The features observed by AFM were not discernable by a noncontact optical profiler (146).

Surface roughness of PS and PS/PVME blend thin films before and after rubbing with velour cloth were measured and correlated with angle-dependent total-reflection x-ray fluorescence (TXRF). The TXRF failed to discern polymer surface changes because of rubbing, although it did characterize the underlying nickel substrate. On the other hand, AFM revealed anisotropic grooves and ridges for the rubbed PS film, and isotropic, sinusoidal roughness for the rubbed blend. The anisotropy of the blend was said to be typical of phase-separated blends. Similar rms roughness of 6.1 nm and peak to peak distances of 170 nm were observed for the rubbed samples (147).

Morphology and Polymer Orientation. Morphology of polymer systems can be indicated by surface AFM measurements. Of great interest in this area is the study of phase-segregated blends, blocks, and partially crystallized materials. Recently, the interpenetration of poly(butylenes succinate) lamella with the spherulites of the poly(vinylidene chloride-*co*-vinyl chloride) blend was determined by AFM (148). Significant morphological changes occur in diacetylene LB films upon the addition of polyallylamine to the subphase during LB deposition (149). This addition was shown to produce microfibrillar structures in the resultant film consisting of “fingerprint” like features. Morphologically interesting phase segregation of phthalocyaninato-polysiloxane with poly(isobutylvinyl ether) have been measured with contact mode AFM (150).

The morphology of polymer surfaces can also be influenced by electrostatics, rubbing and stretching of the materials. Polydiacetylene nanocrystals (151) and ferroelectric liquid crystalline elastomers (152,153) have been observed by AFM. The morphology of these thin films yield interesting photoreactive and photoreponsive behavior. These morphologies are also affected by the rubbing (154) or stretching (153) of the materials. Understanding of molecular alignment is critical for liquid crystal display technology using polymer networks as the active matrix.

Adhesion. As mentioned previously, the AFM force transducer can also be used to determine adhesion and frictional properties at surfaces. Because of the nature of AFM cantilever–polymer surface interactions, it is possible to modify the cantilever tip with chemical agents, and then quantitatively probe the adhesion of these agents to the polymeric material in question. Modified AFM tips were produced by attaching glass spheres to AFM cantilevers. To the glass spheres, sulfonated polysulfone was applied. The interactions between this sulfonated polysulfone and aminosilanes (which had been applied to silicon wafers) were measured using the AFM. Treatment of the aminosilane with boiling water, which destroys the silane network, was shown to significantly reduce silane–polymer adhesive forces (155). Similarly, the authors showed correlation between maximum adhesive forces and silanol and sulfonic acid groups as well as mechanical entanglements (156). Adhesion between glass and HDPE or LDPE (low density polyethylene) was measured using AFM. Grafting of chlorosilane-terminated PE onto the glass, to produce an amorphous interphase, was shown to enhance adhesion (157). Adhesion versus temperature was measured using AFM FCs for a surface of poly(*tert*-butyl acrylate) near its glass–rubber transition (158). By studying compliance and adhesion, these authors concluded that the activation energy for molecular relaxation was the same for bulk versus free surface measurements. This indicates that AFM surface

measurements are accurate and useful measures of molecular scale viscoelasticity, and that when the surface properties do differ from the bulk then the AFM can characterize these properties with near molecular spatial resolution. Moreover, when applied to ultrathin adsorbed polymer layers, the AFM can be used for “nanorheology” so as to understand molecular lubricants at this important length scale (159).

Friction. To measure the frictional characteristics of a surface, the AFM is used in contact mode, where the tip is “dragged” across the surface. The frictional force induced from the load of the tip, torques the cantilever. Higher frictional forces result in higher lateral deflection of the optical lever; these relative changes in deflection can be interpreted as changes in the coefficient of friction, μ , of the sample. In contrast to bulk measurements, AFM studies of friction often contradict Amonton’s “law” whereas the coefficient of friction does depend on load. This is especially true for polymer systems that exhibit significant viscous flow under load such as Hydrogels. Various hydrogels were studied by AFM and μ did depend on load and also correlated with measured adhesive forces indicating a molecular chain attachment and entanglement model (160).

Friction, and more significantly wear, is an exceedingly important parameter for developing advanced polymer materials that must withstand sliding contact operations. Mechanisms of friction involve intermolecular forces, molecular adhesion, subnanometer topography of the sliding contact surfaces, and the elastic and yield moduli of the near-surface region. While studying the friction and adhesion of various polymer bearings (PS, polyacetal, Tarnamid T-27, etc) against a glass-fiber loaded, polyamide composite shaft, the resultant nanometer scale AFM topography was correlated with μ (161). The high spatial resolution topographs of these worn polymer surfaces enabled a far more accurate computational model of the wear process.

Often, new materials are developed from composites, or mixed polymer systems. Since friction has been shown to be a molecularly driven mechanism, a simple weighted average of the material’s constituents will not yield accurate predictions of measured tribological properties. The AFM as a frictional transducer has resolved the submicrometer domains of PS/PMMA blends (162). To accentuate the sensitivity of the AFM probe to very small differences in surface energy and μ , the AFM tip can be functionalized. Hydroxylated tips are far better at discerning these surface changes when contrasting polar versus nonpolar blend components (163).

Modifications. As a method capable of describing both gross polymer features and placement of individual molecules (and small groups of atoms), AFM has been shown to be an important probe in relating chemical and morphological structures. At these varying levels of magnification, AFM has been demonstrated to be able to discern changes in polymers, which result from chemical modification of the starting monomer material.

A series of polymers, including HDPE, PET, PTFE, PI (polyimide), and XPA (cross-linked polyaniline) were imaged before and after Argon plasma or ozone treatment and acrylamide grafting. The basic surface features of the untreated substrates were retained after grafting. In each case, the rms roughness of the surfaces was reduced, as shown in Table 2, because the acrylamide grafts covered surface features (such coverage is similar to that described for monolayer

Table 2. RMS Roughness of Polymers Before/After Acrylamide Grafting

Polymer	Rms roughness, nm Unmodified surface	Acrylamide grafted
HDPE	308	290
PET	17	15
PTFE	165	120
PI	52	44
XPA	10	6.3

coverage of hyperbranched polymers on inorganic surfaces). A broadening of lamellar distances was also observed upon grafting, suggesting that the grafted groups push between the existing lamellae (164).

Corona treatment of iPP (both oriented and biaxially oriented) led to the generation of spherical-shaped features on the sample surface. The size of these features was correlated to the corona dose level, as were the degree of surface oxidation, and the loss of molecular weight. Peel strength also correlated with the surface morphology (165). Poly(vinyl chloride) was oxidized using both air plasma and corona discharge. Significant differences in the surface morphologies of these two oxidized materials were imaged, with the air plasma producing smaller, regular surface nodules, and the corona producing a lower number of much larger features. The authors postulate that the plasma was more effective at removing plasticizer and other additives present in PVC, whereas the corona-generated features were the result of radical chain scissions and subsequent cross-linking of the oxidized polymer chains (166). Cross-linked, unsaturated polyester resins were treated with CF_4 under plasma conditions to produce a fluorinated surface exhibiting a greater moisture barrier than the unmodified resin. Changes in the surface were imaged, showing changes from a rough to a nodular surface upon treatment (167). LDPE and HDPE were also treated with CF_4 under plasma conditions. The degree of surface modification was found to decrease with the crystallinity level of the polymers. The lamellar surface of LDPE was converted into a uniform, nanoporous structure; this change was not observed on the HDPE. In neither case did the modification have any effect beyond the surface region (168). Polyethylene was plasma-treated in the presence of allyl alcohol, to give a hydroxylated surface, followed by silation. AFM shows that the silitated surfaces are similar to one another and consist of much higher levels of graininess than with the allyl alcohol or argon plasma treatments alone. Image analysis suggested to the authors that the silane coverage might be greater than a monolayer (169).

The effectiveness of different wavelengths of light at producing the photochemical cross-linking of poly(ethynyl)carbosilane fibers was probed using AFM. As the light frequency was changed, the depth of photochemical products also changed. Using broadband $\lambda > 300$ nm, photochemical products were observed to a depth of 100 nm, or about 125 molecular layers. When $\lambda = 254$ nm light was used, penetration of the photochemistry to 115 nm (130 layers) was observed. This level of detail is not readily obtained using techniques such as nmr or x-ray structural analysis (170).

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AUTOMOTIVE PLASTICS AND COMPOSITES

Introduction

Plastics play a fundamental role in the construction and comfort of modern automotive vehicles. Because of their low cost, ease in design flexibility, chemical resistance, as well as appearance, plastics usage has increased in the automotive industry. Most commonly used automotive plastics include polyolefin resins (polypropylene, polyethylene), unsaturated polyesters, and polyurethanes. By definition, plastics or polymers are high molecular weight organic compounds that consist of repeated linked units. These occur naturally or are synthesized through polymerization and can be formed into a variety of shapes including solid bodies, foams, films, or filaments for carpet or textiles, among others.

Global Trends. The use and selection of automotive plastics is influenced by global trends in material costs, fuel economy targets, and environmental factors. Price fluctuations in the petroleum market including natural gas and crude oil have had a direct impact on raw material costs for polymers. For example, natural gas is a key source for ethylene and propylene oxide, which are used in the production of polyolefins and polyurethane products. These swings in raw material pricing have an effect on manufacturing these polymers, and the resulting material choices for automotive components.

Demands for improved fuel economy and reduced environmental footprint also have a significant impact on the plastics industry. Historical U.S. trends of adjusted fuel economy and adjusted CO₂ emissions for light-duty vehicles, with gross weight ratings up to 8500 lb, are outlined in Figure 1. These data were presented by the Environmental Protection Agency (EPA) in their report on “Light-Duty Automotive Technology, Carbon Dioxide Emissions, and Fuel Economy Trends: 1975 through 2010” (1).

According to the EPA, CO₂ emissions and fuel economy are at the most favorable levels since 1975. For 2009 model year vehicles, the EPA projected that fuel economy was 22.4 miles per gallon (mpg) and CO₂ emissions were 397 g/mi. These values were reportedly 15% better than values calculated for 2004 comparable vehicles. The economic recession in 2009 contributed to the low vehicle production of only 9.2 million units, the lowest since the database began in 1975. The EPA has also asserted that with the exception of one vehicle manufacturer, the 14 highest selling vehicle producers improved fuel economy from 2008 model year to 2009 model year vehicles. In 2010, the EPA and National Highway Traffic Safety Administration (NHTSA) disclosed standards for light-duty greenhouse gas emissions, as part of the National Program for corporate average fuel economy (CAFE) standards. The projected targets in 2016 for fuel economy and carbon dioxide emissions of light-duty vehicles are 250 g/mi and equivalent of 35.5 mpg, respectively (1).

Factors such as engine efficiency, vehicle weight, driving conditions, and aerodynamic drag play a critical role on the overall fuel economy of a vehicle. One strategy to reduce fuel economy is reducing vehicle weights by size reduction and selection of lightweight materials, including plastics and composites. With increased targets for CAFE standards, plastic components provide a cost-effective

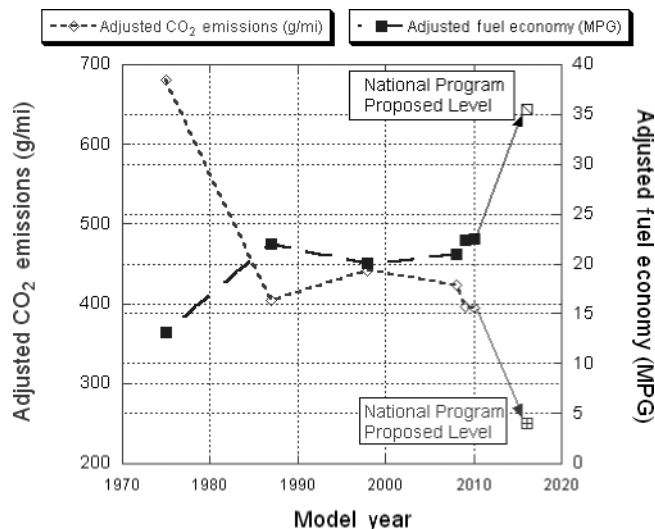


Fig. 1. Fuel economy and carbon dioxide emissions of light duty vehicles (1).

method to manufacture lightweight parts. According to the U.S. Department of Energy, research has shown a rough correlation between vehicle weight and fuel economy for approximately 100 lb in vehicle weight to a 2% change in the fuel economy. This translates to approximately 1-mpg improvement for a weight reduction of 200 lb (2).

In Europe, legislation adopted in 2000 dictates targets for reuse, recovery, and recycling of automotive components and materials. The End-of Life Vehicle (ELV) Directive dictates minimum targets for reuse and recovery as well as reuse and recycling. For vehicles produced prior to 1980, targets for reuse and recovery were set at a minimum of 75% by vehicle weight, and for reuse and recycling to 70%. By 2006, vehicles were to meet targets of 85% and 80% for reuse/recovery and reuse/recycling, respectively. No later than 2015, the minimum required targets have been set to 95% and 85%, respectively. This directive impacts the choice of materials for European vehicles and is anticipated to influence materials selections globally (3).

Usage.

Industry Volumes. Table 1 provides an annual breakdown of materials used in North American light vehicles for a decade ending in 2008, based upon data provided by the American Chemistry Council's report on "Changing Customer Dynamics: Chemistry and Light Vehicles" (4). Regular, high and medium strength steels are the main contributors to vehicle weight by material category, followed by plastics/composites, iron castings, and aluminum.

