1

TRENDS IN SYNTHETIC STRATEGIES FOR MAKING (CO)POLYMERS

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1.1 BACKGROUND AND INTRODUCTION

Polymers have been an inherent part of human life for well over half a century at present. In spite of the comparably poor mechanical properties of polymers with that of metals, polymers encompass the applications of materials ranging from metals to glass and have replaced them in many applications. Light weight in combination with ease of processing as compared to that of metals and glasses are two of the most favorable characteristics of polymers. These characteristics are of great significance in the present circumstances as efforts are being made to lower energy consumption in various processes, and thus such lesser energy consumption would also accompany lesser emissions of CO_2. Polymeric materials with enhanced properties are required in order to meet the ever improving technological needs in various fields. In addition to the demand in technological improvements, health concerns, predominantly about monomers, also bring in legislative changes leading to the disappearance of polymers from the markets, if not completely, in selected sectors of application where, in fact, these polymers were in use for many decades. One recent example is the polycarbonate derived from Bisphenol A. Owing to the suspected nature of Bisphenol A as an endocrine disruptor, its use in drinking water bottles has been banned recently in some of the developed countries. There has been as immense pressure to replace Bisphenol A in other applications as well. Indeed, until now, Bisphenol A is one of the widely employed monomers for making linear polymers like polycarbonates as well as thermosetting resins and adhesives based on bisepoxy compound (Figure 1.1).
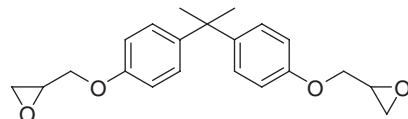
Figure 1.1   Chemical structure of bisepoxy compound.

Although the use of Bisphenol-A-based polymers is likely to face continued intense scrutiny, there are interesting developments with some other polymers that date farther back such as polyethylene. Polyethylene is an interesting case. For a long time, it is the largest volume of synthetic polymer falling under the category of commodity plastic. However, there are recent trends that expand the application of polyethylene into selected specialty areas. The efforts for making ultrahigh molecular weight polyethylene (UHMWPE) and make use of these materials in offshore applications are of particular significance in this regard. With the development of processes for converting bioethanol to ethylene, a green label is being attached to polyethylene in addition to other claims like lower carbon footprint in comparison to other polymers. It is interesting to note that the nondegradable nature of polyolefins and in particular polyethylene is of immense concern for a long time because it is the largest volume of synthetic polymer and thus constitutes a major component in landfill.

Synthesis and the development of synthetic methodologies are the life blood of new materials. The challenges posed by changing and ever demanding technologies and also health and environmental concerns can be met by synthetic methods that evolve with time. It is an objective of this chapter to give an overview of interesting synthetic methods developed in the recent past. In published literature, newer methods and polymers made therefrom abound. However, any new development has to meet many if not all of the following requirements in order for the process and/or product to reach industrial scale manufacturing processes and subsequently the market:

1. Reagents and catalysts employed for making new monomers and polymers should be, preferably, available on industrial scale.
2. Requirement of low consumption of energy, which means that the process be of low or moderately high temperature and pressure in nature.
3. Processes that demand unusual machinery, very high rate of mixing, exotic reagents, solvents, and reaction conditions should be avoided.
4. Methods of purification should be simple and straightforward, preferably free from techniques like column chromatography.
5. Use of nontoxic and recyclable solvents is an important criterion to be considered for industrial scale processes.
6. It is also preferable to have processes in which lesser number of steps is involved to make the desired product.

7. Atom economical and high yielding processes are generally preferred.
8. It is also desirable to have processes that do not generate lot of waste water and do not make use of highly corrosive reagents or catalysts.

The developments discussed in following sections may be looked at by keeping the above requirements for a successful process.

Interestingly, some of the stated objectives of the synthetic methodologies developed in the recent past are as follows:

1. To make polymers of well-defined or predetermined molecular weights and low polydipersities.
2. Control over (co)polymer architectures.
3. Sequence-regulated polymerization.
4. Formation of reversible covalent bonds.
5. Self-healing or self-repairing polymers.
6. Recyclable thermoset polymers.
7. Chain-shuttling polymerization.

