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INTRODUCTION TO POLYMER SCIENCE

Polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of plastics, rubber, adhesives, fibers, and coatings. Only much later did polymer science come to academic life. Perhaps because of its origins, polymer science tends to be more interdisciplinary than most sciences, combining chemistry, chemical engineering, materials, and other fields as well.

Chemically, polymers are long-chain molecules of very high molecular weight, often measured in the hundreds of thousands. For this reason, the term "macromolecules" is frequently used when referring to polymeric materials. The trade literature sometimes refers to polymers as resins, an old term that goes back before the chemical structure of the long chains was understood.

The first polymers used were natural products, especially cotton, starch, proteins, and wool. Beginning early in the twentieth century, synthetic polymers were made. The first polymers of importance, Bakelite and nylon, showed the tremendous possibilities of the new materials. However, the scientists of that day realized that they did not understand many of the relationships between the chemical structures and the physical properties that resulted. The research that ensued forms the basis for physical polymer science.

This book develops the subject of physical polymer science, describing the interrelationships among polymer structure, morphology, and physical and mechanical behavior. Key aspects include molecular weight and molecular weight distribution, and the organization of the atoms down the polymer chain. Many polymers crystallize, and the size, shape, and organization of the

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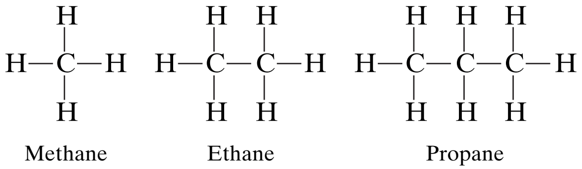
crystallites depend on how the polymer was crystallized. Such effects as annealing are very important, as they have a profound influence on the final state of molecular organization.

Other polymers are amorphous, often because their chains are too irregular to permit regular packing. The onset of chain molecular motion heralds the glass transition and softening of the polymer from the glassy (plastic) state to the rubbery state. Mechanical behavior includes such basic aspects as modulus, stress relaxation, and elongation to break. Each of these is relatable to the polymer's basic molecular structure and history.

This chapter provides the student with a brief introduction to the broader field of polymer science. Although physical polymer science does not include polymer synthesis, some knowledge of how polymers are made is helpful in understanding configurational aspects, such as tacticity, which are concerned with how the atoms are organized along the chain. Similarly polymer molecular weights and distributions are controlled by the synthetic detail. This chapter starts at the beginning of polymer science, and it assumes no prior knowledge of the field.

1.1 FROM LITTLE MOLECULES TO BIG MOLECULES

The behavior of polymers represents a continuation of the behavior of smaller molecules at the limit of very high molecular weight. As a simple example, consider the normal alkane hydrocarbon series



$$\underset{\text{Methane}}{\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}} \quad \underset{\text{Ethane}}{\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}} \quad \underset{\text{Propane}}{\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}} \tag{1.1}$$

These compounds have the general structure

$$\mathrm{H}\!\left(\mathrm{CH_2}\right)_{n}\mathrm{H} \tag{1.2}$$

where the number of —CH_2— groups, n, is allowed to increase up to several thousand. The progression of their state and properties is shown in Table 1.1.

At room temperature, the first four members of the series are gases. n-Pentane boils at 36.1°C and is a low-viscosity liquid. As the molecular weight of the series increases, the viscosity of the members increases. Although commercial gasolines contain many branched-chain materials and aromatics as well as straight-chain alkanes, the viscosity of gasoline is markedly lower than that of kerosene, motor oil, and grease because of its lower average chain length.

These latter materials are usually mixtures of several molecular species, although they are easily separable and identifiable. This point is important

Table 1.1 Properties of the alkane/polyethylene series

Number of Carbons in Chain	State and Properties of Material	Applications
1–4	Simple gas	Bottled gas for cooking
5–11	Simple liquid	Gasoline
9–16	Medium-viscosity liquid	Kerosene
16–25	High-viscosity liquid	Oil and grease
25–50	Crystalline solid	Paraffin wax candles
50–1000	Semicrystalline solid	Milk carton adhesives and coatings
1000–5000	Tough plastic solid	Polyethylene bottles and containers
$3–6 \times 10^5$	Fibers	Surgical gloves, bullet-proof vests

because most polymers are also "mixtures"; that is, they have a molecular weight distribution. In high polymers, however, it becomes difficult to separate each of the molecular species, and people talk about molecular weight averages.

Compositions of normal alkanes averaging more than about 20 to 25 carbon atoms are crystalline at room temperature. These are simple solids known as wax. It must be emphasized that at up to 50 carbon atoms the material is far from being polymeric in the ordinary sense of the term.

The polymeric alkanes with no side groups that contain 1000 to 3000 carbon atoms are known as polyethylenes. Polyethylene has the chemical structure

$$+\!\!\left(CH_2-CH_2 \right)\!\!+_n \tag{1.3}$$

which originates from the structure of the monomer ethylene, $CH_2{=}CH_2$. The quantity n is the number of mers—or monomeric units in the chain. In some places the structure is written

$$+\!\!\left(CH_2 \right)\!\!+_{n'} \tag{1.4}$$

or polymethylene. (Then $n' = 2n$.) The relationship of the latter structure to the alkane series is clearer. While true alkanes have CH_3— as end groups, most polyethylenes have initiator residues.

Even at a chain length of thousands of carbons, the melting point of polyethylene is still slightly molecular-weight-dependent, but most linear polyethylenes have melting or fusion temperatures, T_f, near 140°C. The approach to the theoretical asymptote of about 145°C at infinite molecular weight (1) is illustrated schematically in Figure 1.1.

The greatest differences between polyethylene and wax lie in their mechanical behavior, however. While wax is a brittle solid, polyethylene is a tough plastic. Comparing resistance to break of a child's birthday candle with a wash bottle tip, both of about the same diameter, shows that the wash bottle tip can be repeatedly bent whereas the candle breaks on the first deformation.

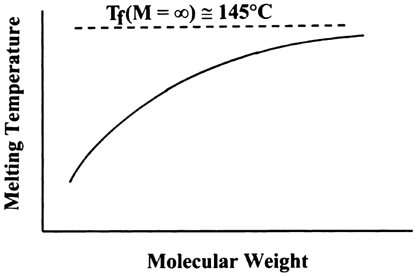


Figure 1.1 The molecular weight-melting temperature relationship for the alkane series. An asymptotic value of about 145°C is reached for very high molecular weight linear polyethylenes.

Polyethylene is a tough plastic solid because its chains are long enough to connect individual stems together within a lamellar crystallite by chain folding (see Figure 1.2). The chains also wander between lamellae, connecting several of them together. These effects add strong covalent bond connections both within the lamellae and between them. On the other hand, only weak van der Waals forces hold the chains together in wax.

In addition a certain portion of polyethylene is amorphous. The chains in this portion are rubbery, imparting flexibility to the entire material. Wax is 100% crystalline, by difference.

The long chain length allows for entanglement (see Figure 1.3). The entanglements help hold the whole material together under stress. In the melt state, chain entanglements cause the viscosity to be raised very significantly also.

The long chains shown in Figure 1.3 also illustrate the coiling of polymer chains in the amorphous state. One of the most powerful theories in polymer science (2) states that the conformations of amorphous chains in space are random coils; that is, the directions of the chain portions are statistically determined.

1.2 MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTIONS

While the exact molecular weight required for a substance to be called a polymer is a subject of continued debate, often polymer scientists put the number at about 25,000 g/mol. This is the minimum molecular weight required for good physical and mechanical properties for many important polymers. This molecular weight is also near the onset of entanglement.