By the late 2000s, passenger vehicles contained an average of 332 lb of plastics and composites, accounting for more than 8% of the vehicle by weight (5). During the decade from 1998 to 2008, plastics/composites usage increased from 278 to 343 pounds per vehicle and rubber usage increased from 166 to 185 pounds per vehicle. Regular stainless steel has shown a drop in usage by 40 pounds per vehicle, most likely due to the increased applications for high and medium strength

Table 1. Annual Breakdown of Materials Content in North American Light Vehicles (pounds per/vehicle)^a

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Total Vehicle Weight (lb)	3867	3861	3918	3921	3939	3969	4045	4040	4069	4093	4070
Regular steel	1669	1662	1655	1652	1649	1646	1650	1634	1622	1644	1629
High and medium strength steel	378	390	408	424	443	460	479	491	502	518	523
Stainless steel	59	60	62	63	64	65	70	71	73	75	75
Other steels	40	30	26	28	30	32	34	35	34	34	34
Iron castings	438	436	432	384	355	336	331	328	331	322	301
Aluminum	245	257	268	286	294	303	315	316	323	317	315
Magnesium	7	7	8	10	9	10	10	10	10	10	11
Copper and brass	70	69	68	66	69	70	71	71	67	66	64
Lead	35	35	36	37	35	35	37	38	39	41	45
Zinc castings	17	14	13	11	10	10	10	10	10	9	10
Powder Metal	33	35	36	38	39	41	43	42	42	43	43
Other metals	4	4	4	4	4	4	5	4	5	5	5
Plastics/composites	278	265	286	298	307	319	338	334	341	331	343
Rubber	166	159	166	163	167	169	172	179	188	190	185
Coatings	26	24	25	26	26	25	28	27	29	29	28
Textiles	43	42	44	45	45	46	51	49	47	46	48
Fluids and lubricants	201	204	207	208	209	210	210	210	211	215	214
Glass	99	101	103	104	104	105	105	104	105	106	106
Other	58	66	71	75	79	83	86	87	89	92	91

^aRef. 1.

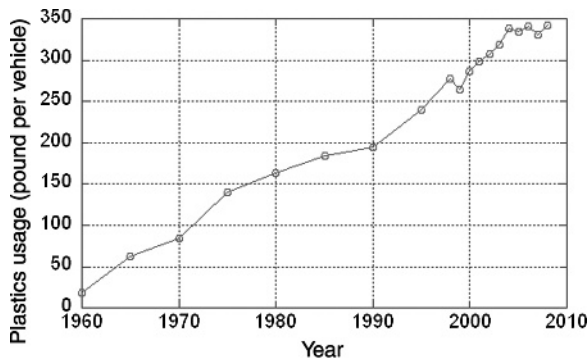


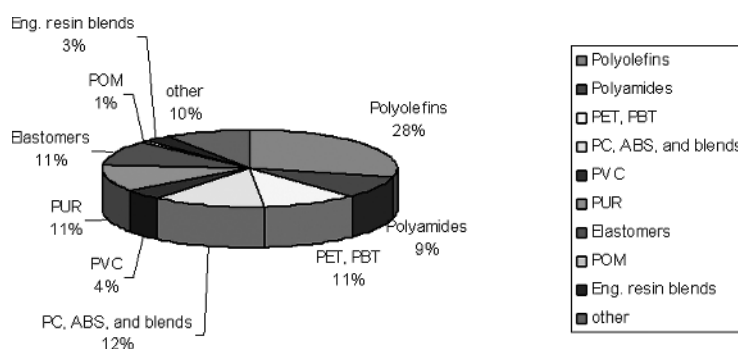
Fig. 2. Total plastics usage per North American vehicle from 1998 to 2008 (1).

steel. Figure 2 provides an overview of total plastics usage in a North American light vehicle per year from 1998 to 2008. With a few limited exceptions, plastics and composites usage has gradually increased year over year during this decade.

Many different types of plastic resins contribute to the approximate 350 pounds per vehicle. Table 2 provides a summary of usage of the main classes of plastic resins used on North American light vehicles from 1998 to 2008.

Table 2. Usage of Plastic Resins in North American Light Vehicles (pounds per vehicle)^a

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Total Plastics Resin	278	265	286	298	307	319	338	334	341	331	343
Polypropylene	59	51	62	66	72	78	79	77	81	80	83
Polyurethanes	56	52	54	58	57	60	64	64	59	56	56
Nylon	33	35	38	37	38	39	43	42	41	35	34
ABS	20	20	20	22	26	25	26	25	23	22	24
Polyvinyl chloride	22	22	22	23	23	23	25	23	27	28	29
Polyethylene	13	12	11	13	12	12	14	13	14	15	17
Polycarbonate	12	11	12	12	11	12	14	14	15	15	18
Other engineering resins	30	29	31	33	33	36	38	38	42	42	43
Polyvinyl butyral	6	5	6	6	6	6	7	7	7	7	7
Other	27	26	30	29	27	28	30	30	31	30	33

^aRef. 1.**Fig. 3.** Breakdown of plastic types in a typical mid-size Ford vehicle in 2010. *Not including tires.

For North American light vehicles produced in 2008, the primary polymeric resins were polypropylene, engineering resins (including PC, ABS, and their blends), polyurethanes, and polyamides. By 2010, overall plastics and composites usage for an average midsize North American vehicle showed a growth to approximately 400 lb (5). Figure 3 provides a breakdown of the key plastic types for this segment in 2010. Polyolefins remained one of the primary resins used in the car. However, the decrease in the use of polyurethanes, for example, emphasizes the trend to reduce weight by making seats thinner and more streamlined.

Vehicle Systems. Plastics and elastomers are used in virtually all areas of automobiles. Figure 4 provides an overview of primary automotive subsystems that utilize polymeric materials: interiors, exteriors, seating, underhood/underbody, and tires. Throughout the interior, polymeric materials comprise applications such as instrument panels, door trim, pillars, and steering wheels. For exterior components, plastic resins are used to mold headlamps, mirror casings, bumpers, fascias, weatherstrips and grill-opening reinforcements. Underhood and underbody applications include power train and chassis components such as air intake manifolds, covers, and a variety of shields. In seating



Fig. 4. Overview of Automotive systems using plastics and composites (courtesy of John Jaranson, Ford Motor Company).

subsystems, polymers are used in applications from fabrics to foams to substructure, among others. Tires are multilayered in construction, including materials such as nylon fabrics and elastomer blends.

Because of the complexity of vehicle construction and integration, numerous types of plastics, elastomers, and composites are used and can be tailored to the specific requirements of each subsystem's application. For more details on specific material choices and applications, see the Design Considerations and Material Types sections.

Resin Costs. Plastic resin costs vary tremendously based upon the type of plastic, processing grade, and whether the resin is neat or filled with talc or glass fibers. Pricing can vary year to year and regionally based upon the current economic conditions. Table 3 provides a directional overview of resin costs for select polymers, based upon truckload quantities (unless indicated otherwise) from data provided by Plastics Technologies (6). The table is organized from low cost, commodity resins to premium cost resins. The polyolefins (PE, PP) are relatively low cost compared to more specialty polymers such as fluoropolymers and polysulfone. While this table provides general direction for pricing, exact costs will vary based upon quantities and pricing index for the period of time.

Design Considerations. Plastics and composites are often selected as a replacement for metal components to reduce weight, provide more freedom in design, and minimize corrosion and durability issues. There are several design considerations that need to be addressed during the evaluation of polymers for different applications. Some plastics and composites exhibit anisotropy, in which their properties such as tensile strength and modulus will vary in the transverse direction. Variations in properties need to be considered during part design and molding processes. Another key consideration is the coefficient of linear thermal expansion (CLTE) of the polymers. Since automotive parts may experience temperature changes of 80° or more during operation and can experience even larger variations during manufacture, part fit and finish requires adjustments to thermal growth and shrinkage of the components. This factor becomes especially

Table 3. Directional Price Comparison for Automotive Plastics and Composites

Resin	Resin Abbreviation
Polystyrene* (G-P crystal)	PS
High density polyethylene ^a (injection molding)	HDPE
High density polyethylene ^a (blow molding)	HDPE
Thermoplastic elastomers (olefinic)	TPE
Phenolic-molding compound	MC
Low density polyethylene ^a (injection molding)	LDPE
Polypropylene ^a (injection molding)	PP
Low density polyethylene ^a (blow molding)	LDPE
Acrylonitrile butadiene styrene (medium impact)	ABS
Acrylonitrile copolymer (injection molding)	SAN
Polyester polybutylene terephthalate (unfilled)	PBT
Nylon (type 6)	PA6
Polycarbonate (extrusion)	PC
Nylon (type 66)	PA66
Polycarbonate (injection molding)	PC
Acrylonitrile butadiene styrene/polycarbonate alloy	ABS/PC
Phenolic-molding compound (reinforced grade)	MC
Polyurethane (ester type)	TP
Polyester thermoset (bisphenol A)	MC
Thermoplastic elastomers (polyester)	TPE
Vinyl ester (heat and corrosion resistant)	VE-MC
Polyurethane (ether type)	TP
Polyethersulfone	PES
Silicones (molding compounds)	SI
Polysulfone	PSU
Fluoropolymer (polytetrafluoroethylene)	PTFE
Polyetherketone	PEK
Polyether ether ketone	PEEK

^aindicates rail car quantity.

critical when plastic parts mate to metal surfaces. Furthermore, once a tool is produced, manufacturers are limited in material choice due to differences in material shrink rates.

Material Selection. Material selection for automotive applications requires understanding of component functionality and requirements as well as material properties and performance. Certain considerations may include: resin type, such as thermoplastic versus thermosetting resin; material type, such as molded composite, foam and textile; and processing methods (7–10). Details on the types of materials and polymer chemistry can be found in the Material Types section. Processing considerations are discussed in the next section.

Processing Considerations. The choice of material and processing method can be dictated by production volumes based on cost and logistics. Manufacturers need to balance associated costs of tooling, cycle time, design, and maintenance. For example, injection molding may provide a fast cycle time and more complex design freedom than compression molding, but has a higher cost for tooling at low volumes. Likewise, SMC (sheet molding compound) provides more design

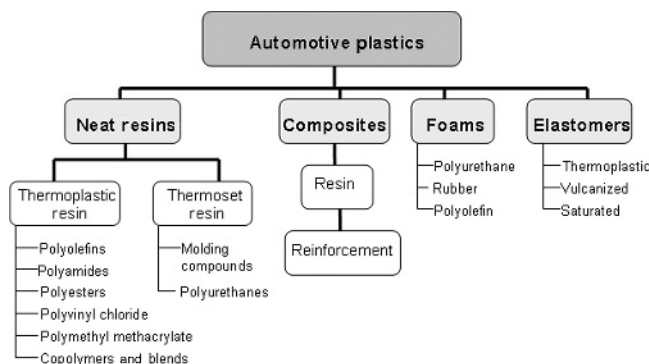


Fig. 5. Overview of types of automotive polymers.

flexibility than stamped metal parts used in applications such as hoods and closures for low volumes, but is limited by cycle time for high volume production.

Material Types

Plastics or polymeric materials are used in many forms including homogeneous polymers, blends of resins, reinforced composites, and formulated resins. In many cases, these polymers are combined with other chemicals or compounds such as impact modifiers, additives, plasticizers, oils, and fillers to improve the properties of the material for a desired application. Figure 5 provides a high level overview of common automotive plastics: neat resins, composites, foams, and elastomers. Each of these topics will be discussed in detail in this section.

Thermoplastics. Thermoplastics are used widely in a variety of automotive applications due to their versatility in design, processing, and recycling (11),(12). Table 4 shows the many different types of thermoplastic materials commonly used in automotive applications, their chemical structures, typical applications, and some key characteristics that dictate material selection.

Polyolefins. Polyolefins, also known as polyalkenes, are thermoplastics that are polymerized from olefin or alkane monomers. Polyolefins comprise two of the most commonly used plastics, polypropylene and polyethylene. Polypropylene is the most used thermoplastic in automotive, with a portfolio of applications ranging from unreinforced interior trim and storage bins to talc-reinforced exterior bumper fascia to underhood fiberglass reinforced battery trays. These polypropylene materials can also be modified for impact by adding a rubbery phase, making it a so-called thermoplastic olefin, or TPO. TPOs are used in bumper fascias and interior trim where impact performance is needed. TPOs can also be used for soft flexible skins on instrument panels and other trim.

Polyethylene (PE) also has a wide range of uses including trim and ductwork, blow-molded fluid reservoirs, and one of the materials in multilayered fuel tanks. PE can be used in its neat, unreinforced state or can be reinforced with minerals or fibers. Other uses of PE include wire coatings, films, and bags.

Table 4. Automotive Thermoplastics and Their Applications

Material	Structure	Applications	Characteristics
Polyolefins			
Polypropylene (PP) 	$\left[\begin{array}{c} \text{H} & \text{H} \\ & \\ -\text{C}- & \text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	Interior trim, battery trays, semi-structural interior components	Chemical resistance, versatile, semi-crystalline
Thermoplastic olefin (TPO)		Bumper fascia, interior trim	Similar to PP but with improved impact performance
High density polyethylene (HDPE) 	$\left[\begin{array}{c} \text{H} & \text{H} \\ & \\ -\text{C}- & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$	HVAC ducts, fluid reservoirs, fuel tanks	Chemical resistance, versatile, low cost, semi-crystalline
Low density polyethylene (LDPE) 		Films, bags	Semi-crystalline to amorphous
Nylon (PA)			
Nylon 6 (PA6)	$\left[\begin{array}{c} \text{H} & \text{O} \\ & \\ -\text{N}-(\text{CH}_2)_5-\text{C}- \end{array} \right]_n$	Engine cover, handles, fans and shrouds	Upper use temperature suitable underhood, fibers for textiles, semi-crystalline

Table 4. (Continued)

Material	Structure	Copolymers and blends	Applications	Characteristics
ABS (acrylonitrile butadiene styrene copolymer) PC/ABS	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{C}\equiv\text{N} \end{array} \right]_m \left[\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}=\text{C}-\text{C} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \right]_n \left[\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right]_o$		Chromed trim, interior substrates Face plates	Good impact, can be painted or chromed, amorphous Can be painted or chromed, good impact
SMA (styrene maleic anhydride)	$\left[\begin{array}{c} \text{O}=\text{C} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n \left[\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right]_m$		Instrument panel substrate	Low cost, high stiffness
Polyvinyl chloride (PVC) 	$\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right]_n$	Other	Vinyl trim for leather	Leather replacement
PMMA (polymethylmethacrylate)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{C}=\text{O} \\ \quad \\ \quad \text{O} \\ \quad \\ \quad \text{CH}_3 \end{array} \right]_n$		Glazings, lenses	Clear, amorphous

Polyolefins can be processed by many different methods, including injection molding, extrusion, blowmolding, thermoforming, rotomolding, and slush molding, among others. Injection molding, extrusion and blowmolding require melt processing of the materials, resulting in higher heat histories. Thermoforming, rotomolding, and slush molding, on the other hand, have reduced heat histories but are also limited in design geometries. These and other processing methods are discussed in more detail in the Processing section.