Although many of the abovementioned developments have generated immense interest only among academic communities and thus resulted in enormous volumes of publications, these are nevertheless worth noting on account of very interesting material characteristics achieved through these developments.

1.2 SIGNIFICANCE OF CONTROL OVER ARRANGEMENT OF MONOMERS IN COPOLYMERS

Developments in controlled radical polymerization had led to the formation of polymers of varying structures such as block copolymers, cylindrical brushes, gradient copolymers, graft copolymers, hyperbranched polymers, macrocycles, and miktoarm stars. Each of these polymers possessed unique characteristics that were absent in the corresponding linear polymers, although in terms of chemical composition they were alike. An interesting case is the gradient copolymers whose physical properties differed considerably from the corresponding block and random copolymers of similar chemical composition as given in Table 1.1 [1].

1.3 CHAIN-GROWTH CONDENSATION POLYMERIZATION

Among the various polymerization techniques, step-growth or condensation polymerization has its own place in making polymeric materials with unique properties. A large majority of condensation polymers are engineering thermoplastics well known for their high temperature properties, crystallinity, excellent mechanical properties, and so on. Polyesters as represented by poly(ethylene and butylene terephthalate)s, aromatic and aliphatic polyamides, polyimides, a wide

TABLE 1.1   Comparison of Block and Gradient Copolymers of Poly(styrene-*co*-methylacrylate)

| Type of Copolymer	T_g, °C	Dynamic Mechanical Analysis Results
PS-*b*-PMA	~100, ~10	Two distinct segmental relaxation processes
PS-*ran*-PMA	75	
PS-*grad*-PMA	>10 (rapidly cooled)	Single, extremely broad segmental relaxation
PS-*grad*-PMA	>10, ~70 (annealed above 50 °C)	

variety of poly(arylene ether)s such as polyether ether ketone (PEEK) and other poly(ether ketone)s, poly(ether sulfone), and poly(benzimiazole)s are some of the well-known examples of polymers formed by condensation polymerization. Condensation polymerization that typically involves AA- and BB-type monomers or AB-type monomers, where A and B represent different reacting functionalities during polymerization, generally yields polymers with polydispersity of 2 or more. However, recently, Yokozawa et al. [2] have introduced a new concept termed as *chain-growth* condensation polymerization whereby the molecular weights of condensation polymers such as polyamides, polyesters, and polyethers have been controlled and polydispersity of these polymers is well below the theoretically predicted 2. Some special *para*-substituted AB-type aromatic monomers were employed for this purpose (Scheme 1.1). By introducing an activated functional group in the AB-type monomer, a preferred reaction site was created that resulted in sequential addition of monomers.

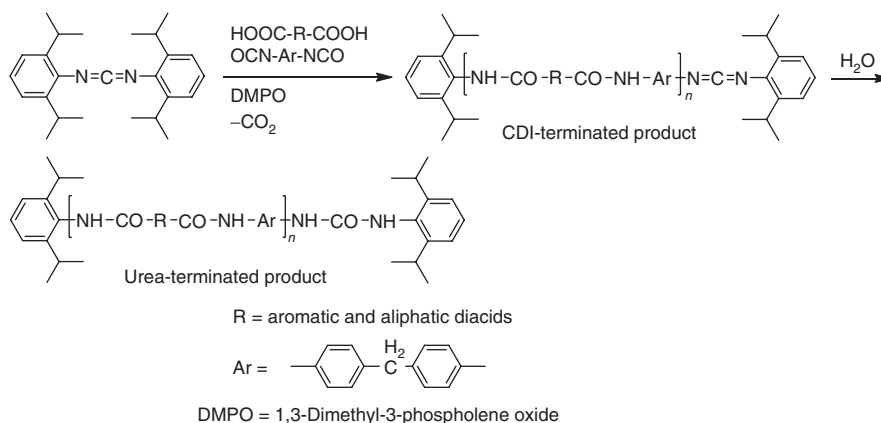### 1.3.1   Sequential Self-Repetitive Reaction (SSRR)