1.2.1 Effect on Tensile Strength

The tensile strength of any material is defined as the stress at break during elongation, where stress has the units of Pa, dyn/cm^2, or lb/in^2; see Chapter 11.

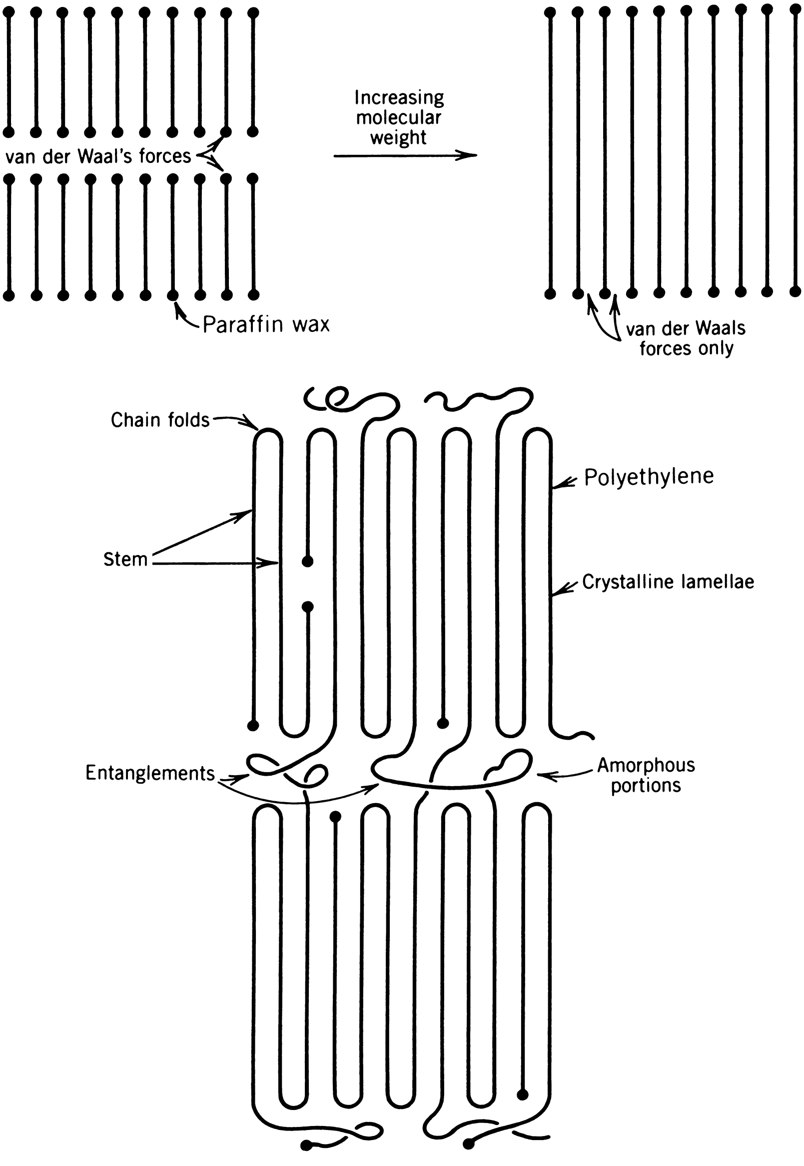


Figure 1.2 Comparison of wax and polyethylene structure and morphology.

The effect of molecular weight on the tensile strength of polymers is illustrated in Figure 1.4. At very low molecular weights the tensile stress to break, σ_b, is near zero. As the molecular weight increases, the tensile strength increases rapidly, and then gradually levels off. Since a major point of weakness at the molecular level involves the chain ends, which do not transmit the covalent bond strength, it is predicted that the tensile strength reaches an asymptotic

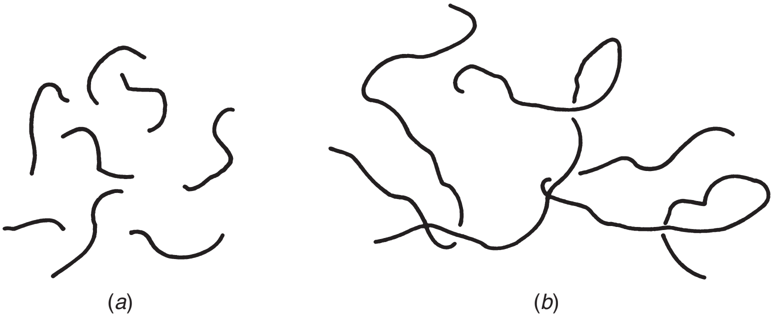


Figure 1.3 Entanglement of polymer chains. (*a*) Low molecular weight, no entanglement. (*b*) High molecular weight, chains are entangled. The transition between the two is often at about 600 backbone chain atoms.

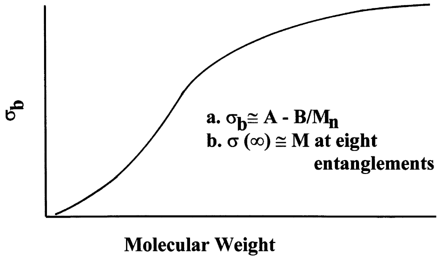


Figure 1.4 Effect of polymer molecular weight on tensile strength.

value at infinite molecular weight. A large part of the curve in Figure 1.4 can be expressed (3,4)

$$\sigma_b = A - \frac{B}{M_n} \tag{1.5}$$

where M_n is the number-average molecular weight (see below) and A and B are constants. Newer theories by Wool (3) and others suggest that more than 90% of tensile strength and other mechanical properties are attained when the chain reaches eight entanglements in length.

1.2.2 Molecular Weight Averages

The same polymer from different sources may have different molecular weights. Thus polyethylene from source A may have a molecular weight of 150,000 g/mol, whereas polyethylene from source B may have a molecular weight of 400,000 g/mol (see Figure 1.5). To compound the difficulty, all common synthetic polymers and most natural polymers (except proteins) have a distribution in molecular weights. That is, some molecules in a given sample

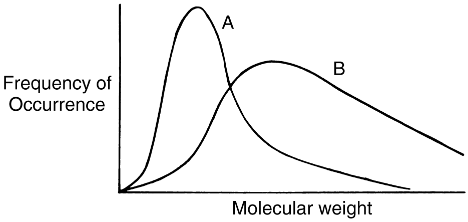


Figure 1.5 Molecular weight distributions of the same polymer from two different sources, A and B.

of polyethylene are larger than others. The differences result directly from the kinetics of polymerization.

However, these facts led to much confusion for chemists early in the twentieth century. At that time chemists were able to understand and characterize small molecules. Compounds such as hexane all have six carbon atoms. If polyethylene with 2430 carbon atoms were declared to be "polyethylene," how could that component having 5280 carbon atoms also be polyethylene? How could two sources of the material having different average molecular weights both be polyethylene, noting A and B in Figure 1.5?

The answer to these questions lies in defining average molecular weights and molecular weight distributions (5,6). The two most important molecular weight averages are the number-average molecular weight, M_n,

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{1.6}$$

where N_i is the number of molecules of molecular weight M_i, and the weight-average molecular weight, M_w,

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{1.7}$$

For single-peaked distributions, M_n is usually near the peak. The weight-average molecular weight is always larger. For simple distributions, M_w may be 1.5 to 2.0 times M_n. The ratio M_w/M_n, sometimes called the polydispersity index, provides a simple definition of the molecular weight distribution. Thus all compositions of $\text{+}CH_2\text{—}CH_2\text{+}_n$ are called polyethylene, the molecular weights being specified for each specimen.