Modulus values of polypropylene (PP) homopolymers can range from 800 to 1100 MPa, depending on the molecular weight and degree of crystallinity, as well as the presence of additives and modifiers. The continuous upper use temperature of PP is approximately 90°C. Reinforced grades can increase the modulus as high as 2500 MPa and the upper use temperature to 110°C. Polyethylenes have moduli in the range of 200–400 MPa for LDPE, 300–750 MPa for LLDPE, and 600–1400 MPa for HDPE. Like PP, the modulus is a function of molecular weight, crystalline content, and additives. Upper use temperatures are lower than PP at approximately 75°C.

Polyamides. Polyamides, commonly known as nylons, are engineering thermoplastics that are used for applications requiring more functional and high heat performance. Most polyamides are semicrystalline materials. Nylon 6 (PA6) is commonly used in both injection-molding applications, as well as fibers for carpeting and textiles. Nylon 6,6 (PA66) has higher stiffness, strength, and heat stability and is often used in underhood applications. Nylon 4,6 (PA46) has the highest temperature resistance of the polyamides as well as good mar and wear resistance, so is often used in gear applications. Because of their excellent chemical resistance and moisture resistance, nylon 11 (PA11) and nylon 12 (PA12) are used in fuel system applications such as fuel lines.

The majority of automotive applications in polyamides are processed by injection molding for rigid parts and by fiber spinning for textiles. Fuel lines are typically extruded. Because they are hygroscopic, drying of polyamide resins is generally recommended prior to processing. Furthermore, because of the relatively high equilibrium moisture content for some of the grades, mechanical properties are often reported from both dry-as-molded (DAM) and conditioned specimens.

Modulus values can vary quite a bit, depending on type of polyamide, filler/reinforcement type and loading, as well as crystalline content. Unreinforced PA6 and PA66 resins have modulus values ranging from 1700 to 2500 MPa, whereas 30% glass fiber reinforced grades can boost the modulus up to approximately 9500 MPa. Continuous upper use temperatures range from 150 to 170°C. While PA66 has higher HDT (heat deflection temperature) and lower moisture absorption than PA6, the latter has better long-term high temperature stability. Both PA6 and PA66 are subject to significant moisture absorption, so the properties reported here are for DAM materials.

Polyesters. There are several types of polyesters ranging from general purpose to engineering plastics. The most common of the types are detailed below:

Polyethylene Terephthalate. The most widely used polyester is polyethylene terephthalate (PET). The largest use of PET is fibers for carpeting applications, followed by water and soda bottles. It is the most recycled postconsumer plastic. PET can be processed by fiber spinning, injection molding, sheet extrusion, and

blow molding. In the automotive industry, PET is most commonly used for textiles such as seat coverings, floor mats, and carpeting, as well as films for labels. A limited number of injection-molded trim applications also exist.

PET has modulus values in the range of 2500–3100 MPa and an upper use temperature of 70–100°C.

Polybutylene Terephthalate. Polybutylene terephthalate (PBT) is an engineering thermoplastic with excellent mechanical and thermal properties, chemical resistance, and good dimensional stability. Its low moisture absorption is a benefit when compared to polyamides for engineering applications. PBT resins and blends are primarily processed by injection molding or extrusion. Automotive uses include housings and brackets, as well as underhood applications. PBT is often blended with other resins such as PC to give a balance of properties. PBT is chosen over PET for high temperature and underhood applications. PBT resins are also available in platable grades for metallic appearance in automotive applications.

Unreinforced and glass fiber reinforced properties of PBT grades can range in modulus from 2700 to 10,00 MPa with upper use temperatures of 130–150°C.

Polycarbonate. Polycarbonate (PC) is an amorphous thermoplastic with excellent optical clarity and excellent toughness. The most common form of this polyester is that formed through a condensation polymerization with bisphenol A and carbonyl chloride. Its automotive use is primarily in lenses and glazings. It is often used in blends with other thermoplastics such as ABS and PBT. These blends offer a balance of properties including low temperature toughness and improved chemical resistance.

PC resins and blends are primarily injection molded for automotive applications. However, they can also be processed by extrusion, blow molding, and structural foam molding. In applications taking advantage of the optical clarity, injection molding is used with special attention to mold surface.

The Young's modulus of PC is in the range of 2200–2500 MPa. PC has an upper use temperature of approximately 125°C.

Polyvinyl Chloride. Polyvinyl chloride (PVC) is a very durable resin that can be used in a wide variety of applications. Many applications exist in the building industry for pipes and connectors, as well as flexible applications for leather substitute. In the automotive industry, PVC finds common use as a leather substitute for instrument panel skin and various trim applications. The predominant process for producing PVC skins is by slush molding. Rigid-molded PVC is processed by injection molding. The modulus of PVC can vary tremendously depending on addition of impact modifiers and/or plasticizers. PVC's upper use temperature is approximately 60°C.

Polymethyl Methacrylate. Polymethyl methacrylate (PMMA), also known by the trade name of Plexiglas, is an amorphous, clear resin that is commonly used in interior lighting applications and lenses. A more economical alternative to PC, it does not have as high optical clarity or toughness. PMMA has a modulus of approximately 2900 MPa and an upper use temperature of 60–80°C.

Copolymers and Blends.

ABS. ABS is acrylonitrile butadiene styrene copolymer. It has an excellent balance of properties, including impact strength, stiffness, and thermal stability. It consists of a two-phase blend, a continuous styrene–acrylonitrile phase for

Table 5. Physical Properties of Molding Compounds

Property	Vinyl Ester SMC	Unsaturated Polyester SMC	Polyester Resin BMC	Phenolic Fiber Reinforced MC
Glass content, %	35	30	15	30
Filler content, %	79	65–71	— ^a	71
Density, g/cm ³	1.75–2.05	1.72–1.82	1.7–2.0	1.95–2.00
Tensile strength, MPa	87	25	27.6	25
Flexural modulus, GPa	11	6.4	— ^a	9
Flexural strength, MPa	207	100	83	65
Impact strength, notched Izod, kJ/m ²	64	28	0.27	10
Heat deflection temperature, °C	250	200	— ^a	160

^aproperties unavailable.

stiffness and thermal resistance and a discontinuous rubbery butadiene phase for impact and toughness. The balance of properties can also be changed by varying the ratios of the three monomers (see the chemical structure in Table 4 for more detail), as well as by additives and reinforcements. Furthermore, ABS can be readily electroplated, lending the material to appearance applications in interior and exterior automotive trim. ABS is often blended with PC to give a balance of properties.

ABS is primarily processed by injection molding. Secondary processing methods include electroplating for a metallic finish. Properties of ABS depend on copolymer formulation, blend makeup, and reinforcing agents. General purpose ABS has a modulus range of 2300–2900 MPa but can be as low as 1500 MPa for impact grades. The upper use temperature of ABS is in the range of 80–100°C.

SMA. Styrene maleic anhydride (SMA) is a copolymer of styrene and maleic anhydride monomers. This engineering resin is characterized by high heat performance and good dimensional stability. It is used mainly in glass fiber reinforced form for structural components in automotive. SMA is processed by injection molding. Unreinforced grades of SMA have Young's modulus of approximately 1900–2400 MPa and has an upper use temperature more than 100°C.

Thermosets.

Molding Compounds. There are several thermoset molding compounds used in automotive composites including sheet molding compounds (SMC), bulk molding compounds (BMC), resin transfer molding compounds (RTM), and phenolic resin molding compound (MC). Resins for SMC can be based upon several different chemistries including vinyl ester, epoxy vinyl esters, and unsaturated polyesters. Representative properties of several molding compounds are compared in Table 5 (13,14).

Compared to steel parts, thermoset-molding compounds can offer part weight reductions of up to 30%, superior corrosion resistance, reduced complexity due to integrating parts, and reduced tooling costs. Standard formulations for molding compounds include the thermoset polymer resin, calcium carbonate fillers, catalysts, pigments and mold release compounds, and reinforcements. Most composites use glass fibers to reinforce the molding compounds and can

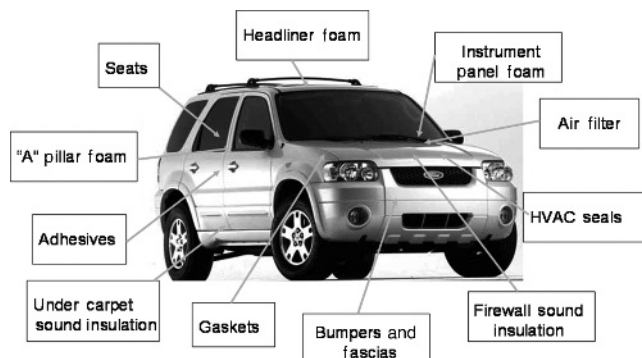


Fig. 6. Common Applications using polyurethanes in automotive components.

be incorporated as a woven fabric, mat, or as tow. More discussion on reinforcement fiber type and forms can be found in the Composites section. Common applications include pickup truck boxes, valve covers, structural body panels, hoods, front-end structural supports, and fenders.

SMC, for example, can be used both in surface appearance and structural components. According to the Automotive Composites Alliance, automotive usage of SMC in 2006 was approximately 400 million lb, of which approximately one third of that quantity used for structural applications (15). Structural components such as GORs (grill opening reinforcements) or GOPs (grill opening panels) utilize 48–52 wt% of glass fibers as reinforcement within the molding compound. Phenolic resins are often chosen for applications requiring resistance to higher temperatures or superior fire retardant properties. Typical applications include components for engine compartments or drivelines.

Polyurethanes. Next to polyolefins, polyurethanes (PUR or commonly, PU) are the next most prevalent polymer used in automotive parts. Polyurethanes are used in a variety of applications such as bumpers, seating, windshields, and seals. This versatile material can be manufactured using several different processing methods to create different forms of the polymer: reaction injection molded (RIM) polyurethane, foams, coatings, and elastomers. Figure 6 provides an overview of the diverse applications for polyurethanes within the automotive vehicles.

Reaction Injection Molding. RIM polyurethane parts offer the advantages of being lightweight, corrosion resistant, and having the ability to be molded into complex shapes. Due to their ability to absorb energy, they are often used in applications such as bumpers, fascias, and spoilers. These parts are made by mixing the isocyanate and polyol blend (polyol with additives and cure package) using an impingement mixing process. The blended mixture is injected at high pressure into a mold, where it reacts and expands.

Structural Reaction Injection Molding and Reinforced Reaction Injection Molding. Two related forms of this PU material are reinforced reaction injection molding (RRIM) and structural reaction injection molding (SRIM) urethanes. RRIM uses glass fiber or mica for reinforcement within the rigid foam. In SRIM, a glass fiber mesh is used to reinforce the urethane matrix. These materials are used in structural applications such as body panels.

Table 6. Typical Properties of Automotive Polyurethanes

PU Type	Density, kg/m ³	Tensile Strength, kPa	Elongation, % ASTM D 1564	Tear Resistance, N/m ASTM D3574
Flexible foam	28–40	70–100	120–170	200–250
TPU	1190–1210	25,000	450	95,000

Thermoplastic Polyurethane Elastomers. Polyurethanes are also used as a base material in several o-rings and seals in an elastomeric form. In addition to applications as bulk resins, polyurethanes can also be applied as adhesives and thin coatings. Polyurethane coatings are thin layers that are applied to windshields as a glazing to increase their strength and provide scratch resistance. Thermoplastic polyurethane elastomers (TPU) provide flexibility over a wide temperature range while also providing a soft feel to the plastic.

The form of polyurethane used has a significant impact on its material characteristics and applications. Table 6 provides a comparison of key properties of polyurethanes used in two forms: thermoplastic polyurethane elastomers and flexible foams (see the Polyurethane Foam section).

Composites. Polymeric composites for automotive applications encompass both thermoplastic and thermoset resins reinforced with minerals and/or fibers. Resin types are discussed in preceding sections, whereas reinforcements and fillers will be discussed in the following section (13).

Reinforcement Type. Fiberglass and minerals comprise the majority of reinforcing agents for automotive composites, followed by carbon fiber and natural fibers.

In thermoplastic matrices, talc and wollastonite minerals are most common for applications that require moderate stiffness enhancement and higher HDT over unfilled resin, followed by calcium carbonate and nanoclays. These applications may include interior and exterior trim, fascias, and ducts. The level of reinforcement provided by the reinforcing agents depends on several factors including compatibility between phases as well as the aspect ratio and size of reinforcement particles. Nanoclays, commonly derived from montmorillonite silicates, will provide excellent reinforcement to the loading ratio, primarily due to their high aspect ratio and small size. Most natural fiber reinforcements possess similar performance to common mineral reinforcement, while concurrently providing a density savings (15). More detailed discussion of natural fibers and fillers can be found in the Natural Fibers and Fillers section. For more load-bearing applications such as instrument panel retainers and grill-opening reinforcements, glass fibers (including both long glass and short glass) may be selected. Carbon fibers provide similar performance to glass fiber reinforcements while providing a significant density reduction. Less common reinforcing fibers are those formed from minerals, such as basalt fibers. Basalt can provide good reinforcement at a lower density. Combinations of reinforcement types may also be used.

In thermosetting systems, the most common composite type is SMC, discussed in the Molding Compounds section. Standard formulations of SMC contain fiberglass and calcium carbonate reinforcements. Lightweight versions of

SMC for automotive applications utilize carbon fibers or hollow glass spheres. As mentioned previously, individual glass fibers and glass fiber mesh can be used in RIM composites. As in the thermoplastic case, natural fibers, basalt fibers, or carbon fibers can be substituted into these types of composites as well to reduce composite density.