Dai et al. [3] reported a sequential self-repetitive reaction by which the condensation of diisocyanate with diacid in the presence of a carbodiimide catalyst like 1,3-dimethyl-3-phospholene oxide (DMPO) led to the formation of polyamide (Scheme 1.2). The reaction is so called because of the occurrence of repetitive reactions sequentially by the following three steps:

1. Condensation of two isocyanates to yield carbodiimide.
2. Addition of carboxylic acid to carbodiimide leading to the formation of *N*-acyl urea.
3. Thermal fragmentation of *N*-acyl urea that results in amide and isocyanate fragments in half or the original molar quantities.

Carbodiimide formation and the addition of carboxylic acid to carbodiimide took place in a facile manner at an ambient temperature. On the contrary, fragmentation of *N*-acyl urea occurred above 140 °C. In order to form the
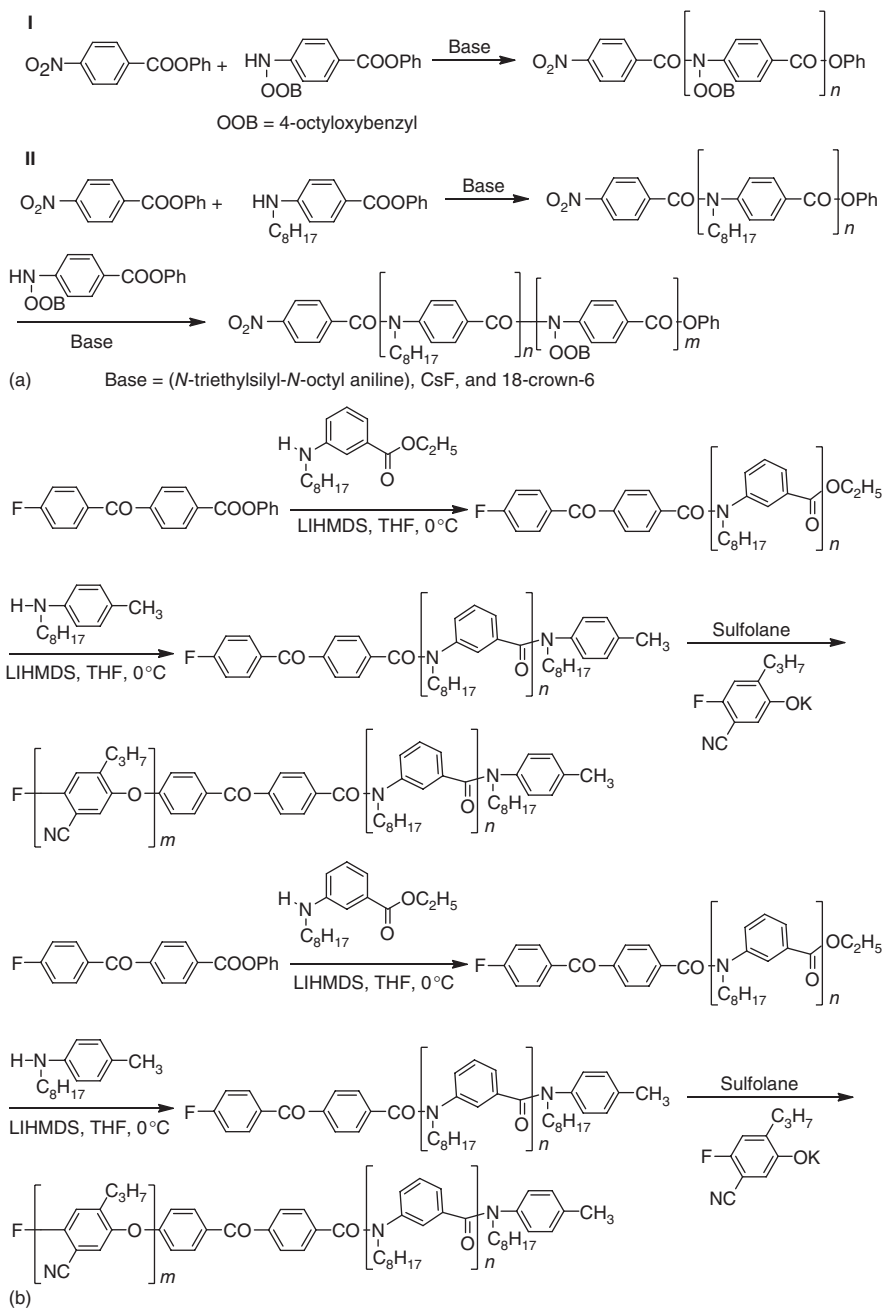
Scheme 1.1 (a) Polyamides (I) and block copolyamides (II) prepared by step-growth polymerization. (Reprinted with permission from [2l]. Copyright © 2002 American Chemical Society.) (b) Preparation of diblock copolymers, poly(amide-*block*-ether) by chain-growth condensation polymerization. (Reprinted with permission from [2m]. Copyright © 2009 Wiley Periodicals Inc.)