For many polymers a narrower molecular distribution yields better properties. The low end of the distribution may act as a plasticizer, softening the material. Certainly it does not contribute as much to the tensile strength. The high-molecular-weight tail increases processing difficulties, because of its enormous contribution to the melt viscosity. For these reasons, great emphasis is placed on characterizing polymer molecular weights.

1.3 MAJOR POLYMER TRANSITIONS

Polymer crystallinity and melting were discussed previously. Crystallization is an example of a first-order transition, in this case liquid to solid. Most small molecules crystallize, an example being water to ice. Thus this transition is very familiar.

A less classical transition is the glass–rubber transition in polymers. At the glass transition temperature, T_g, the amorphous portions of a polymer soften. The most familiar example is ordinary window glass, which softens and flows at elevated temperatures. Yet glass is not crystalline, but rather it is an amorphous solid. It should be pointed out that many polymers are totally amorphous. Carried out under ideal conditions, the glass transition is a type of second-order transition.

The basis for the glass transition is the onset of coordinated molecular motion is the polymer chain. At low temperatures, only vibrational motions are possible, and the polymer is hard and glassy (Figure 1.6, region 1) (7). In the glass transition region, region 2, the polymer softens, the modulus drops three orders of magnitude, and the material becomes rubbery. Regions 3, 4, and 5 are called the rubbery plateau, the rubbery flow, and the viscous flow regions, respectively. Examples of each region are shown in Table 1.2.

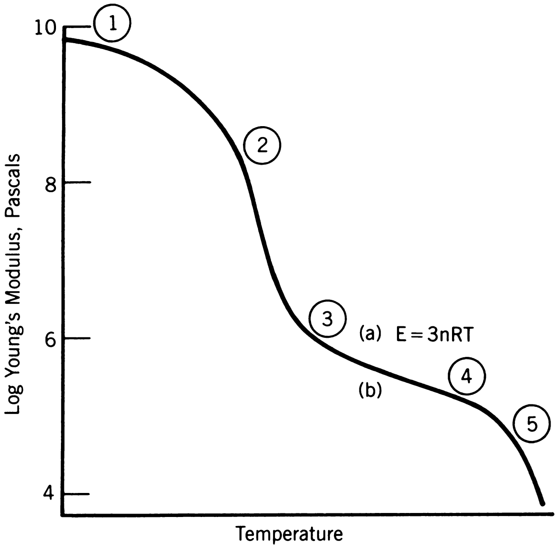


Figure 1.6 Idealized modulus–temperature behavior of an amorphous polymer. Young's modulus, stress/strain, is a measure of stiffness.

Table 1.2 Typical polymer viscoelastic behavior at room temperature (7a)

Region	Polymer	Application
Glassy	Poly(methyl methacrylate)	Plastic
Glass transition	Poly(vinyl acetate)	Latex paint
Rubbery plateau	*Cross*-poly(butadiene–*stat*–styrene)	Rubber bands
Rubbery flow	Chicle[a]	Chewing gum
Viscous flow	Poly(dimethylsiloxane)	Lubricant

[a] From the latex of *Achras sapota*, a mixture of *cis*- and *trans*-polyisoprene plus polysaccharides.

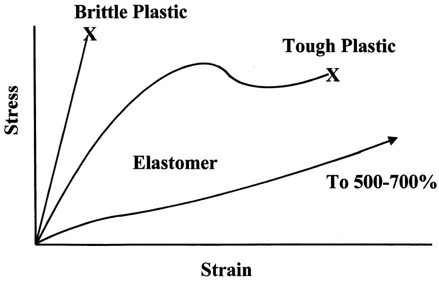


Figure 1.7 Stress–strain behavior of various polymers. While the initial slope yields the modulus, the area under the curve provides the energy to fracture.

Depending on the region of viscoelastic behavior, the mechanical properties of polymers differ greatly. Model stress–strain behavior is illustrated in Figure 1.7 for regions 1, 2, and 3. Glassy polymers are stiff and often brittle, breaking after only a few percent extension. Polymers in the glass transition region are more extensible, sometimes exhibiting a yield point (the hump in the tough plastic stress–strain curve). If the polymer is above its brittle–ductile transition, Section 11.2.3, rubber-toughened, Chapter 13, or semicrystalline with its amorphous portions above T_g, tough plastic behavior will also be observed. Polymers in the rubbery plateau region are highly elastic, often stretching to 500% or more. Regions 1, 2, and 3 will be discussed further in Chapters 8 and 9. Regions 4 and 5 flow to increasing extents under stress; see Chapter 10.

Cross-linked amorphous polymers above their glass transition temperature behave rubbery. Examples are rubber bands and automotive tire rubber. In general, Young's modulus of elastomers in the rubbery-plateau region is higher than the corresponding linear polymers, and is governed by the relation $E = 3nRT$, in Figure 1.6 (line not shown); the linear polymer behavior is illustrated by the line (*b*). Here, n represents the number of chain segments bound at both ends in a network, per unit volume. The quantities R and T are the gas constant and the absolute temperature, respectively.

Polymers may also be partly crystalline. The remaining portion of the polymer, the amorphous material, may be above or below its glass transition

Table 1.3 Examples of polymers at room temperature by transition behavior

	Crystalline	Amorphous
Above T_g	Polyethylene	Natural rubber
Below T_g	Cellulose	Poly(methyl methacrylate)

temperature, creating four subclasses of materials. Table 1.3 gives a common example of each. While polyethylene and natural rubber need no further introduction, common names for processed cellulose are rayon and cellophane. Cotton is nearly pure cellulose, and wood pulp for paper is 80 to 90% cellulose. A well-known trade name for poly(methyl methacrylate) is Plexiglas®. The modulus–temperature behavior of polymers in either the rubbery-plateau region or in the semicrystalline region are illustrated further in Figure 8.2, Chapter 8.

Actually there are two regions of modulus for semicrystalline polymers. If the amorphous portion is above T_g, then the modulus is generally between rubbery and glassy. If the amorphous portion is glassy, then the polymer will be actually be a bit stiffer than expected for a 100% glassy polymer.

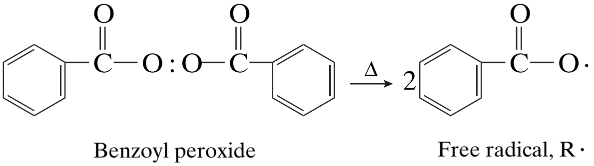
1.4 POLYMER SYNTHESIS AND STRUCTURE

1.4.1 Chain Polymerization

Polymers may be synthesized by two major kinetic schemes, chain and stepwise polymerization. The most important of the chain polymerization methods is called free radical polymerization.

1.4.1.1 Free Radical Polymerization The synthesis of poly(ethyl acrylate) will be used as an example of free radical polymerization. Benzoyl peroxide is a common initiator. Free radical polymerization has three major kinetic steps—initiation, propagation, and termination.

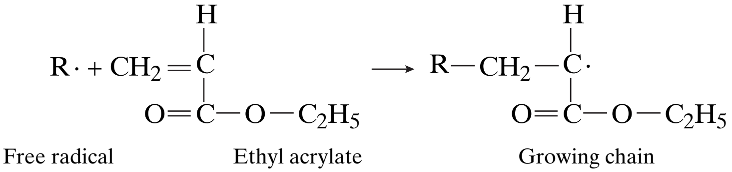
1.4.1.2 Initiation On heating, benzoyl peroxide decomposes to give two free radicals:



(1.8)

In this reaction the electrons in the oxygen–oxygen bond are unpaired and become the active site. With R representing a generalized organic chemical group, the free radical can be written R·. (It should be pointed out that hydrogen peroxide undergoes the same reaction on a wound, giving a burning sensation as the free radicals "kill the germs.")