Reinforcement Preparation. Reinforcing fibers can be prepared by several methods for introduction into the composite system. The type of preparation chosen will influence both the composite performance as well as the processing method for producing parts.

In thermoplastic composites, the most common forms of fiberglass reinforcements are short glass (SG) and long glass (LG or LF). Short glass composites are prepared through extrusion compounding of sized fiberglass and can sometimes contain additional mineral reinforcements. Long glass fiber reinforced thermoplastics (LFRT) are prepared by melt pultrusion, where a continuous tow of fiberglass is pulled through the resin melt. This process aids in maintaining the fiber length in the composite pellets. Both short and long glass thermoplastic composites can be prepared by injection molding (as discussed in the Injection Molding section), although LFRT requires low shear injection molding to maintain fiber length. Long glass composites can also be prepared by direct long fiber technology, wherein a continuous fiberglass tow is compounded using an inline extruder followed directly by injection molding or compression molding. This process aids in maintaining fiber length, as it significantly reduces thermal and shear history on the material by combining compounding and molding operations into a single process. Other melt-processing methods discussed in the Processing section can also be used. Natural fiber and carbon fiber reinforced thermoplastics can also be prepared through melt compounding. For natural fibers, the most common form of composite currently used in automotive applications is the nonwoven mat. Here, reinforcing fibers are combined with thermoplastic resin fibers such as PP or PET by wet lay, dry lay, and air lay methods into a web and then needle punched to form a mat that can be consolidated and compressed with heat. Glass fibers can be prepared by this method as well.

In thermoset composites, fibers can be chopped and disoriented or can be woven and highly oriented. When chopped, the processing methods such as those used for sheet molding compound and RRIM can be used for producing composite applications. For woven fibers of glass, carbon, and or natural fibers, SRIM, RTM, and compression molding methods are used to first impregnate the preforms with resin and then to cure. The woven fiber reinforced composites are used in automotive applications that have structural requirements.

Foam. Several polymer resins can be used to make foam for automotive applications including polyurethanes, polypropylene, polyethylene, and rubber. Foams provide an excellent form of plastics for NVH (noise, vibration, harshness) reduction, comfort for seating and sealing applications. These materials are often chosen due to their lightweight nature, flexibility in design, and resiliency.

Polyurethane Foam. Polyurethane foams are available in three primary categories: flexible foams, semirigid foams, and rigid foams. In a typical passenger vehicle, about 30 lb of flexible foam are used. Flexible polyurethane foams are most commonly used in seat cushions, seat backs, headliners, armrests, steering wheels, instrument panels, and headrests. These foams are characterized by

their low density, 30–50 kg/m³, and are produced from polyols with a molecular weight in the range of 2000–10000 g/mol. In comparison, semirigid foams and rigid foams use polyols with molecular weights around 700–2000 and 250–700 g/mol, respectively. Rigid foams are used in applications such as sound and noise, vibration, harshness dampening, and energy management systems.

Thermoplastic Foam. Many thermoplastic resins, including polypropylene (PP) and polystyrene (PS), can be expanded with either a chemical or physical blowing agent (BA) to form voids within the resin matrix. A chemical BA is added to the resin such that upon melt processing, the heat and/or pressure will trigger a chemical reaction that forms carbon dioxide or nitrogen gas. The formation of the vapor results in voids that are trapped within the plastic or composite material when the resin solidifies. A physical BA is added to the resin in the melt phase during melt processing at a high pressure. When the resin–gas mixture enters a mold or is extruded at a lower pressure, the gas expands, resulting in a foamed material. These processes are used both in extrusion as well as injection molding of the plastics.

Expanded thermoplastic foams are used in energy management systems such as bumpers, fascias, and structural pillars of the vehicle. Common thermoplastic foams for energy management are EPP (expanded polypropylene), EPS (expanded polystyrene), and EPE (expanded polyethylene). Because of their increased energy absorption capacity, expanded foams can also serve to insulate for temperature and sound in the same way that polyurethane foams can. Beads of thermoplastic resin are first preexpanded by either a chemical or physical BA and then consolidated in a steam chest to mold into the desired shape.

A subset of thermoplastic foams is microcellular foams, in which the void size is smaller than several hundred microns. Figure 7 shows scanning electron micrographs of a polypropylene composite processed by microcellular injection molding. The microcellular molding process results in a part with a solid skin layer (shown in Figure 7a) and a foamed center core (see Fig. 7b) with small, uniform cells. Microcellular foams can be formed by either chemical or physical BAs. When the void fraction of a microcellular foamed material is limited to a low level with a fine and uniform cell structure, these materials can maintain similar mechanical performance to their solid counterparts. A new trend in the automotive industry is to use a microcellular foaming technology to reduce the weight and processing energies of molded components without changing the material.

In addition to weight, energy, and cost reductions, foam-molded thermoplastics also tend to have improved dimensional stability than solid molded counterparts due to the elimination of the pack phase (see the Injection Molding section).

Elastomers. Elastomers are a subset of polymers that are characterized by their ability to recover without permanent deformation, after being stretched to a great extent (eg, twice their original length). Elastomers are more commonly referred to as rubber. For amorphous polymers, elastomers will have a glass transition temperature (T_g) below room temperature, thus making it soft and rubbery at room temperature. Table 7 provides an overview of several of the key elastomers used in automotive applications with their abbreviations and typical properties. These properties will change as the base material is formulated with other elastomers, oils or fillers.

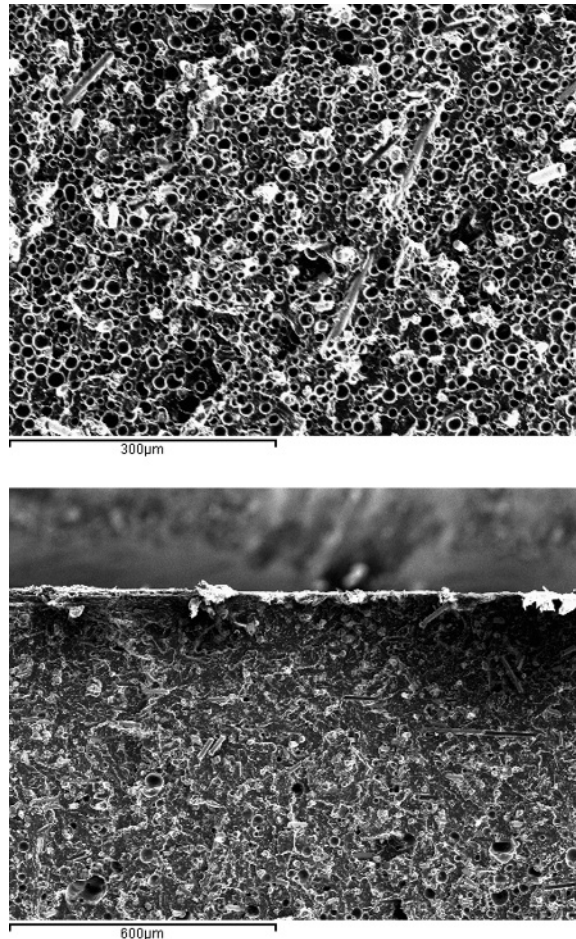


Fig. 7. (a) Scanning electron micrograph (SEM) of microcellular foamed talc reinforced polypropylene. A solid skin layer is shown to be 180 μm . (b) Higher magnification SEM of sample, showing a uniform microcellular structure of the core.

Rubber is obtained from two primary sources: natural rubber trees and chemical or natural gas sources. Natural rubber is produced by tapping the trunk of mature rubber trees (*Havea brasiliensis*) to collect the latex drainage. The latex is combined with diluted acid and rolled to remove water and provide texture to the rubber. After drying the latex, it is ready to be used or combined with other ingredients. Synthetic rubber is obtained from the refinement of oil, coal, or natural gas to produce styrene and isoprene monomers. Through a solution polymerization or emulsion polymerization process, the monomers are linked into long chains of an elastic polymer.

There are several subcategories of elastomers that are used throughout the automotive vehicle: thermoplastic elastomers (TPE), vulcanized elastomers, and saturated elastomers.

Table 7. Properties of Common Automotive Elastomers

Elastomer Type	Abbreviation	Elongation, %	Hardness (Durometer A)	Tensile Strength, MPa
Silicone	SI	100	65–75	4.2
Fluoroelastomers	FKM	70–90	94–98	13–16
Ethylene propylene diene monomer	EPDM	300	70–80	8.3
Nitrile butadiene rubber	NBR	350	60–70	12.0
Epichlorohydrin rubber	ECO	400	55–65	10.4

Thermoplastic Elastomers. Thermoplastic elastomers are used in a variety of applications including interior soft trim, instrument panels, door panels, airbag covers, and steering wheels. A common thermoplastic elastomer known as TEO (thermoplastic elastomeric olefin) is EPDM (ethylene propylene diene monomer) rubber-modified polyolefin, which is frequently used for seals, gaskets, and edge strips for interior applications. Typical properties would be hardness in the range of 60–85 hardness (Shore A durometer), 100–250% elongation at break, and 15–40 kN/m tear strength.

Vulcanized Elastomers. Vulcanized rubber is used extensively in the vehicle. Several of the common unsaturated elastomers or rubber that are sulfur vulcanized include natural rubber (NR), polyisoprene (IR), polybutadiene (BR), styrene butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber, and chloroprene. One of the main applications for these materials is in the tire construction. Most tread layers use either SBR or a blend with some combination of BR and NR. The innerliner of the tire uses halogenated butyl rubber. Rubber for tire applications accounts for approximately one half of the rubber usage in the United States.

For tire applications, rubber is often blended together with processing aids, fillers, accelerators, and antidegradants. As an example, typical tire tread formulations will use blends of 75/25 parts per hundred rubber by weight of SBR and BR. For 100 g of rubber, formulations will include approximately 70 g of filler such as carbon black and silica, 33 g of processing oil and around 20 g of additives. Table 8 provides a sample formulation of the different chemicals that are used in a compounded rubber formulation (16–18).

Saturated Elastomers. For seals, gaskets, and underbody shield applications, saturated rubbers are commonly chosen. EPDM is one of the key elastomers for seals and underbody shields due to its excellent weatherability, temperature resistance, and ultraviolet and ozone resistance. EPDM is a terpolymer of ethylene, propylene and either dicyclopentadiene, 1,4-hexadiene or ethylidene norbornene (ENB). For example, in an automotive grade EPDM, the ethylene to propylene (E/P) ratio may be approximately 68/32 and ENB weight percentage is 3.9. The amount of ethylene in the rubber can be adjusted to provide a range in physical properties based upon the application. Increasing the ethylene content aids in polymer crystallization and enhances properties, whereas lowering of its content results in an amorphous form that can be processed more easily (19).

Table 8. Sample Rubber Formulation Expressed in phr (Parts per Hundred Rubber, by Weight)

Rubber Formulation	
Component	phr
Solution styrene butadiene rubber	75.0
Polybutadiene rubber	25.0
Filler—carbon black	10.0
Filler—silica	60.0
Silane-coupling agent	4.8
Processing oil	33.12
Zinc oxide	1.9
Microcrystalline wax	2.0
Antidegradants	2.5
Stearic acid	1.5
Process aid	2.0
Sulfur	1.5
Accelerators	2.8

EPDM rubber is also used as an impact modifier in polyolefins, such as TPOs and TPEs.

Fluoroelastomers and perfluoroelastomers are often used in seals where resistance to chemicals and heat aging degradation is critical for performance. Automotive applications of fluoroelastomers include fuel hoses, o-rings, and valve cover seals. Silicone rubber is used in applications such as oil pan seals, vacuum lines for engine components, and sealants. Epichlorohydrin rubber is used for seals, gaskets, hoses, and belts within the automotive industry. This elastomer is polymerized with ethylene oxide, thus providing exceptional physical properties for chemical and fuel resistance for a wide range of temperatures.

Processing

The processing of plastic and composite materials allows for certain design freedoms over metal components. Plastic composites and polymeric materials can generally be divided into two distinct categories of thermoplastics and thermosets. Thermoplastic materials can be taken between solid and liquid phases by melt processing, whereas thermosets are formed to shape irreversibly. Thermoplastics can therefore be recycled and reprocessed. On the other hand, thermosets will not melt, but if heated above a critical point will start to degrade or decompose.

Thermoplastics. Several processing methods are available to thermoplastic resins and composites. Those used most frequently for automotive applications include injection molding, extrusion, blow molding, thermoforming, slush molding or rotational sintering, and fiber spinning.

Injection Molding. Injection molding provides the most design freedom, allowing for complex designs and consolidation of parts as well as multiple layers.

In this process, molten resin is injected into a steel mold with one or more cavities with the net shape of the desired part. As the resin solidifies and contracts, molten resin is continuously packed in to fully fill the cavity. After solidification is complete, the finished part is removed from the mold. Injection molding also comprises co- and multishot injection for two or more materials, in-mold decoration, as well as microcellular injection molding. Semistructural and trim applications for interior and exterior automotive components, as well as underhood components such as engine covers and air induction system components are examples of injection-molded automotive parts.

In microcellular foam injection molding, the packing phase of conventional injection molding is eliminated or greatly reduced, resulting in both a faster cycle time as well as a reduction in molded-in stresses. While the pack phase in solid molding ensures that the injection-molded part does not sink due to density changes during solidification, packing of the component is achieved in foam molding by the expansion of the bubbles (foam). The elimination of packing and hold time also results in reduced clamping tonnage. Typical processing conditions for microcellular foaming with nitrogen blowing agent are presented in Table 9 for various thermoplastic composites. The blowing agent concentration is reported in the table as a weight percentage and is denoted as "scN₂" for "supercritical nitrogen." The delivery pressure indicates the pressure of the gaseous blowing agent as it is injected into the molten resin.