Scheme 1.2   Synthesis of polyamides by sequential self-repetitive reaction. (Reprinted with permission from [3a]. Copyright © 2002 American Chemical Society.)

polyamide, the aforementioned three steps were carried out by heating the reaction mixture with sufficient acid.

1.3.2   Poly(phenylene Oxide)s by Chain-Growth Condensation Polymerization

Kim et al. [4] reported the synthesis of well-defined poly(phenylene oxide)s bearing trifluoromethyl ($-CF_3$) groups through nucleophilic aromatic substitution (S_NAr) reaction (Scheme 1.3). For the chain-growth condensation polymerization to proceed in a controlled manner, the correct choice of initiator was a prerequisite. If the initiator chosen was far more reactive, chain transfer reactions occurred during the course of polymerization. As a result of this, multimodal gel permeation chromatograms were observed indicating the inhomogeneous nature of polymers that were produced by this process. For example, when 4-nitro-3-(trifluoromethyl)benzonitrile was employed as an initiator in the chain-growth condensation polymerization of 4-fluoro-3-(trifluoromethyl)potassium phenolate, transetherification prevailed in the reaction because of the more activated nature of initiator. However, the polymerization proceeded in a controlled manner when 2-nitrobenzotrifluoride was used as an initiator. Gel permeation chromatographic analysis of polymers of the reaction between 2-nitrobenzotrifluoride and 4-fluoro-3-(trifluoromethyl)potassium phenolate revealed that the molecular weight increased linearly with conversion and the observed molecular weight was close to the theoretically estimated molecular weight. The polydispersity lowered with conversion and the polydispersity of final polymers were relatively narrow.