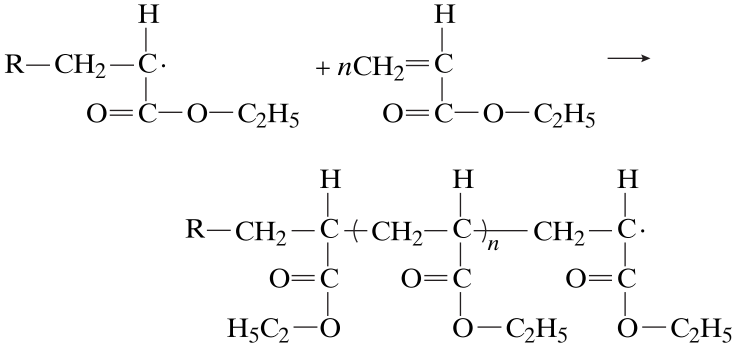
The initiation step usually includes the addition of the first monomer molecule:



$$\mathrm{R\cdot} + \mathrm{CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}} \longrightarrow \mathrm{R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}\cdot} \tag{1.9}$$

In this reaction the free radical attacks the monomer and adds to it. The double bond is broken open, and the free radical reappears at the far end.

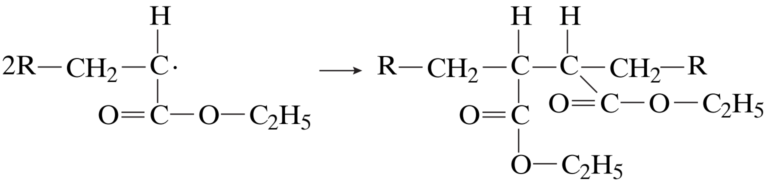
1.4.1.3 Propagation After initiation reactions (1.8) and (1.9), many monomer molecules are added rapidly, perhaps in a fraction of a second:



$$\mathrm{R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}\cdot} + n\mathrm{CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}} \longrightarrow \mathrm{R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}\underset{\displaystyle H_5C_2{-}O}{C}}{C}}\!\left(CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}\underset{\displaystyle O{-}C_2H_5}{C}}{C}}\right)_{\!n}\!{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}\underset{\displaystyle O{-}C_2H_5}{C}}{C}}\cdot} \tag{1.10}$$

On the addition of each monomer, the free radical moves to the end of the chain.

1.4.1.4 Termination In the termination reaction, two free radicals react with each other. Termination is either by combination,



$$2\mathrm{R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}\cdot} \longrightarrow \mathrm{R{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}\underset{\displaystyle O{-}C_2H_5}{C}}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{C}}{-}CH_2{-}R} \tag{1.11}$$

where R now represents a long-chain portion, or by disproportionation, where a hydrogen is transferred from one chain to the other. This latter result produces in two final chains. While the normal mode of addition is a head-to-tail reaction (1.10), this termination step is normally head-to-head.

As a homopolymer, poly(ethyl acrylate) is widely used as an elastomer or adhesive, being a polymer with a low T_g, –22°C. As a copolymer with other acrylics it is used as a latex paint.

1.4.1.5 *Structure and Nomenclature* The principal method of polymerizing monomers by the chain kinetic scheme involves the opening of double bonds to form a linear molecule. In a reacting mixture, monomer, fully reacted polymer, and only a small amount of rapidly reacting species are present. Once the polymer terminates, it is "dead" and cannot react further by the synthesis scheme outlined previously.

Polymers are named by rules laid out by the IUPAC Nomenclature Committee (8,9). For many simple polymers the source-based name utilizes the monomer name prefixed by "poly." If the monomer name has two or more words, parentheses are placed around the monomer name. Thus, in the above, the monomer ethyl acrylate is polymerized to make poly(ethyl acrylate). Source-based and IUPAC names are compared in Appendix 1.1.

Table 1.4 provides a selected list of common chain polymer structures and names along with comments as to how the polymers are used. The "vinyl" monomers are characterized by the general structure $CH_2{=}CHR$, where R represents any side group. One of the best-known vinyl polymers is poly(vinyl chloride), where R is —Cl.

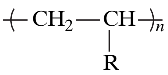
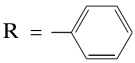
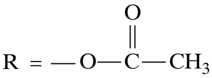
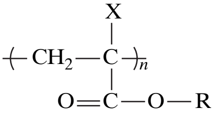
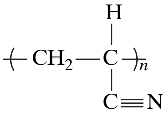
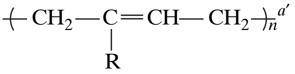
Polyethylene and polypropylene are the major members of the class of polymers known as *polyolefins*; see Section 14.1. The term *olefin* derives from the double-bond characteristic of the alkene series.

A slight dichotomy exists in the writing of vinyl polymer structures. From a correct nomenclature point of view, the pendant moiety appears on the left-hand carbon. Thus poly(vinyl chloride) should be written $\text{+}CHCl{-}CH_2\text{+}_n$. However, from a synthesis point of view, the structure is written $\text{+}CH_2{-}CHCl\text{+}_n$, because the free radical is borne on the pendant moiety carbon. Thus both forms appear in the literature.

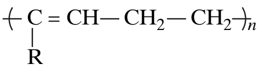
The diene monomer has the general structure $CH_2{=}CR{-}CH{=}CH_2$, where on polymerization one of the double bonds forms the chain bonds, and the other goes to the central position. The vinylidenes have two groups on one carbon. Table 1.4 also lists some common copolymers, which are formed by reacting two or more monomers together. In general, the polymer structure most closely resembling the monomer structure will be presented herein.

Today, recycling of plastics has become paramount in preserving the environment. On the bottom of plastic bottles and other plastic items is an identification number and letters; see Table 1.5. This information serves to help in separation of the plastics prior to recycling. Observation of the properties of the plastic such as modulus, together with the identification, will help