Extrusion. Processing consists of melting a resin in a heated barrel, conveyed and/or mixed by a single or twin screws, through an orifice. This process can be used to mix or blend additives of several plastics together, as well as to produce sheet material or profiles. Seals, gaskets, and tubes are commonly extruded profiles.

Thermoforming. Transforming is a process in which a sheet of resin is heated but kept below its melting temperature, formed over a mold, and trimmed to its final state. The sheet can vary in thickness and composition to range from a rigid formed part to a flexible skin application. Pickup truck bedliners, wheel well liners, and headliners are often thermoformed.

Blow Molding. Blow molding is a process used in conjunction with injection molding or extrusion. In this process, a preform or a tube is first formed by injection molding or extrusion. Air is then blown into the preform or tube prior to solidification of the resin to stretch or draw the material down to a thinner gage or wall thickness. Hollow objects such as tubes or bottles are formed by this method. Multilayered structures can also be processed by blow molding. A commonly blow-molded multilayered automotive component is the fuel tank.

Slush Molding or Rotational Sintering. Slush molding or rotational sintering is an excellent process for producing open or hollow parts and skins. In this process, a solution or powder is poured into a heated mold and partially fused by application of heat. The excess liquid or unfused material is removed, and the part is heated again to complete the sintering. Slush molding is a common process for producing the soft skin covering for automotive instrument panels.

Fiber Spinning and Melt Spinning. Fiber spinning and melt spinning are methods to produce fibers from thermoplastic resins. A polymer solution or molten resin is passed through spinneret die heads to form several hundred filaments at once. The filaments are stretched to achieve the desired denier and

Table 9. MuCell Processing Parameters for Thermoplastic Resins and Composites

Material	scN ₂ concentration, %	Delivery Press, psi	Comments
Polyolefins			
HDPE	0.75–1.25	2500	Highly susceptible to voids
Unfilled PP	0.75–1.25	2500	Nitrogen can reach 2% at high length-to-thickness ratios
Talc-filled PP	0.4–0.6	1700–2300	Glass promotes cell growth more effectively than talc.
Glass-filled PP	0.3–0.5	1700–2300	
Amorphous			
PS and PC	0.4–0.6	2500–3000	Very good foamability
HIPS, ABS, and impact-modified.	0.6–0.8	2800–3300	Impact modifiers adversely affect cell structure
Glass-filled amorphous resins	0.2–0.7	2000	Independent of impact modifiers
Semicrystalline Engineering Resins			
Unfilled PA	0.5–0.7	2500	Excellent cell structure control
Glass-filled PA, PBT, and PET	0.2–0.4	1000–1500	
High Heat Resins			
Unfilled polysulfone, PEEK, and similar	0.5–0.7	2500	Excellent cell structure control
Glass-filled polysulfone, PEEK, and similar	0.3–0.4	2500	

taken up on a roll. Filaments are further processed into fiber and textile applications such as carpeting and seat coverings, to name a few.

Thermosets. Because thermosets are irreversibly formed upon curing, the methods of processing depend greatly on the material type, as well as the final desired component or shape. Structural composites can be processed by RIM, RTM, and SMC (sheet-molding compound) processing.

Reaction Injection Molding. RIM, RRIM, and SRIM are processes by which rigid polyurethane can be molded by reacting two liquid components within a tool. This process enables urethanes to be molded with a range of characteristics including foam to a solid structure and from a flexible to rigid part.

Resin Transfer Molding. RTM is a process used for structural composites that are reinforced with woven fiberglass or carbon fiber mats. This process involves heating and injecting a low viscosity thermoset resin through the sprue and runners into the closed mold cavity. The resin wets the reinforcing fibers as it fills out the mold and is heat cured in place.

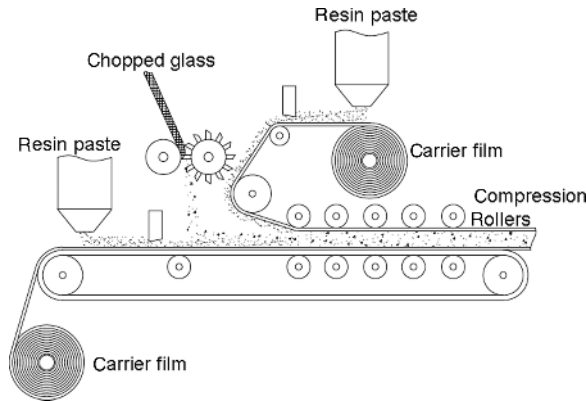


Fig. 8. Schematic of sheet molding compound processing (courtesy of Jeff Dahl, Ford Motor Company).

Sheet Molding Compound. SMC and its relative BMC are produced through a compression-molding process in which a charge of uncured thermoset resin with fiber reinforcement is placed on the mold cavity. The charge of material is prepared by the compounding process shown in Figure 8, where resin paste is applied to a carrier film and glass fibers are chopped to 1–2-inch length and are dropped onto the resin film. The material is covered with another resin layer via a second carrier film and is inserted through compaction rollers to fully wet the fibers with the resin. After allowing the resin paste to mature and build viscosity for a period of time, 24–72 h, the material or “charge” is cut into pieces according to the mold design. The mold is closed and heated to enable the resin to spread throughout the mold and cure into its final shape.

Discussion of elastomer processing and polyurethane foaming is specific to these material types and will be discussed in more detail in upcoming sections.

Polyurethanes.

Thermoplastic Polyurethanes. TPUs are often processed with standard extrusion and injection-molding equipment. In some cases, TPU is used as the skin layer in instrument panels and may be processed using thermoforming of sheets, or from slush or rotational molding from granules.

Flexible Polyurethane Foams. Flexible polyurethane foams are manufactured using a two part mixing process of liquid chemicals into a closed mold. Polyurethanes are formed by reacting two main constituents: isocyanate and a prepolymer or polyol (hydroxylated oil). During the chemical process, there are two competing reactions that take place, called a gel reaction and blow reaction. Figure 9 provides a high level schematic of these reactions and the required balance between them. If the blow reaction is accelerated compared to the gel reaction, the evolution of carbon dioxide will be too rapid and form large voids, resulting in collapsed foam. Alternatively, if the gel reaction exceeds the blow reaction in excess, the foam rise will be restricted and the resulting urethane will have a higher density. Polyurethanes are formulated with other ingredients such as surfactants, catalysts, and blowing agents to control these reactions and resulting foam properties.

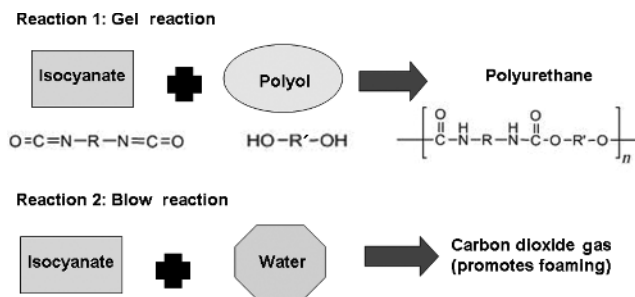


Fig. 9. Schematic of polyurethane processing reactions.

To initiate the polyurethane reaction, the chemicals are metered together such that the ratio of the isocyanate to polyol can be adjusted to the appropriate index for control of foam stiffness. The stream of chemicals is dispensed into an open mold, which is closed as the foam begins to rise. After a few minutes, the mold is opened and the foam is demolded from the tool.

Another method to manufacture polyurethane foam is known as free rise processing. In this method, the chemicals are poured onto a processing film using a controlled doctor blade method. During the reaction, the foam is not constrained by a tool and is able to free rise into a large bun that passes through a curing oven with a conveyor belt. Layers of the foam are cut from the bun according to the application. This process is used for manufacturing headliners and NVH foams.

Elastomers. Elastomers are often processed with a two-step approach: formulation compounding and rubber molding.

Rubber Compounding. Rubber compounding is one of the first stages in processing elastomers. Raw rubber is commonly processed with fillers, oils, and additives using a multistage approach, which can include blending the rubber with a Banbury mixer, two-roll mill, and extruder. As an example, on a Banbury mixer, a typical filler factor is 70% and the rubber is mixed with fillers, processing oil, and coupling agents on the first pass. Cure activators, antidegradants, and processing aid can be added to the masterbatch in the second pass. Often, the primary and secondary accelerators and sulfur are mixed with the masterbatch in the final (productive) pass.

The rubber is processed on a two-roll mill after each Banbury mixing stage to form a flat sheet of the rubber. In this form, the rubber “slug” can be further processed to form the desired end product. The two primary applications of rubber in vehicles are tires and molded rubber goods (19). In tires, rubber sheets are warmed prior to processing them through tread extruders. The rubber is then incorporated in a layered tire build process. Similarly, for molded rubber goods, sheets are warmed, extruded, cut to shape, and pressed into final form. Rubber formulations will affect the rate of extrusion, which is a mid processing step to convert the rubber compound into pellets or sheet form.

Rubber Molding. Rubber molding is the method to cure the rubber after the compounding stage. Once compounded, rubber is extruded and molded in a heated, closed mold to the desired shape. For vulcanized rubber, the temperature–time profile of the molding stage will influence the rubber’s

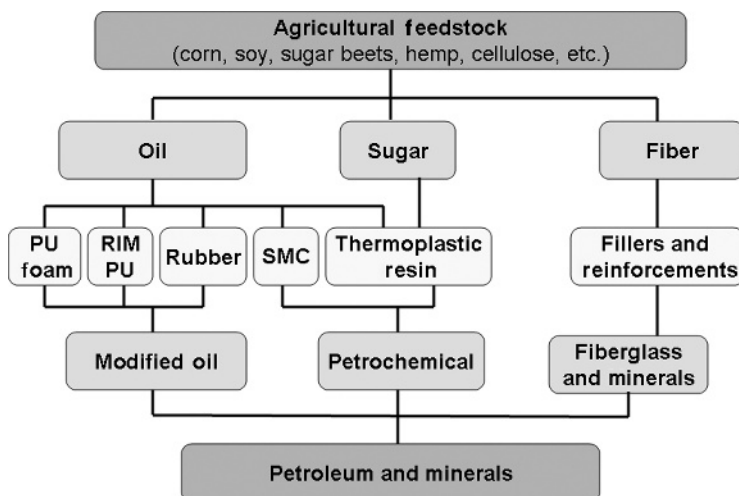


Fig. 10. Potential sources and routes for developing biobased plastics.

cross-link density and final mechanical properties. The cure rate information can be determined following ASTM D 2084 using an oscillating disk rheometer. In the formulation stage, accelerators are added to the formulation to control the rate of sulfur or peroxide cure. Rubber-molding operators will monitor several key parameters including rubber scorch time (t_s), time to 90% cure (t_{c90}), and resulting torque of curing rubber. The scorch time provides processing information of time available once the vulcanization process has initiated. The rubber can be extruded or placed into a compression mold to complete molding of the rubber into the final part.

Sustainable Materials

Plastics can be derived from either petroleum products, such as crude oil and natural gas, or from natural sources, such as sugar or latex. A current trend in automotive materials is to increase sustainability, reaching beyond recycled content to renewable materials. Beginning in the late 1990s, development and use of renewable feedstocks for plastic resins and fillers became more prevalent in the polymer industries. These sustainable materials have shown benefits ranging from improved environment footprints to enhanced processing to financial stability of certain plastics (20).

Renewable composite materials encompass both resins derived from agricultural feedstocks or biomass as well as natural fillers and reinforcements. Figure 10 provides an overview of potential raw material routes for producing biobased plastics, including resins, fillers, and oils.

During the commercial processes for petroleum-based plastics, the raw source of oil or gas is separated into basic building blocks of ethylene and propylene or their derivatives through a cracking process. By controlling the architecture of the polymer chains as the monomers are bonded together, a variety of

plastic resins can be manufactured. This process enables chemical companies to tailor the properties of the polymers for the desired application.

Alternatively, plastic resins, fibers, and reinforcements as well as oils may be obtained from agricultural feedstocks. For example, soybeans can be crushed and expeller pressed or hexane extracted to obtain the soy oil. The oil is often chemically modified or refined prior to incorporation in a variety of plastics or composite formulations. Crops such as corn or sugar beets provide a favorable yield in extracting sugar to obtain the lactic acid from the plant. The lactic acid can be polymerized to form a thermoplastic resin.

Biobased Thermoplastic Resins. These resins are derived in part or in whole from oils, sugars, or other biomass in lieu of petroleum. In terms of their uses for automotive applications, they can be subcategorized into the following groups: biodegradable and compostable, durable, and bioderived replacements. The first two categories comprise new polymeric compounds that are substantially different than the synthetic polymers derived from petroleum. The last category includes the synthetic polymers that are derived from biomass but are chemically identical to those derived from petroleum.

Biodegradable and Compostable Resins. Biodegradable polymers are those that decompose to form CO₂, water, and biomass in a natural environment. Compostable materials also decompose to form CO₂, water, and biomass, but usually in the presence of specific microbes at an elevated temperature and humidity level. In addition, compostability requires no ecotoxicity in the finished compost. Biodegradable and compostable resins can be derived both from petroleum as well as renewable feedstocks. The biobased materials in this category include polylactide (PLA), polyhydroxyalkanoates (PHA), and polyhydroxybutyrate (PHB). PLAs have mechanical stiffness in the range of ABS-, PC/ABS-, and glass-reinforced PP, but have poor impact resistance. PLAs fall into the compostable resin category. PHAs and PHBs have similar mechanical properties to polypropylene and are biodegradable (21–23).

Durable Biobased Resins. Durable resins from biobased feedstocks include poly(trimethylene terephthalate) (PTT) and biobased nylons including polyamide 4,10 (PA410), polyamide 10,10 (PA1010), polyamide 6,10 (PA610), and polyamide 11 (PA11). PTT is a commercially available resin that is up to 37% renewably sourced from corn. Its automotive applications include carpeting, mats, and seat covers. In rigid molded form, PTT has properties similar to PBT. The biobased polyamides have a range of properties similar to the petroleum-based PA6, PA66, and PA12 and have renewable content up to 100%. PA11 is derived completely from castor bean oil and is currently extensively used in fuel line applications.