1.3.3   Hydroxybenzoic Acids as AA′ Type Monomer in Nucleophilic Aliphatic Substitution Polymerization

Hydroxybenzoic acids such as 4-hydroxybenzoic acid are well-known AB-type monomers capable of undergoing self-polymerization yielding, in some cases,
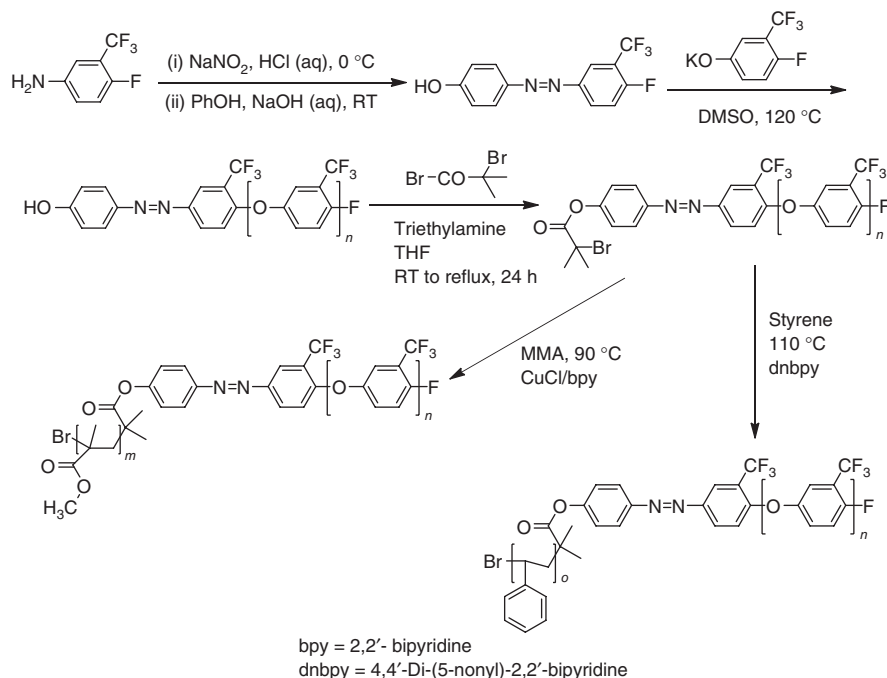
Scheme 1.3 Synthesis of rod–coil block copolymers by chain-growth condensation polymerization. (Reprinted with permission from [4a]. Copyright © 2010 Wiley Periodicals Inc.)

polymers with interesting and useful characteristics such as liquid crystallinity. However, this AB-type monomer has been reported to function as AA′-type monomer in the reaction with *trans*-1,4-dibromo-2-butene, yielding a new class of materials [5] (Scheme 1.4) with high molecular weights (Table 1.2). Both phenoxide and carboxylate anions of hydroxybenzoic acid took part in the nucleophilic substitution nearly simultaneously. As expected, the reaction between AB_n-type hydroxybenzoic acid and *trans*-1,4-dibromo-2-butene yielded network polymers. Reduction of unsaturated bond in such poly(ether ester)s yielded an interesting class of polymers whose chemical structure was comparable to that of poly(butylene terephthalate), except that one of the ester linkages of latter polymer was replaced by an ether (−O−) linkage in the former. Such substitution led to substantial reduction in melting transitions, about 100 °C, but also induced crystallization during heating as well as upon cooling.

1.4 SEQUENCE-CONTROLLED POLYMERIZATION

Nature's way of making polymers, in particular polypeptides, is often envied because of the control with which such polymers are made precisely in terms of
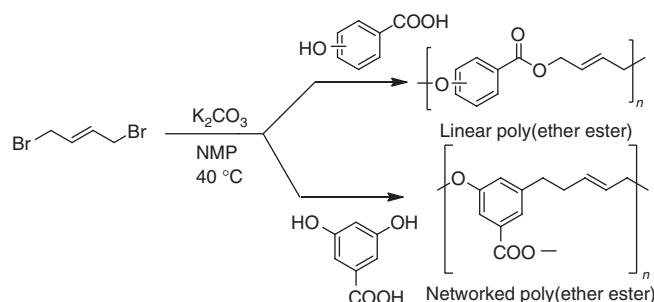
Scheme 1.4 Linear and networked polymers formed by using hydroxybenzoic acid as AA′-type comonomer. (Reprinted with permission from [5a]. Copyright © 2011 Wiley Periodicals Inc.)

TABLE 1.2   Hydroxy Benzoic acid as AA′-Type Comonomer in Aliphatic Nucleophilic Substitution Reaction[a]

HBA monomer (solvent)	Reaction time (h) and temperature (°C)	$\langle M_n \rangle$	$\langle M_w \rangle$	PD
4-HBA (DMA)	48, 40	22,200	35,850	1.60
4-HBA (NMP)	64, RT	10,800	17,300	1.60
4-HBA (NMP)	24, RT	8,300	12,120	1.50
4-HBA (NMP)	48, 40	22,530	33,750	1.50
4-HBA (NMP)	64, 40	26,460	39,220	1.50
4-HBA (NMP)	48, 50	9,970	15,590	1.60
3-HBA (NMP)	48, 40	25,550	38,080	1.50
HNA (NMP)	48, 40	Insoluble		