Table 1.4 Selected chain polymer structures and nomenclature

Structure	Name	Where Used
 $(\mathrm{CH_2}-\underset{\mathrm{R}}{\underset{\vert}{\mathrm{CH}}})_n$	"Vinyl" class	
R = —H	Polyethylene	Plastic
R = —$\mathrm{CH_3}$	Polypropylene	Rope
	Polystyrene	Drinking cups
R = —Cl	Poly(vinyl chloride)	"Vinyl," water pipes
 $\mathrm{R} = -\mathrm{O}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{CH_3}$	Poly(vinyl acetate)	Latex paints
R = —OH	Poly(vinyl alcohol)	Fiber
 $(\mathrm{CH_2}-\overset{\mathrm{X}}{\overset{\vert}{\underset{\mathrm{O=C-O-R}}{\underset{\vert}{\mathrm{C}}}}})_n$	X = —H, acrylics X = —$\mathrm{CH_3}$, methacrylics	
X = —H, R = —$\mathrm{C_2H_5}$	Poly(ethyl acrylate)	Latex paints
X = —$\mathrm{CH_3}$, R = —$\mathrm{CH_3}$	Poly(methyl methacrylate)	Plexiglas®
X = —$\mathrm{CH_3}$, R = —$\mathrm{C_2H_5}$	Poly(ethyl methacrylate)	Adhesives
 $(\mathrm{CH_2}-\overset{\mathrm{H}}{\overset{\vert}{\underset{\mathrm{C\equiv N}}{\underset{\vert}{\mathrm{C}}}}})_n$	Polyacrylonitrile[a]	Orlon®
 $(\mathrm{CH_2}-\underset{\mathrm{R}}{\underset{\vert}{\mathrm{C}}}=\mathrm{CH-CH_2})_n$[a']	"Diene" class	
R = —H	Polybutadiene	Tires
R = —$\mathrm{CH_3}$	Polyisoprene	Natural rubber
R = —Cl	Polychloroprene	Neoprene
$(\mathrm{CX_2-CR_2})_n$	Vinylidenes	
X = —H, R = —F	Poly(vinylidene fluoride)	Plastic
X = —H, R = —F	Polytetrafluoroethylene	Teflon®
X = —H, R = —$\mathrm{CH_3}$	Polyisobutene[b]	Elastomer
	Common Copolymers	
EPDM	Ethylene–propylene–diene–monomer	Elastomer
SBR	Styrene–butadiene–rubber Poly(styrene–*stat*–butadiene)[c]	Tire rubber
NBR	Acrylonitrile–butadiene–rubber Poly(acrylonitrile–*stat*–butadiene)	Elastomer
ABS	Acrylonitrile–butadiene–styrene[d]	Plastic

[a] Polyacrylonitrile is technically a number of the acrylic class because it forms acrylic acid on hydrolysis.

[a'] IUPAC recommends  $(\underset{\mathrm{R}}{\underset{\vert}{\mathrm{C}}}=\mathrm{CH-CH_2-CH_2})_n$

[b] Also called polyisobutylene. The 2% copolymer with isoprene, after vulcanization, is called butyl rubber.

[c] The term–*stat*–means statistical copolymer, as explained in Chapter 2.

[d] ABS is actually a blend or graft of two random copolymers, poly(acrylonitrile–*stat*–butadiene) and poly(acrylonitrile–*stat*–styrene).

Table 1.5 The plastics identification code

Code	Letter I.D.	Polymer Name
♳	PETE	Poly(ethylene terephthalate)
♴	HDPE	High-density polyethylene
♵	V	Poly(vinyl chloride)
♶	LDPE	Low-density polyethylene
♷	PP	Polypropylene
♸	PS	Polystyrene
♹	Other	Different polymers

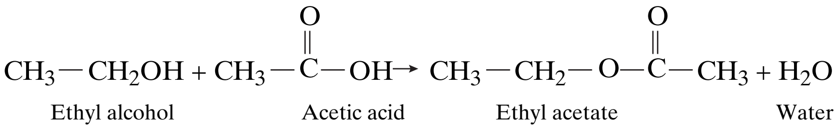
Source: From the *Plastic Container Code System*, The Plastic Bottle Information Bureau, Washington, DC.

the student understand the kinds and properties of the plastics in common service.

1.4.2 Step Polymerization

1.4.2.1 A Polyester Condensation Reaction The second important kinetic scheme is step polymerization. As an example of a step polymerization, the synthesis of a polyester is given.

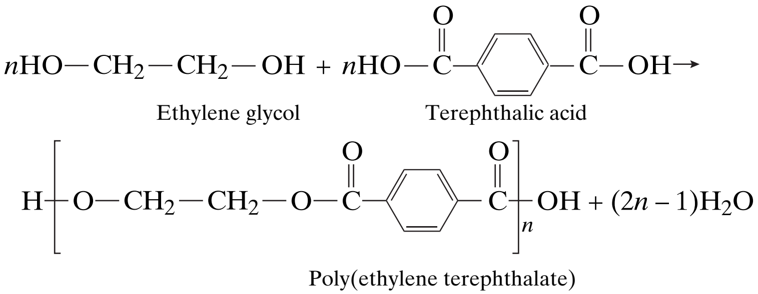
The general reaction to form esters starts with an acid and an alcohol:



$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2OH} + \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \rightarrow \underset{\text{Ethyl acetate}}{CH_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + \underset{\text{Water}}{H_2O} \tag{1.12}$$

where the ester group is $-O-\overset{\overset{\displaystyle O}{\|}}{C}-$, and water is eliminated.

The chemicals above cannot form a polyester because they have only one functional group each. When the two reactants each have bifunctionality, a linear polymer is formed:

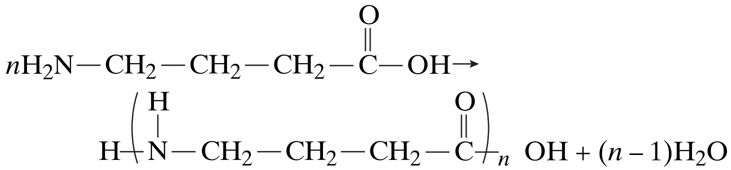


(1.13)

In the stepwise reaction scheme, monomers, dimers, trimers, and so on, may all react together. All that is required is that the appropriate functional groups meet in space. Thus the molecular weight slowly climbs as the small molecule water is eliminated. Industrially, $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ is replaced by $-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$. Then, the reaction is an ester interchange, releasing methanol.

Poly(ethylene terephthalate) is widely known as the fiber Dacron®. It is highly crystalline, with a melting temperature of about +265°C.

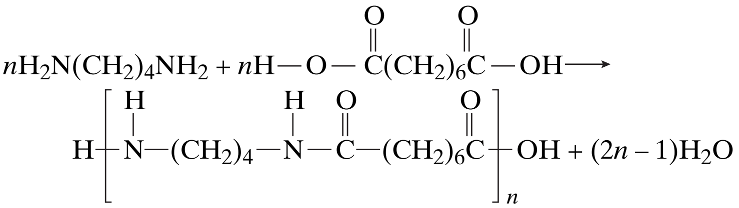
Another well-known series of polymers made by step polymerization reactions is the polyamides, known widely as the nylons. In fact there are two series of nylons. In the first series, the monomer has an amine at one end of the molecule and a carboxyl at the other. For example,



$$nH_2N-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightarrow H\left(\overset{\overset{\displaystyle H}{|}}{N}-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\right)_n OH + (n-1)H_2O \tag{1.14}$$

which is known as nylon 4. The number 4 indicates the number of carbon atoms in the mer.

In the second series, a dicarboxylic acid is reacted with a diamine:



$$nH_2N(CH_2)_4NH_2 + nH-O-\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_6\overset{\overset{\displaystyle O}{\|}}{C}-OH \longrightarrow H\left[\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_4-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_6\overset{\overset{\displaystyle O}{\|}}{C}\right]_n OH + (2n-1)H_2O \tag{1.15}$$

which is named nylon 48. Note that the amine carbon number is written first, and the acid carbon number second. For reaction purposes, acyl chlorides are frequently substituted for the carboxyl groups. An excellent demonstration experiment is described by Morgan and Kwolek (10), called the nylon rope trick.

1.4.2.2 Stepwise Nomenclature and Structures Table 1.6 names some of the more important stepwise polymers. The polyesters have already been mentioned. The nylons are known technically as polyamides. There are two important subseries of nylons, where amine and the carboxylic acid are on different monomer molecules (thus requiring both monomers to make the polymer) or one each on the ends of the same monomer molecule. These are numbered by the number of carbons present in the monomer species. It must be mentioned that the proteins are also polyamides.

Other classes of polymers mentioned in Table 1.6 include the polyurethanes, widely used as elastomers; the silicones, also elastomeric; and the cellulosics, used in fibers and plastics. Cellulose is a natural product.