Conventional Polymers from Biofeedstocks. A newer trend in renewable polymers and composites is the production of traditionally petro-based polymers from monomers and chemical precursors that have been derived from biobased sources. In this category, the polymer is chemically identical to that which is derived from petroleum. In terms of sustainability, however, the biobased material has an advantage of carbon sequestration by the use of biomass. One such example is polyethylene derived from sugarcane. In this process, the fermentation of sugarcane produces ethanol, which is in turn dehydrated to form ethylene, and finally polymerized to produce PE. Other examples include biobased

butanediol for PBT, propanediol for urethanes and coolants and biobased ethylene glycol for PET.

Biobased Thermoset Resins.

Biobased Thermoset Polyesters. Thermoset polyester resins for sheet-molding compounds are derived from petroleum-based oil products. Several universities and companies have demonstrated technical and commercial success in using soy or other crops as a feedstock for unsaturated polyester resins for SMC and BMC. Ashland Chemical Company and John Deere and Company have developed and implemented the use of soy oil based resin containing up to 18% biocontent for use in SMC body panels for agricultural equipment (24).

In addition to using bioderived resin for thermoset-molding compounds, replacing part or all of the glass reinforcements with natural fibers provides another mechanism to produce a biobased part. Since SMC/BMC uses up to 50% glass fibers by weight, use of lightweight fiber alternatives can have a positive impact on weight and tool abrasion. Recent research on using natural fibers in SMC/BMC has included a variety of fiber forms including rovings, mats, and chopped fibers (25),(26). In addition, researchers are also investigating natural replacements for SMC filler, calcium carbonate, by incorporating soy, corn, and cellulose fillers into the composites. The use of natural fibers and fillers can pose issues with water absorption and paint surface appearance (27).

Biobased Polyurethane Foams. Natural oil or biobased polyols such as soy polyol and castor oil have shown promising alternatives to polyether polyols in urethane foams. Soy polyols are produced by modifying degummed soy oil, a triglyceride of fatty acids, with the addition of hydroxyl functionality. Castor oil is a unique option for biopolyols in that it can be used directly in urethane formulations without chemical modifications.

These naturally based polyols offer several advantages over petroleum-based polyols: low cost, favorable life cycle assessments, renewable raw materials and reduced energy usage in their manufacture. In a study conducted by OmniTech International (28), soy-based polyols were preferred over petroleum-based polyols for most environmental categories including global warming potential, fossil fuel depletion, and smog formation potential. For 1000-kg output, the soy-polyols required 1.6E+04 total fuel energy compared to 5.5E+04 total fuel energy required to produce petroleum polyols.

A variety of chemical companies and universities have developed commercial polyols from oils sources such as soybeans, rapeseed, sunflowers, and palms (29). Early introduction of these products showed several issues such as odor concerns, reduced reactivity, and poor green strength of the resulting foam. Further developments alleviated these issues, and successful implementation was noted in both the automotive industry as well as furniture and building industries.

The use of natural oil polyols in urethane foams began commercial usage in the automotive industry in the late 2000s.

In 2007, soy-based polyurethane foam was first implemented in passenger vehicle seats and has increased in usage within 3–4 years. In 2011, one major automotive company is using the technology on all vehicles produced in North America (30). This expansion of usage has had a significant impact on estimated carbon dioxide reductions as well. During a 2-year time frame, it is estimated that approximately 16 million pounds of CO₂ are reduced annually. Since these first

Table 10. Basic Polyurethane Foam Recipe Using Biobased Polyols

Component	Part by Weight
Biobased polyol	40
Petroleum polyol	60
Water (blowing agent)	3–4
Silicone surfactants	1–1.5
Amine catalysts	0.5–1.0
Cross-linker	0.25–0.35
Isocyanate	100 index

introductions, soy-based urethane foams have shown commercial success by several original equipment manufacturers for seating, as well as other applications including headrests and headliners. Opportunities exist to increase the biocontent in these urethanes as well as to expand to other applications including rigid foams and adhesives (31,32).

Table 10 provides a general recipe for biobased polyurethane foam formulation used in flexible foam applications. Recipes are similar to those of petroleum-based polyurethanes and include the use of polyol blends, blowing agents, surfactants, and catalysts.

Natural Fibers and Fillers. Natural fibers and fillers from renewable sources can be used to replace conventional reinforcements such as glass fiber, talc, and other minerals in both thermoplastic and thermoset composites. The reduction in fiber density, and thus composite density, is especially favorable for automotive applications, where component and vehicle weight is often a concern. In addition to their lower cost and lower density, natural fibers are a renewable material and are less energy intensive to produce (grow) than glass fibers. Furthermore, glass fibers tend to be abrasive to tooling and can be irritating to operators, such that a change to natural fibers can reduce tool maintenance and worker issues. The natural fibers and fillers that are most commonly used in automotive composites currently are based on bast or stems. These include hemp, flax, jute, and wood, among others (33–35).

Natural fibers are used extensively in compression molded and thermofomed composites wherein the fiber is intermingled with thermoplastic fibers such as PP or PE into a nonwoven mat (36). These composites can be reinforced with a natural fiber loading of 50% by weight and can be used in applications from door trim components to trunk liners. Because of the aesthetics, however, these applications are limited to components that are covered with vinyl or carpet. As mentioned previously, natural fibers and fillers in SMC and BMC can significantly reduce the component weight while offering a renewable reinforcement for applications such as underbody shields.

More recent developments for natural fiber reinforced composites include injection moldable grades of material. Because of the reduced thermal resistance of natural fibers compared to glass, these composites have been limited to polyolefin systems. One such example is wheat straw reinforced PP, which has applications and properties similar to talc/PP or ABS and can be used in applications such as interior storage bins and underhood trays.

Recycled Plastics. Many plastic resins are able to be recycled into new parts through either a mechanical recycling or chemical recycling process.

Sources for the plastic include both postindustrial recycled resins (scrap from a molding plant) known as PIR, or postconsumer recycled resins (reuse from a consumer part) known as PCR. The recycling of plastics provides the benefit of reducing landfill usage as well as decreasing demands on petroleum oil and natural gas.

The idea of mechanical recycling of plastics has been well adopted in consumer markets for PET and HDPE bottles, beginning in the 1980s. Within the automotive industry, similar processing steps take place. Reclaimed plastic parts are collected, sorted, and chopped into flakes. The reclaimed resin is blended with virgin resin and processed into new plastic components. Chemical recycling, on the other hand, breaks down the polymer chains into the monomers or starting materials. Condensation polymers such as polyethylene terephthalate and nylon are two common examples of plastics that are able to be chemically recycled.

For automotive applications, recycled plastics have been used extensively for applications ranging from seat fabrics to engine fan components to sound dampening materials. According to General Motors Corporation, the company uses recycled materials from several plastic sources including soda bottles, used tires, recycled vehicle bumpers, and nylon carpet (37). At Ford Motor Company, the European Ford Focus uses several recycled material components including wheel arch liners with 100% recycled polypropylene, fan shrouds with 25% recycled content, and air cleaner assembly with 25% recycled plastics (38).

With greater environmental demands on end-of-life vehicles in North America and in line with the ELV directive in the European Union, recycled content in plastics has been demonstrated in a wide range of applications. One of the key challenges is developing plastic components with the same physical properties as those produced from virgin resins. Recycling companies continue to seek solutions for developing cost-effective methods of collecting, separating, and processing plastics in an economical manner.

Conclusion

Plastics provide an important material choice in the design, construction, safety, and comfort of modern automobiles. These materials are used in virtually all subsystems of the vehicle including power train, interiors, exteriors, seating, chassis, and transmissions. Plastics are readily adaptable for different applications and requirements because of the relative ease in modifying polymer chemical structures and blending the material with other resins, fillers, or fibers. Over the past decade, usage of plastics has remained constant at about 340 pounds per vehicle. Because of their lightweight and versatility in design and manufacturing, plastics are anticipated to play a vital role in future automobiles.

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AZO COMPOUNDS

Introduction

Azo compounds are organo-nitrogen derivatives with the characteristic —N=N— functionality and the general formula R—N=N—R' where R and R' can be the same or different organic groups. In the polymer industry, azo compounds are used as dyes, blowing agents, and free-radical polymerization initiators. The use of azo compounds as dyes and blowing agents is covered elsewhere in this *Encyclopedia* (see DYEING; BLOWING AGENTS). This article describes the azo compounds used as free-radical initiators (see INITIATORS, FREE-RADICAL).

Simple symmetrical azo compounds have been named by adding the prefix azo- to the name of the parent molecule, eg, azomethane for $\text{CH}_3\text{—N=N—CH}_3$. Azo compounds with simple substituents were named by prefixing the substituent and locant, eg, 1-methylazoethane for $\text{C}_2\text{H}_5\text{—N=N—CH(CH}_3)_2$. However, starting with *Chemical Abstracts* Volume 76 (1972), azo compounds are indexed as derivatives of diazene, H—N=N—H , eg, diazene, dimethyl-. Previously, “diimide” had been used instead of diazene in naming certain other azo compounds, eg,

diimide, diacetyl for $\text{CH}_3\overset{\text{O}}{\parallel}\text{C—N=N—C}\overset{\text{O}}{\parallel}\text{CH}_3$ which is now indexed as diazene, diacetyl.

Azo compounds containing a functional group in addition to the azo moiety (eg, alcohol, amide, carboxylic acid, imidamide, nitrile, sulfonic acid) are named as derivatives of that functional group. In naming symmetrical azo compounds of

Table 1. Commercial Azo Initiators

Compound	Structure number	Structure	Mp, °C	10-h $t_{1/2}$, °C	Refs.
<i>Symmetrical</i>					
2,2'-azobis(4-methoxy-2,4-dimethylpentanenitrile)	(1)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{OCCH}_2\text{C}-\text{N}=\text{N}-\text{CCH}_2\text{COCH}_3 \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CN} \quad \text{CH}_3 \end{array} $	55–86	40	2,14
2,2'-azobis(2,4-dimethylpentanenitrile)	(2)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{CHCH}_2\text{C}-\text{N}=\text{N}-\text{CCH}_2\text{CHCH}_3 \\ \quad \quad \quad \\ \text{CN} \quad \text{CN} \quad \text{CN} \quad \text{CN} \end{array} $	46–65	52	1–4
2,2'-azobis(2-methylpropanimidamide) dihydrochloride	(3)	$ \begin{array}{c} \text{NH} \quad \text{CH}_3 \quad \text{NH} \\ \quad \quad \\ \text{H}_2\text{NC}-\text{C}-\text{N}=\text{N}-\text{C}-\text{CNH}_2 \cdot 2\text{HCl} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} $	160–169	56 ^a	5
2,2'-azobis(isobutyronitrile)	(4)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{C}-\text{N}=\text{N}-\text{CCH}_3 \\ \quad \\ \text{CN} \quad \text{CN} \end{array} $	103–104	64	1,3,4,6–9
2,2'-azobis(2-methylbutanenitrile)	(5)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2\text{C}-\text{N}=\text{N}-\text{CCH}_2\text{CH}_3 \\ \quad \\ \text{CN} \quad \text{CN} \end{array} $	49–51	67	1,2,4
4,4'-azobis (4-cyanopentanoic acid)	(6)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{HOOCCH}_2\text{CH}_2\text{C}-\text{N}=\text{N}-\text{CCH}_2\text{CH}_2\text{COOH} \\ \quad \\ \text{CN} \quad \text{CN} \end{array} $	112–116	66 ^a	1,10
1,1'-azobis(cyclohexanecarbonitrile)	(7)		114–115	88	1,2,3
2,2'-azobis(2-acetoxypentane)	(8)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{COOC}-\text{N}=\text{N}-\text{COOCCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	101–103	189	8,9,11–13

Unsymmetrical

2-(<i>tert</i> -butylazo)-4-methoxy-2,4-dimethylpentanenitrile	(9)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{CH}_3\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_2\text{COCH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CH}_3 \end{array} $	-11	55	3,15,16
2-(<i>tert</i> -butylazo)-2,4-dimethylpentanenitrile	(10)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_2\text{CHCH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CH}_3 \end{array} $	-16	70	3,15,16
4-(<i>tert</i> -butylazo)-4-cyanopentanoic acid	(11)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_2\text{CH}_2\text{COOH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CN} \end{array} $	83-85	73 ^a 76	16
2-(<i>tert</i> -butylazo)isobutyronitrile	(12)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CN} \end{array} $	17	79	3,7,8,15,16
2-(<i>tert</i> -butylazo)-2-methylbutanenitrile	(13)	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_2\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CN} \quad \text{CN} \end{array} $	-25	82	3,15,16
1-(<i>tert</i> -amylazo)cyclohexanecarbonitrile	(14)	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{C}-\text{N}=\text{N}-\text{C}(\text{CN})-\text{C}_6\text{H}_{10} \\ \\ \text{CH}_3 \end{array} $	-12	94	3,16
1-(<i>tert</i> -butylazo)cyclohexanecarbonitrile	(15)	$ \begin{array}{c} (\text{CH}_3)_3\text{C}-\text{N}=\text{N}-\text{C}(\text{CN})-\text{C}_6\text{H}_{10} \end{array} $	27-28	96	3,8,15
1-(<i>tert</i> -butylazo)formamide	(16)	$ \begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_3\text{C}-\text{N}=\text{N}-\text{C}-\text{NH}_2 \end{array} $	105	105	17

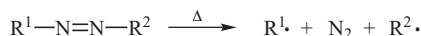
^aIn water

this type, the name of the unsubstituted parent compound is preceded by the prefix azobis- (formerly azodi-). For example: 2,2'-azobis(2-methylpropanenitrile) (**4**)

for $(\text{CH}_3)_2\overset{\text{CN}}{\underset{|}{\text{C}}}-\text{N}=\text{N}-\overset{\text{CN}}{\underset{|}{\text{C}}}(\text{CH}_3)_2$. In naming unsymmetrical azo compounds $\text{R}^1-\text{N}=\text{N}-\text{R}^2$, a parent molecule R^1H is treated as substituted by a radical $\text{R}^2-\text{N}=\text{N}-$. The R group with a functional group, or the more complex R group, is chosen as the parent. For example: 2-[(1,1-dimethylethyl)azo]-2-methylpropanenitrile (**12**)

for $(\text{CH}_3)_3\overset{\text{CN}}{\underset{|}{\text{C}}}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2$. Acceptable common or trivial names are generally used for simplicity, eg, 2,2'-azobis(isobutyronitrile) (**4**), 2-(*tert*-butylazo)isobutyronitrile (**12**), 4,4'-azobis(4-cyanovaleric acid) (**6**), and 2,2'-azobis(2-acetoxyp propane) (**8**).