4-HBA, 4-hydroxy benzoic acid; 3-HBA, 3-hydroxy benzoic acid; HNA, 6-hydroxy-2-naphthoic acid; NMP, N-methyl-2-pyrrolidinone; DMA, N,N-dimethyl acetamide. [a][5].

sequence and tacticity [6]. In such natural process, it is very common that polypeptides are made up of 20 or more amino acids in repeat unit sequence. Developments reported thus far and the following description need to be considered cautiously, because in comparison to the natural processes, the polymeric systems reported are too simple and also are restricted to just two different monomer sequences.

1.4.1   Sequence-Controlled Copolymers of N-Substituted Maleimides

The reactivity difference between styrene and various N-substituted maleimides has been utilized for making copolymers (Scheme 1.5) [7].

1.4.2   Alternating Copolymers by Ring-Opening Polymerization

By making use of bis(phenolate) group 3 metal complexes as initiators, highly alternating copolymers were prepared by ring-opening polymerization of a mixture of
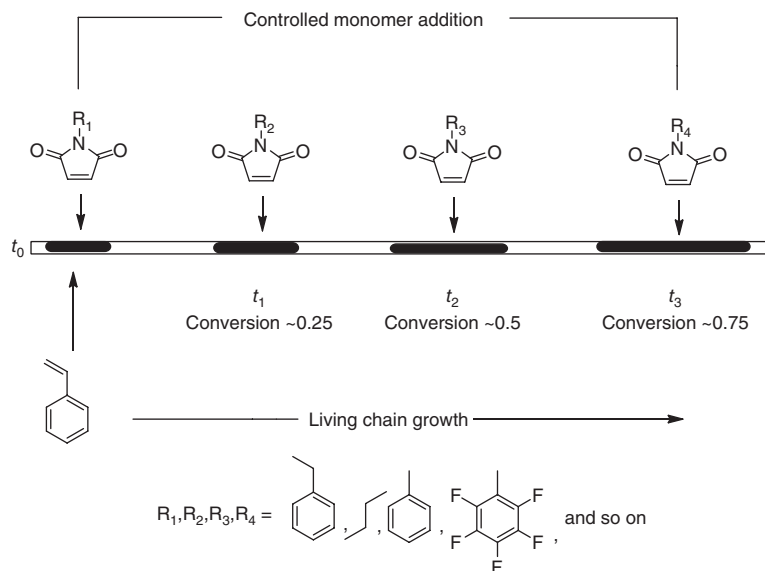
Scheme 1.5 Sequence-controlled chain-growth polymerization. (Reprinted with permission from [6]. Copyright © 2010 Royal Society of Chemistry.)

enantiomerically pure but different monomers (Scheme 1.6) [8]. The co-catalyzed carbonylation of epoxides yielded optically active β-lactone. The β-lactone in presence of yttrium initiators formed alternating copolymers.

### 1.4.3 Selective Radical Addition Assisted by a Template

A template-dependent recognition was noticed in the copolymerization of sodium methacrylate (NaMA) and methacryloyloxyethyl trimethylammonium chloride (ACMA) (Scheme 1.7) [9].

### 1.4.4 Alternating AB-Type Sequence-Controlled Polymers

A naphthalene template was used for making alternating copolymer of methyl methacrylate and acrylate [10]. The monomeric units methacrylate and acrylate were anchored spatially close to each other in the *peri*-position (1,8-position) of naphthalene to form the A−B templated divinyl monomer that was polymerized under dilute conditions by metal-catalyzed living radical polymerization. After polymerization, the naphthalene template was removed by hydrolysis, and the polymers were methylated again to yield alternating AB-type copolymer of poly(methyl methacrylate-*alt*-acrylate).