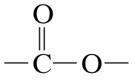
Another class of polymers are the polyethers, prepared by ring-opening reactions. The most important member of this series is poly(ethylene oxide),

$$-\!\!\left(\text{CH}_2-\text{CH}_2-\text{O}\right)\!\!-_n$$

Because of the oxygen atom, poly(ethylene oxide) is water soluble.

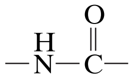
To summarize the material in Table 1.6, the major stepwise polymer classes contain the following identifying groups:

Polyesters



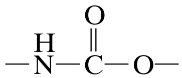
$$-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{O}-$$

Polyamides



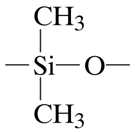
$$-\overset{\displaystyle \text{H}}{\text{N}}-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-$$

Polyurethanes



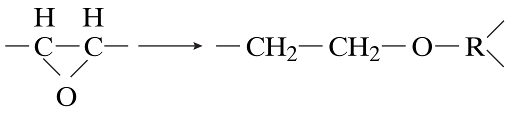
$$-\overset{\displaystyle \text{H}}{\text{N}}-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{O}-$$

Silicones



$$-\underset{\underset{\displaystyle \text{CH}_3}{|}}{\overset{\overset{\displaystyle \text{CH}_3}{|}}{\text{Si}}}-\text{O}-$$

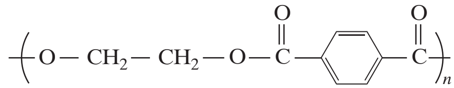
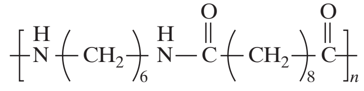
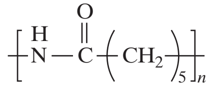
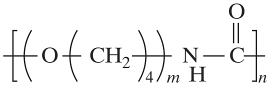
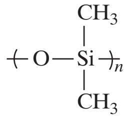
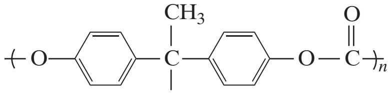
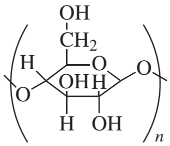
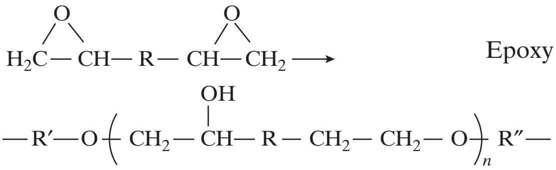
Epoxy resins



Polyethers $-\text{O}-$

1.4.2.3 Natural Product Polymers Living organisms make many polymers, nature's best. Most such natural polymers strongly resemble step-polymerized materials. However, living organisms make their polymers enzymatically, the structure ultimately being controlled by DNA, itself a polymer.

Table 1.6 Selected stepwise structures and nomenclature

Structure[a]	Name	Where Known
	Poly(ethylene terephthalate)	Dacron®
 $\left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_8-\overset{O}{\overset{\Vert}{C}}\right]_n$	Poly(hexamethylene sebacamide)	Polyamide 610[b]
 $\left[\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5\right]_n$	Polycaprolactam	Polyamide 6
$\left[O-CH_2\right]_n$	Polyoxymethylene	Polyacetal
$\left[O-(CH_2)_4\right]_n$	Polytetrahydrofuran	Polyether
 $\left[\left(O-(CH_2)_4\right)_m\underset{H}{N}-\overset{O}{\overset{\Vert}{C}}\right]_n$	Polyurethane[c]	Spandex Lycra®
 $\left(O-\underset{CH_3}{\overset{CH_3}{Si}}\right)_n$	Poly(dimethyl siloxane)	Silicone rubber
	Polycarbonate	Lexan®
	Cellulose	Cotton
	Epoxy resins	Epon®

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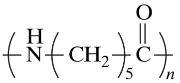
[a] Some people see the mer structure in the third row more clearly with



$$\left(\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}\right)_n$$

Some other step polymerization mers can also be drawn in two or more different ways. The student should learn to recognize the structures in different ways.

[b] The "6" refers to the number of carbons in the diamine portion, and the "10" to the number of carbons in the diacid. An old name is nylon 610.

[c] The urethane group usually links polyether or polyester low molecular weight polymers together.

Table 1.7 Some natural product polymers

Name	Source	Application
Cellulose	Wood, cotton	Paper, clothing, rayon, cellophane
Starch	Potatoes, corn	Food, thickener
Wool	Sheep	Clothing
Silk	Silkworm	Clothing
Natural rubber	Rubber tree	Tires
Pitch	Oil deposits	Coating, roads

Some of the more important commercial natural polymers are shown in Table 1.7. People sometimes refer to these polymers as natural products or renewable resources.

Wool and silk are both proteins. All proteins are actually copolymers of polyamide-2 (or nylon-2, old terminology). As made by plants and animals, however, the copolymers are highly ordered, and they have monodisperse molecular weights, meaning that all the chains have the same molecular weights.

Cellulose and starch are both polysaccharides, being composed of chains of glucose-based rings but bonded differently. Their structures are discussed further in Appendix 2.1.

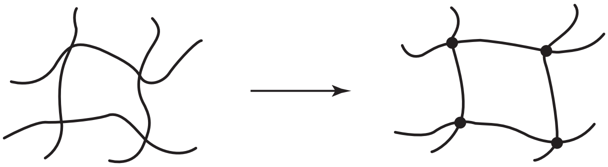
Natural rubber, the hydrocarbon polyisoprene, more closely resembles chain polymerized materials. In fact synthetic polyisoprene can be made either by free radical polymerization or anionic polymerization. The natural and synthetic products compete commercially with each other.

Pitch, a decomposition product, usually contains a variety of aliphatic and aromatic hydrocarbons, some of very high molecular weight.

1.5 CROSS-LINKING, PLASTICIZERS, AND FILLERS

The above provides a brief introduction to simple homopolymers, as made pure. Only a few of these are finally sold as "pure" polymers, such as polystyrene drinking cups and polyethylene films. Much more often, polymers are sold with various additives. That the student may better recognize the polymers, the most important additives are briefly discussed.

On heating, linear polymers flow and are termed thermoplastics. To prevent flow, polymers are sometimes cross-linked (•):



(1.16)

The cross-linking of rubber with sulfur is called vulcanization. Cross-linking bonds the chains together to form a network. The resulting product is called a thermoset, because it does not flow on heating.

Plasticizers are small molecules added to soften a polymer by lowering its glass transition temperature or reducing its crystallinity or melting temperature. The most widely plasticized polymer is poly(vinyl chloride). The distinctive odor of new "vinyl" shower curtains is caused by the plasticizer, for example.

Fillers may be of two types, reinforcing and nonreinforcing. Common reinforcing fillers are the silicas and carbon blacks. The latter are most widely used in automotive tires to improve wear characteristics such as abrasion resistance. Nonreinforcing fillers, such as calcium carbonate, may provide color or opacity or may merely lower the price of the final product.

1.6 THE MACROMOLECULAR HYPOTHESIS

In the nineteenth century, the structure of polymers was almost entirely unknown. The Germans called it *Schmierenchemie*, meaning grease chemistry (11), but a better translation might be "the gunk at the bottom of the flask," that portion of an organic reaction that did not result in characterizable products. In the nineteenth century and early twentieth century the field of polymers and the field of colloids were considered integral parts of the same field. Wolfgang Ostwald declared in 1917 (12):

> All those sticky, mucilaginous, resinous, tarry masses which refuse to crystallize, and which are the abomination of the normal organic chemist; those substances which he carefully sets toward the back of his cupboard . . . , just these are the substances which are the delight of the colloid chemist.