Azo compounds used commercially as free-radical initiators are listed in Table 1; all contain at least one tertiary carbon (sp^3 hybridized) attached to azo nitrogen. Such azo compounds, appropriately substituted, decompose upon heating by homolytic cleavage of two carbon–nitrogen bonds to generate two free radicals and nitrogen:



These free radicals are reactive intermediates (half-lives ($t_{1/2}$) of less than 10^{-3} s) and have been used to initiate a variety of commercial processes, such as vinyl monomer polymerizations and copolymerizations; curing resins; grafting vinyl monomers onto polymer backbones; autoxidation of hydrocarbons; anti-Markovnikov additions to terminal olefins; halogenations; and telomerizations (1,3,9,18–26). Although the initiating species in these processes is the free radical, the term free-radical initiator is used synonymously with the precursor azo compound.

Azo compounds are also photosensitive and absorb ultraviolet radiation in relatively high quantum yield. However, the quantum yield for radical generation is low because the absorbed radiant energy primarily excites and isomerizes ground-state trans azo compounds to excited-state cis and trans azo structures, which are partly deactivated to the ground state and partly decomposed to free radicals and nitrogen. Most radicals are generated from the cis forms, which are thermally less stable than the trans forms. Although many studies have been carried out on the photodecomposition of azo compounds (27), commercial azo compounds are used primarily as thermal sources of free radicals.

Properties

The commercial symmetrical initiators given in Table 1 are solids with melting points ranging from 46 to 169°C and limited solubility in common organic solvents (2,5,6) (see Table 2). The unsymmetrical azonitriles without a carboxy substituent are liquids or low melting solids with good solubility in organic

Table 2. Solubility Rating^a of Azo Initiators at 20°C^b

Azo cmpd	Water	Isopropyl alcohol	Acetone	Benzene	Aliphatic hydrocarbon	Methylene chloride, chloroform	Ethyl ether	Ethyl acetate
(8)	ins	ins	sl		ins	s		
(3)	s		sl	ins		ins		
(4)	ins	ins ^c	ms ^d	ms ^c	ins	s	sl	ms
(2)	ins		s		sl		s	
(12)	ins	vs	vs	vs	vs	vs	vs	vs
(15)	ins	vs	vs	vs	vs	vs	vs	vs

^aKey: ins = insoluble (<1%); sl = slightly soluble (1–5%); ms = moderately soluble (5–15%); s = soluble (15–50%); and vs = very soluble (>50%).

^bUnless otherwise stated.

^cAt 25°C.

^dAt 0°C.

solvents; the highest melting are 2-(*tert*-butylazo)isobutyronitrile (**12**) and 1-(*tert*-butylazo)cyclohexanecarbonitrile (**15**) (15).

Upon heating, azo initiators generate two free radicals and nitrogen. The decomposition kinetics are controlled by the nature of the R groups. Activity is affected by the stability of the radicals formed, ie, the more stable the radicals, the less stable the azo initiator. Strained azo compounds are less stable since decomposition relieves strain. These influences are manifested in the *A* and *E* factors in the Arrhenius first-order equation (28):

$$k = A \times \exp(-E/RT)$$

Symmetrical azonitriles are less stable than unsymmetrical ones. This can be seen in Table 1 by comparing the 10-h half-life ($t_{\frac{1}{2}}$) temperatures of analogous symmetrical and unsymmetrical compounds. For example, the 10-h $t_{\frac{1}{2}}$ of the symmetrical compound (**4**) is 64°C compared to 79°C for (**12**) and 52°C for the symmetrical (**2**) compared to 70°C for the unsymmetrical compound (**10**). This effect is due to the fact that α -cyanoalkyl radicals are more stable than the *tert*-butyl radical generated from the unsymmetrical azonitriles (**12**) and (**10**). The α -cyano group has a resonance stabilization effect on radicals.

This alpha effect on stability of radicals is further illustrated in Tables 1 and 3, which show the effect on decomposition kinetics of azo compounds differing only in a single alpha substituent. The following is the order of decreasing radical stability: cyano > phenyl > carbamyl > alkylthio > alkoxy > alkyl > acetoxy.

The influence of alkyl branching is shown in Table 4. Branching on the β -carbon has very little effect on the decomposition kinetics as evidenced from the first four compounds listed. In spite of the fact that one alkyl group of 2-(*tert*-butylazo)-2-cyanoalkane contains one, two, three, or no methyl groups on the β -carbon, the 10-h $t_{\frac{1}{2}}$ varied only from 79 to 83°C without apparent pattern. However, branching on the γ -carbon has a very significant effect as illustrated by the last two compounds in Table 4. With one methyl branch on the γ -carbon, the

Table 3. Effect of Alpha-Substituent on Activity of Azo Compounds

$\begin{array}{c} \text{X} \\ \\ (\text{CH}_3)_3\text{C}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2 \end{array}$	
X	10-h $t_{\frac{1}{2}}$, °C
CH ₃ —	160
RO—	143–154
RS—	111–128
H ₂ NC(O)—	110
C ₆ H ₅ —	84
NC— ^a	79

^aCompound (12).**Table 4. Effect of Alkyl Branching on Activity of Azo Compounds**

$\begin{array}{c} \text{R} \\ \\ (\text{CH}_3)_3\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_3 \\ \\ \text{CN} \end{array}$		
R	Compound	10-h $t_{\frac{1}{2}}$, °C
CH ₃ —	(12)	79
C ₂ H ₅ —	(13)	82
(CH ₃) ₂ CH—		83
(CH ₃) ₃ C—		80
(CH ₃) ₂ CHCH ₂ —	(10)	70
(CH ₃) ₃ CCH ₂ —		52

Table 5. Effect of Ring Size on Activity of Azo Compounds

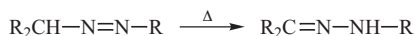
$\begin{array}{c} (\text{CH}_3)_3\text{C}-\text{N}=\text{N}-\text{C} \\ \diagup \quad \diagdown \\ \text{NC} \quad \text{---} \text{C} \text{---} (\text{CH}_2)_n \end{array}$	
n	10-h $t_{\frac{1}{2}}$, °C
5 ^a	96
4	78
6	68
7	55

^aCompound (15).

10-h $t_{\frac{1}{2}}$ of the azonitrile was lowered from about 79 to 70°C, and with two methyl branches the 10-h $t_{\frac{1}{2}}$ dropped to 52°C.

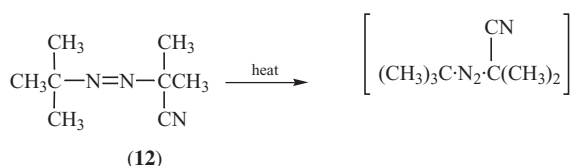
The effect of ring size on cyclic azonitriles is illustrated in Table 5. Cyclohexanone derivatives are the most stable of all azonitriles, whereas cyclooctanone derivatives are among the least stable. It should be noted, incidentally, that the effects of gamma branching and ring size are common to all aliphatic azo compounds.

Although such compounds can be found in the patent literature (29), none of the commercial initiators are primary or secondary alkylazo compounds because they rearrange to hydrazones upon heating:

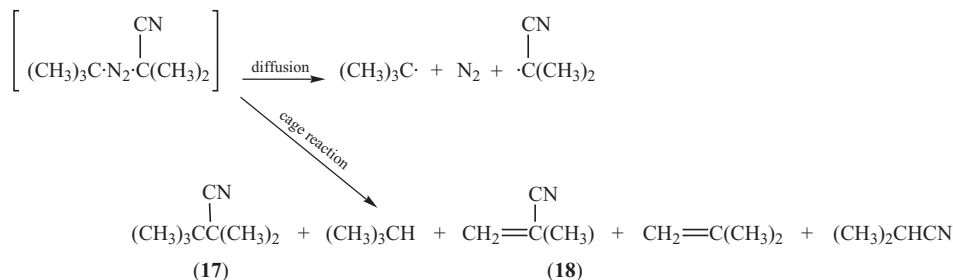


Furthermore, compounds where the azo function is in a ring are not suitable as free-radical initiators because they decompose to diradicals, which couple to cycloalkanes or disproportionate to olefins (30).

In normal applications, azo initiators decompose in a cage of solvent or monomer molecules illustrated by the brackets in the following equation:

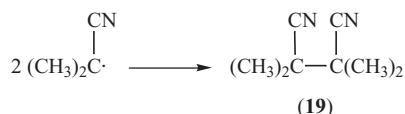


A certain percentage of the radicals react in the cage to form nonradical cage products by coupling and disproportionation. Only those radicals that escape or diffuse out of the cage or react with the cage wall are effective in initiating free-radical reactions. Certain azo compounds give more cage products than others, and this is generally related to the structure of the azo compound. Environment also plays a role; eg, more cage products are formed in highly viscous systems:



In decomposition studies on the unsymmetrical azonitrile (12), all five possible cage products were present in the decomposition products, ie, 2,3,3-trimethyl-2-cyanobutane (17) obtained by coupling the *tert*-butyl and 2-cyanoisopropyl radicals; isobutane and methacrylonitrile (18) from the disproportionation reaction whereby the *tert*-butyl radical removes a β -hydrogen from the 2-cyanoisopropyl radical; and isobutylene and isobutyronitrile from the disproportionation reaction whereby the 2-cyanoisopropyl radical removes a β -hydrogen from the *tert*-butyl radical. In an inert solvent, radicals escaping from the cage interact in coupling and disproportionation terminating reactions and form 2,2,3,3-tetramethylbutane by coupling two *tert*-butyl radicals and

tetramethylsuccinonitrile (**19**) by coupling two 2-cyanoisopropyl radicals:



However, in an efficient radical-scavenging environment (eg, vinyl monomer) such interactions do not occur. The methacrylonitrile (**18**) cage product is an efficient radical scavenger and is usually isolated as an oligomer in an inert solvent or functions as a comonomer in vinyl monomer polymerizations.

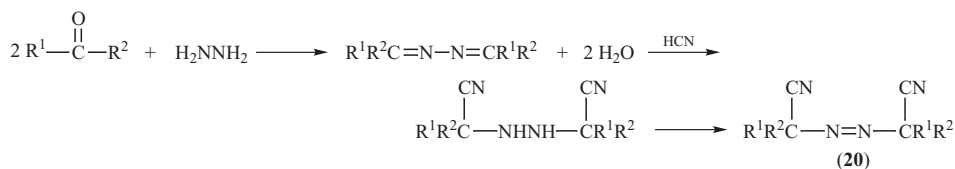
The symmetrical azonitrile (**4**) produces two 2-cyanoisopropyl radicals in the cage and consequently always produces (**19**) in the cage reaction. With unsymmetrical azonitriles, disproportionation is favored over coupling, whereas with symmetrical azonitriles, coupling is preferred. Decomposition studies on (**4**) have shown that 84–90% of the 2-cyanoisopropyl radicals couple to (**19**) (31).

Although azonitriles are effective initiators in vinyl monomer polymerizations and copolymerizations, their efficiency in radical generation is generally less than 50% because the radicals initially generated undergo self-termination reactions in the cage. Decomposition of (**4**) in the presence of radical scavengers gives 54% cage-recombination products (32). This can be important with regard to decomposition fragments in the finished product since (**19**) obtained from (**4**) is highly toxic. Tetrasubstituted succinonitriles from other symmetrical azonitriles such as 2,2'-azobis(2-methylbutanenitrile) (**5**) are, however, not as toxic.

Preparation

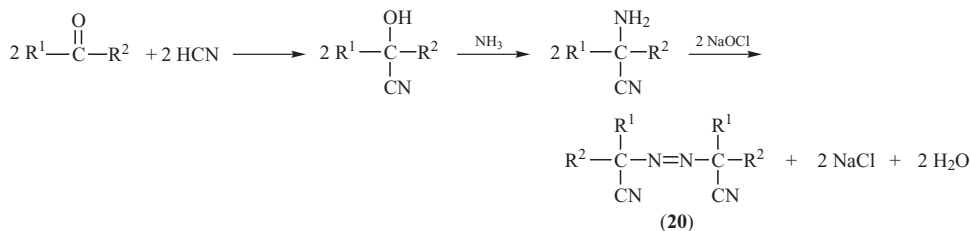
Azo compounds have been synthesized by a variety of methods; details can be found in the General References.

The symmetrical azonitriles in Table 1 are produced by two general routes: (1) Reaction of a ketone with hydrazine to form an azine to which hydrogen cyanide is added to produce an intermediate 1,2-disubstituted hydrazine, which is oxidized to the symmetrical azonitrile (**20**) (14,33)



(2) Reaction of a ketone with HCN to form a cyanohydrin, which reacts with ammonia to produce an aminonitrile; this is coupled to form the symmetrical

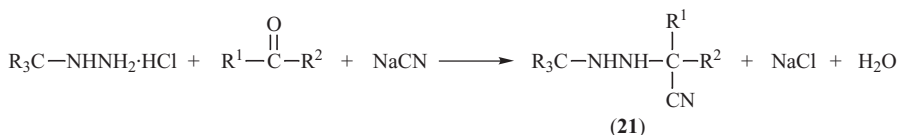
azonitrile (**20**) by hypohalite oxidation (34–40):



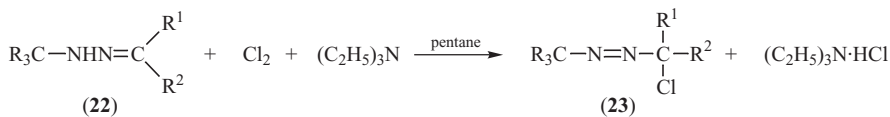
Except for simple aminonitriles (eg, from acetone and methyl ethyl ketone), the oxidative coupling requires cationic surfactants (38–40). Mixtures of symmetrical and asymmetrical azodinitriles have been prepared by oxidative coupling of a mixture of two different aminonitriles (41).