Indeed, those old organic colloids (now polymers) and inorganic colloids such as soap micelles and silver or sulfur sols have much in common (11):

1. Both types of particles are relatively small, 10^{-6} to 10^{-4} mm, and visible via ultramicroscopy[†] as dancing light flashes, that is, Brownian motion.
2. The elemental composition does not change with the size of the particle.

Thus, soap micelles (true aggregates) and polymer chains (which repeat the same structure but are covalently bonded) appeared the same in those days. Partial valences (see Section 6.12) seemed to explain the bonding in both types.

[†] Ultramicroscopy is an old method used to study very small particles dispersed in a fluid for examination, and below normal resolution. Although invisible in ordinary light, colloidal particles become visible when intensely side-illuminated against a dark background.

In 1920 Herman Staudinger (13,14) enunciated the *Macromolecular Hypothesis*. It states that certain kinds of these colloids actually consist of very long-chained molecules. These came to be called polymers because many (but not all) were composed of the same repeating unit, or mer. In 1953 Staudinger won the Nobel prize in chemistry for his discoveries in the chemistry of macromolecular substances (15). The Macromolecular Hypothesis is the origin of modern polymer science, leading to our current understanding of how and why such materials as plastics and rubber have the properties they do.

1.7 HISTORICAL DEVELOPMENT OF INDUSTRIAL POLYMERS

Like most other technological developments, polymers were first used on an empirical basis, with only a very incomplete understanding of the relationships between structure and properties. The first polymers used were natural products that date back to antiquity, including wood, leather, cotton, various grasses for fibers, papermaking, and construction, wool, and protein animal products boiled down to make glues and related material.

Then came several semisynthetic polymers, which were natural polymers modified in some way. One of the first to attain commercial importance was cellulose nitrate plasticized with camphor, popular around 1885 for stiff collars and cuffs as celluloid, later most notably used in Thomas Edison's motion picture film (11). Cellulose nitrates were also sold as lacquers, used to coat wooden staircases, and so on. The problem was the terrible fire hazard existing with the nitrates, which were later replaced by the acetates.

Other early polymer materials included Chardonnet's artificial silk, made by regenerating and spinning cellulose nitrate solutions, eventually leading to the viscose process for making rayon (see Section 6.10) still in use today.

The first truly synthetic polymer was a densely cross-linked material based on the reaction of phenol and formaldehyde; see Section 14.2. The product, called Bakelite, was manufactured from 1910 onward for applications ranging from electrical appliances to phonograph records (16,17). Another early material was the General Electric Company's Glyptal, based on the condensation reaction of glycerol and phthalic anhydride (18), which followed shortly after Bakelite. However, very little was known about the actual chemical structure of these polymers until after Staudinger enunciated the Macromolecular Hypothesis in 1920.

All of these materials were made on a more or less empirical basis; trial and error have been the basis for very many advances in history, including polymers. However, in the late 1920s and 1930s, a DuPont chemist by the name of Wallace Carothers succeeded in establishing the reality of the Macromolecular Hypothesis by bringing the organic-structural approach back to the study of polymers, resulting in the discovery of nylon and neoprene. Actually the first polymers that Carothers discovered were polyesters (19). He reasoned that if the Macromolecular Hypothesis was correct, then if one mixed a molecule with dihydroxide end groups with a another molecule with diacid end

Table 1.8 Commercialization dates of selected synthetic polymers (20)

Year	Polymer	Producer
1909	Poly(phenol–*co*–formaldehyde)	General Bakelite Corporation
1927	Poly(vinyl chloride)	B.F. Goodrich
1929	Poly(styrene–*stat*–butadiene)	I.G. Farben
1930	Polystyrene	I.G. Farben/Dow
1936	Poly(methyl methacrylate)	Rohm and Haas
1936	Nylon 66 (Polyamide 66)	DuPont
1936	Neoprene (chloroprene)	DuPont
1939	Polyethylene	ICI
1943	Poly(dimethylsiloxane)	Dow Corning
1954	Poly(ethylene terephthalate)	ICI
1960	Poly(*p*-phenylene terephthalamide)[a]	DuPont
1982	Polyetherimide	GEC

[a] Kevlar; see Chapter 7.

groups and allowed them to react, a long, linear chain should result if the stoichiometry was one-to-one.

The problem with the aliphatic polyesters made at that time was their low melting point, making them unsuitable for clothing fibers because of hot water washes and ironing. When the ester groups were replaced with the higher melting amide groups, the nylon series was born. In the same time frame, Carothers discovered neoprene, which was a chain-polymerized product of an isoprene-like monomer with a chlorine replacing the methyl group.

Bakelite was a thermoset; that is, it did not flow after the synthesis was complete (20). The first synthetic thermoplastics, materials that could flow on heating, were poly(vinyl chloride), poly(styrene–*stat*–butadiene), polystyrene, and polyamide 66; see Table 1.8 (20). Other breakthrough polymers have included the very high modulus aromatic polyamides, known as Kevlar™ (see Section 7.4), and a host of high temperature polymers.

Further items on the history of polymer science can be found in Appendix 5.1, and Sections 6.1.1 and 6.1.2.

1.8 MOLECULAR ENGINEERING

The discussion above shows that polymer science is an admixture of pure and applied science. The structure, molecular weight, and shape of the polymer molecule are all closely tied to the physical and mechanical properties of the final material.

This book emphasizes physical polymer science, the science of the interrelationships between polymer structure and properties. Although much of the material (except the polymer syntheses) is developed in greater detail in the remaining chapters, the intent of this chapter is to provide an overview of the subject and a simple recognition of polymers as encountered in everyday life. In addition to the books in the General Reading section, a listing of handbooks, encyclopedias, and websites is given at the end of this chapter.

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Case-Western Reserve University, Department of Macromolecular Chemistry: *http://abalone.cwru.edu/tutorial/enhanced/main.htm*

Chemical Abstracts: *http://www.cas.org/EO/polymers.pdf*

Conducts classroom teachers polymer workshops: *http://www.polymerambassadors.org*

Educational materials about polymers: *http://matse1.mse.uiuc.edu/~tw/polymers/polymers.html*

History of polymers, activities, and tutorials: *http://www.chemheritage.org/EducationalServies/faces/poly/home.htm*

Online courses in polymer science and engineering: *http://agpa.uakron.edu*

Pennsylvania College of Technology, Pennsylvania State University, and University of Massachusetts at Lowell: *http://www.pct.edu/prep/*

Polymer education at the K-12 level: *http://www.uwsp.edu//chemistry/ipec.htm*

Recycling of plastics: *http://www.plasticbag.com/environmental/pop.html*

Teacher's workshops in materials and polymers: *http://matse1.mse.uiuc.edu/~tw*

Teaching of plastics and science: *http://www.teachingplastics.org*

The American Chemical Society Polymer Education Committee site: *http://www.polyed.org*

The National Plastics Center & Museum main page; museum, polymer education, PlastiVan: *http://www.plasticsmuseum.org*

The Society of Plastics Engineers main page; training and education, scholarships: *http://www.4spe.org*

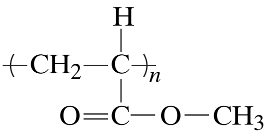
The Society of the Plastics Industry main page; information about plastics, environmental issues: *http://www.plasticsindustry.org/outreach/environment/index.htm*

University of Southern Mississippi, Dept. of Polymer Science, *The Macrogalleria: http://www.psrc.usm.edu/macrog/index.html*

World Wide Web sites for polymer activities and information: *http://www.polymerambassadors.org/WWWsites2.htm*

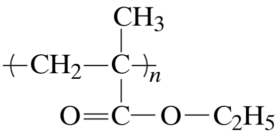
STUDY PROBLEMS

1. Polymers are obviously different from small molecules. How does polyethylene differ from oil, grease, and wax, all of these materials being essentially —CH_2—?
2. Write chemical structures for polyethylene, polyproplyene, poly(vinyl chloride), polystyrene, and polyamide 66.
3. Name the following polymers:



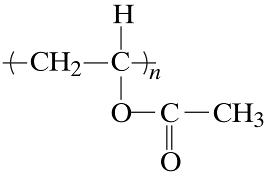
$$\left(CH_2-\underset{\underset{\displaystyle O=C-O-CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} \right)_n$$

(a)



$$\left(CH_2-\underset{\underset{\displaystyle O=C-O-C_2H_5}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} \right)_n$$

(b)



$$\left(CH_2-\underset{\underset{\displaystyle O-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} \right)_n$$

(c)

$\left(CH_2-CF_2 \right)_n$

(d)

4. What molecular characteristics are required for good mechanical properties? Distinguish between amorphous and crystalline polymers.
5. Show the synthesis of polyamide 610 from the monomers.
6. Name some commercial polymer materials by chemical name that are (a) amorphous, cross-linked, and above T_g; (b) crystalline at ambient temperatures.
7. Take any 10 books off a shelf and note the last page number. What are the number-average and weight-average number of pages of these books? Why is the weight-average number of pages greater than the number-average? What is the polydispersity index? Can it ever be unity?
8. Draw a log modulus–temperature plot for an amorphous polymer. What are the five regions of viscoelasticity, and where do they fit? To which regions do the following belong at room temperature: chewing gum, rubber bands, Plexiglas®?
9. Define the terms: Young's modulus, tensile strength, chain entanglements, and glass–rubber transition.
10. A cube 1 cm on a side is made up of one giant polyethylene molecule, having a density of 1.0 g/cm^3. (a) What is the molecular weight of this molecule? (b) Assuming an all trans conformation, what is the contour length of the chain (length of the chain stretched out)? Hint: The mer length is 0.254 nm.

APPENDIX 1.1 NAMES FOR POLYMERS

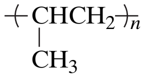
The IUPAC Macromolecular Nomenclature Commission has developed a systematic nomenclature for polymers (A1, A2). The Commission recognized, however, that a number of common polymers have semisystematic or trivial names that are well established by usage. For the reader's convenience, the recommended trivial name (or the source-based name) of the polymer is given under the polymer structure, and then the structure-based name is given. For example, the trivial name, polystyrene, is a source-based name, literally "the polymer made from styrene." The structure-based name, poly(1-phenylethylene), is useful both in addressing people who may not be familiar with the structure of polystyrene and in cases where the polymer is not well known. This book uses a source-based nomenclature, unless otherwise specified. The following structures are IUPAC recommended.

$-\!\!\left(\mathrm{CH_2CH_2}\right)\!\!-_n$

polyethylene
poly(methylene)

$-\!\!\left(\mathrm{CH{=}CHCH_2CH_2}\right)\!\!-_n$

polybutadiene[a]
poly(1-butenylene)

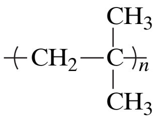


$-\!\!\left(\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\right)\!\!-_n$

polypropylene
poly(1-methylethylene)

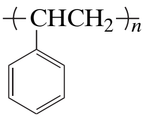
$-\!\!\left(\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CHCH_2CH_2}\right)\!\!-_n$

polyisoprene[b]
poly(1-methyl-1-butenylene)



$-\!\!\left(\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{C}}}}}\right)\!\!-_n$

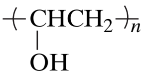
polyisobutylene
poly(1,1-dimethylethylene)



polystyrene
poly(1-phenylethylene)

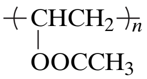
$-\!\!\left(\underset{\displaystyle \mathrm{CN}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\right)\!\!-_n$

polyacrylonitrile
poly(1-cyanoethylene)



$-\!\!\left(\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\right)\!\!-_n$

poly(vinyl alcohol)
poly(1-hydroxyethylene)

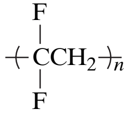


$-\!\!\left(\underset{\displaystyle \mathrm{OOCCH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\right)\!\!-_n$

poly(vinyl acetate)
poly(1-acetoxyethylene)

$-\!\!\left(\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\right)\!\!-_n$

poly(vinyl chloride)
poly(1-chloroethylene)



$-\!\!\left(\overset{\displaystyle \mathrm{F}}{\overset{|}{\underset{\displaystyle \mathrm{F}}{\underset{|}{\mathrm{C}}}}}\mathrm{CH_2}\right)\!\!-_n$

poly(vinylidene Fluoride)
poly(1,1-difluoroethylene)

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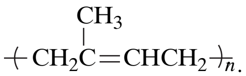
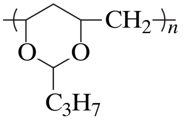
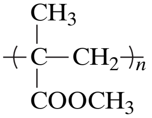
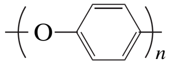
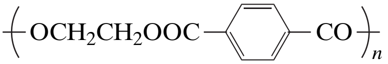
[a] Polybutadiene is usually written $-\!\!\left(\mathrm{CH_2CH{=}CHCH_2}\right)\!\!-_n$, that is, with the double bond in the center. The structure-based name is given.

[b] Polyisoprene is usually written



$-\!\!\left(\mathrm{CH_2}\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CHCH_2}\right)\!\!-_n.$

$\left(\mathrm{CF_2CF_2}\right)_n$ poly(tetrafluoroethylene) poly(difluoromethylene)	 poly(vinyl butyral) poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]
 $\left(\underset{\displaystyle \mathrm{COOCH_3}}{\mathrm{CH}}\mathrm{CH_2}\right)_n$ poly(methyl acrylate) poly[1-(methoxycarbonyl)ethylene]	 $\left(\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{COOCH_3}}{\mathrm{C}}}\mathrm{-CH_2}\right)_n$ poly(methyl methacrylate) poly[1-(methoxycarbonyl)-1-methylethylene]
$\left(\mathrm{OCH_2}\right)_n$ polyformaldehyde poly(oxymethylene)	 poly(phenylene oxide) poly(oxy-1,4-phenylene)
$\left(\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}\right)_n$ polyamide 66[a] poly(hexamethylene adipamide) poly(iminohexamethyleneiminoadipoyl)	$\left(\mathrm{OCH_2CH_2}\right)_n$ poly(ethylene oxide) poly(oxyethylene)
 poly(ethylene terephthalate) poly(oxyethyleneoxyterephthaloyl)	$\left(\mathrm{NHCO(CH_2)_5}\right)_n$ polyamide 6[b] poly(ε-caprolactam) poly[imino(1-oxohexamethylene)]

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[a] Common name. Other ways this is named include nylon 6,6, 66-nylon, 6,6-nylon, and nylon 66.

[b] Common name.

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A1. E. S. Wilks, *Polym. Prepr.*, **40(2)**, 6 (1999).

A2. N. A. Platé and I. M. Papisov, *Pure Appl. Chem.*, **61**, 243 (1989).