The unsymmetrical azonitriles in Table 1 have been synthesized by the reaction of a tertiary alkylhydrazine (eg, *tert*-butylhydrazine) with a ketone to form the tertiary alkylhydrazone $\text{R}_3\text{C}-\text{NHN}=\text{CR}^1\text{R}^2$ (**22**) to which HCN is added

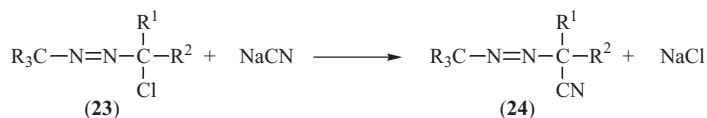
to produce the unsymmetrical 1,2-disubstituted hydrazine $\text{R}_3\text{C}-\text{NHNH}-\overset{\text{CN}}{\underset{|}{\text{C}}}\text{R}^1\text{R}^2$ (**21**); this is oxidized to the unsymmetrical tertiary azonitrile (**24**). With water-soluble ketones, the first two steps to form (**21**) can be combined conveniently by using sodium cyanide and a mineral acid salt of the tertiary alkylhydrazine (16,42):



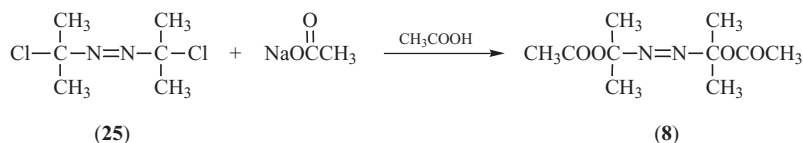
Alternatively, a ketone tertiary alkylhydrazone (**22**) and a tertiary amine (such as triethylamine) react in an inert solvent (pentane) with chlorine at 0–5°C to form a tertiary alkyl α -chloroazo compound (**23**):



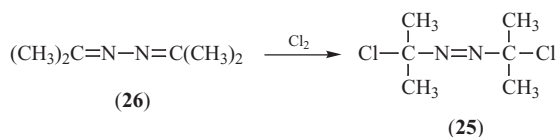
Compound (**23**) reacts with an aqueous methanol solution of NaCN to form the unsymmetrical azonitrile (**24**) (16,42):



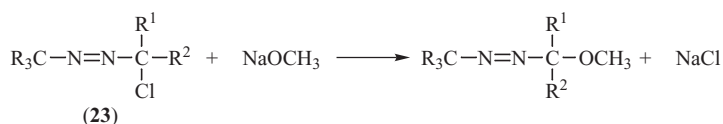
2,2'-Azobis(2-acetoxypropane) (**8**) is produced from sodium acetate and 2,2'-azobis(2-chloropropane) (**25**) in acetic acid (**12**):



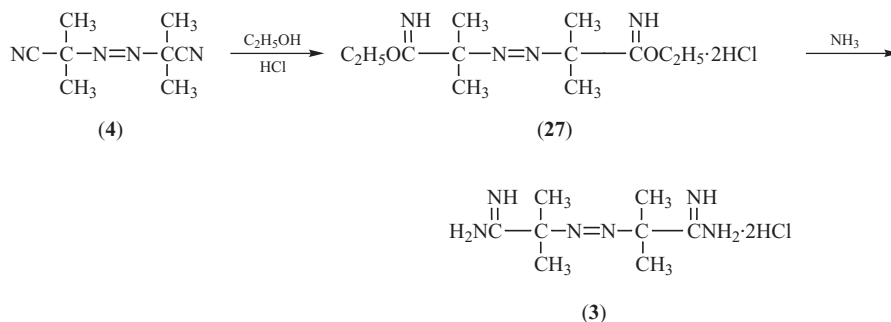
The intermediate (**25**) is prepared by the addition of chlorine to acetone azine (**26**) (**13**):



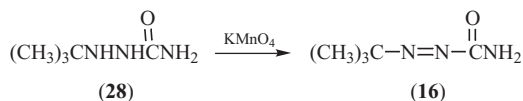
A variety of other nucleophiles (such as imido (**43**), organothio (**44**), hydroperoxy (**45**), alkylperoxy (**46**), azido, cyanato, isocyanato, isothiocyanato, alkoxy, and aryloxy) react with α -chloroazo intermediates (**23**) and (**25**) to form other symmetrical and unsymmetrical azo and bisazo (**47**) compounds, some of which may have commercial value (**12,42,48**):



2,2'-Azobis(2-methylpropanimidamide) dihydrochloride (**3**) listed in Table 1 is prepared by the reaction of 2,2'-azobis(isobutyronitrile) (**4**) with ethanol and hydrogen chloride, followed by treating the intermediate iminoester dihydrochloride (**27**) with ammonia (**49**):

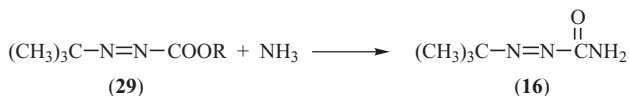


1-(*tert*-Butylazo)formamide (**16**) has been prepared by oxidizing 1-*tert*-butylsemicarbazide (**28**) with potassium permanganate (42,50):

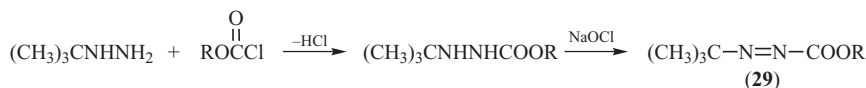


The intermediate (**28**) can be produced from *t*-butylhydrazine and urea or potassium cyanate (51).

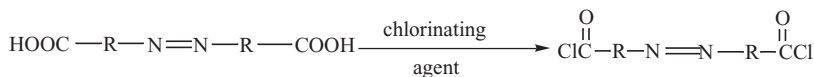
In another process, an alkyl *tert*-butylazocarboxylate (**29**) reacts with ammonia (42,50):



The intermediate (**29**) is prepared from *t*-butylhydrazine and the alkyl chloroformate, followed by oxidation with hypohalite (42,51):



Symmetrical and unsymmetrical azo compounds containing acylating functions (acid chloride, chloroformate, anhydride) have been prepared (52):



Such multifunctional azo compounds have been used as intermediates to synthesize azo polymers (qv) (53), sequential polyazo initiators (54), sequential azo peroxide initiators (55,56), azo monomers (57), and azo initiators with chemically bound uv-stabilizer groups (56,58).

Economic Aspects

2,2'-Azobis(isobutyronitrile) (**4**), often referred to as AIBN, has been the most popular and widely used azo initiator. Although now available elsewhere, AIBN was first produced in the United States by DuPont and offered on the domestic market in 1962 under the trade name Vazo 64.

DuPont later introduced 2,2'-azobis(2-methylbutanenitrile) (**5**) under the trade name Vazo 67 as a less toxic and more soluble replacement for AIBN.

The second largest volume azo initiator is 2,2'-azobis(2,4-dimethylpentanenitrile) (**2**) often referred to as ABVN, a popular initiator for vinyl chloride polymerization produced by Japan Hydrazine Company. In the United States, this initiator is produced by DuPont under the trade name Vazo 52.

The higher temperature 1,1'-azobis(cyclohexanecarbonitrile) (**7**) was introduced by DuPont under the trade name Vazo 88 for the acrylic coating and styrene copolymer markets; it is also available elsewhere.

2,2'-Azobis(2-methylpropanimidamide) dihydrochloride (**3**) is a low volume, water-soluble azo initiator previously marketed by Crescent Chemical Co., Inc. under the trade designation V-50. 2,2'-Azobis(2-acetoxyp propane) (**8**) is another low volume product manufactured in Germany and marketed by Luperox GmbH, Pennwalt, under the trade name Luazo AP as a high temperature polymer modifier.

The unsymmetrical azo initiators 2-(*tert*-butylazo)isobutyronitrile (**12**), 2-(*tert*-butylazo)-2-methylbutanenitrile (**13**), and 1-(*tert*-butylazo)cyclohexane-carbonitrile (**15**) were produced by the Lucidol Division of Pennwalt Corporation under the trade names Luazo 79, Luazo 82, and Luazo 96. The other initiators in Table 1 are low volume or development-type products.

Health and Safety Factors

Azo initiators decompose with dangerous rapidity when overheated and may cause explosions in closed containers. The decomposition of azonitriles is exothermic, eg, 210 kJ/mol (50.2 kcal/mol) for (**4**), and if this heat is not removed, the decomposition may become uncontrollable. Since initiators vary in their decomposition kinetics (see $t_{1/2}$, in Tables 1–5), the manufacturer's literature should be followed carefully.

Azonitrile decomposition products include organonitriles, most of which are toxic. Decomposition products of (**4**), (the symmetrical azonitrile of lowest molecular weight and highest cyano content) are highly toxic, eg, the lethal oral dose of tetramethylsuccinonitrile (**19**) is ca 60 mg/kg (**6**). Decomposition products from higher molecular weight azonitriles are less toxic. Azonitriles also produce saturated organonitriles from radical disproportionation reactions, such as isobutyronitrile from (**4**) and cyclohexyl cyanide from 1,1'-azobis(cyclohexane-carbonitrile) (**7**) and from (**15**). These lower molecular weight organonitriles are volatile and toxic (eg, LD₅₀ oral = 102 mg/kg for isobutyronitrile and 285 mg/kg for cyclohexyl cyanide). Precautions should be taken to avoid exposure to fumes from decomposing azonitriles.

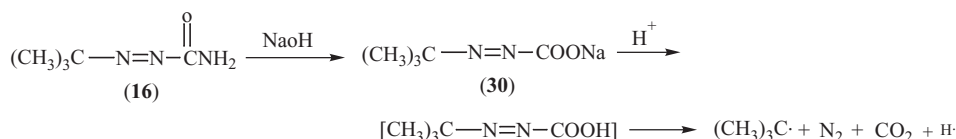
Azonitriles are readily ignited with an open flame, and dispersions of solid azonitriles in air are explosive. Care should be taken to avoid dusty conditions; environments should always be sparkproof.

Applications

The azonitriles in Table 1 are used for bulk, solution, suspension, and dispersion polymerization of most common vinyl monomers (styrene, vinyl chloride, vinyl acetate, methyl methacrylate, methyl acrylate, acrylonitrile, vinylidene chloride, and ethylene). Azonitriles have the following advantages over organic

peroxide initiators: (1) they are not susceptible to radical-induced decompositions; (2) their decomposition rates are little affected by the environment, eg, pH, transition-metal ions, or other additives or contaminants; (3) azonitriles are generally safer than peroxides of comparable activity; (4) they do not form oxygenated residues in the polymer, which consequently exhibits better color stability; and (5) azonitriles generate highly selective tertiary alkyl radicals, which do not attack polymer backbones. This reduces chain branching and permits the use of azonitriles for polymerizing susceptible compounds, such as unsaturated amines, thioethers, and aldehydes (2,6,15,16).

Initiation of water-solution and emulsion polymerizations have been reported for the water-soluble azo compound (3) shown in Table 1 (5). The azonitriles (6) and (11) are especially soluble in basic systems, Unsymmetrical (16) has been used to initiate water-solution and emulsion polymerizations of acrylic acid and ethyl acrylate via conversion to sodium *t*-butylazоformate (30), which decomposes to free radicals, especially at lower pH (59):

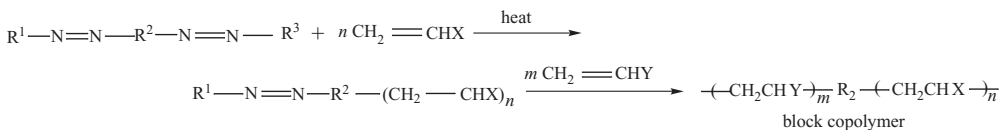


The azonitriles and (16) have been used as initiators for curing unsaturated polyester resin/styrene blends (2,6,15,16,27,28). To avoid surface pinholing (from the nitrogen), blends containing about 10% unsymmetrical lower temperature azonitriles with higher temperature peroxides give accelerated cures without sacrificing shelf-life of precatalyzed unsaturated polyester resins (60).

Although azonitriles are not useful as cross-linking agents because the radicals they generate are poor hydrogen abstractors, azo compounds with α -alkoxy and acetoxy substituents have been found to be fairly efficient cross-linking agents for polymers such as polyethylene (61). Azo compounds with α -acetoxy substituents are the most stable commercial free-radical initiators and can be used in very high temperature applications; the symmetrical α -acetoxy azo compound (8) has been used to modify super high density polyethylene (HDPE).

Azo compounds containing α -substituents other than cyano groups are used as initiators for curing unsaturated polyester resins and for polymerizing vinyl monomers (62).

Polymers containing chemically bound azo initiators are prepared from initiators with acylating groups attached (53) and from sequential polyazo and azo-peroxide initiators by carrying out vinyl monomer polymerizations using only the lower temperature active part of the sequential initiator. Block copolymers are then formed by using the azo polymer as an initiator for another vinyl polymerization (63).



For example, styrene-methacrylate block copolymers have been prepared by this route (see also BLOCK COPOLYMERS). Azo initiators with chemically bound uv-stabilizer (UVLS) groups are used to prepare polymers with bound uv-stabilizer groups, which retain their stabilizing properties because they cannot leach out (56,58):



Azonitriles are used as initiators for free-radical additions to olefins, au-toxidations, telomerizations, and halogenations (1,3,6,9,18-26). Monomers are grafted onto polyols with the aid of azonitrile initiators. The products give polyurethanes with improved properties. Apparently these graft polyols cannot be prepared with peroxide initiators because of their susceptibility to degradation (64) (see also GRAFT COPOLYMERS).

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