1.4.5 Metal-Templated ABA Sequence Polymerization

A palladium template structure was designed to achieve selective, intramolecular, and directional double cyclopolymerization at the template. ABA-type
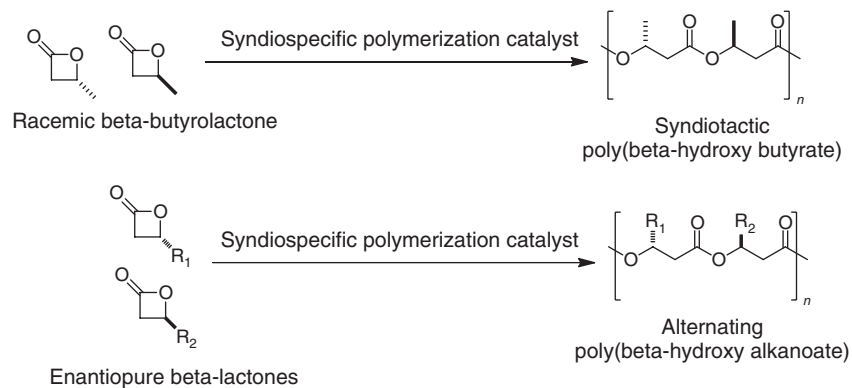
Scheme 1.6 Sequence-controlled ring-opening polymerization. (Reprinted with permission from [8]. Copyright © 2009 American Chemical Society.)
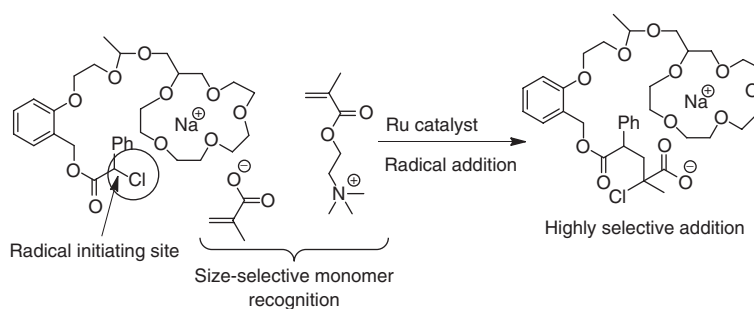

Scheme 1.7 Template-assisted size-selective monomer recognition. (Reprinted with permission from [9]. Copyright © 2010 American Chemical Society.)

alternating copolymers of styrene-4-vinylpyridine-styrene were prepared by this approach (Scheme 1.8) [11]. It is important to note that the polymerization was not straightforward and insoluble polymers were obtained generally due to cross-linking reactions. Polymerization in a bulky fluoroalcohol like 1,1,1,3,3,3-hexafluorophenyl-2-propanol (HFFP) at temperatures −5 to −60 °C proceeded smoothly. However, the reaction time required was very long ranging from 48 to 120 h.

1.4.6 Sequence-Controlled Vinyl Copolymers

In an atom transfer radical polymerization reaction, the chain end was made inactive by atom transfer radical addition of allyl alcohol to yield a primary alcohol. The chain end was again activated by the oxidation of primary alcohol to carboxylic acid followed by esterification to induce polymerization again. These sequence of reactions were repeated with the introduction of different side groups
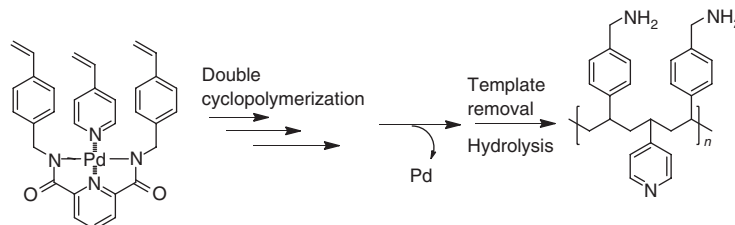
Scheme 1.8 Sequence-regulated metal-templated polymerization of ABA monomer. (Reprinted with permission from [11]. Copyright © 2011 Wiley Periodicals Inc.)
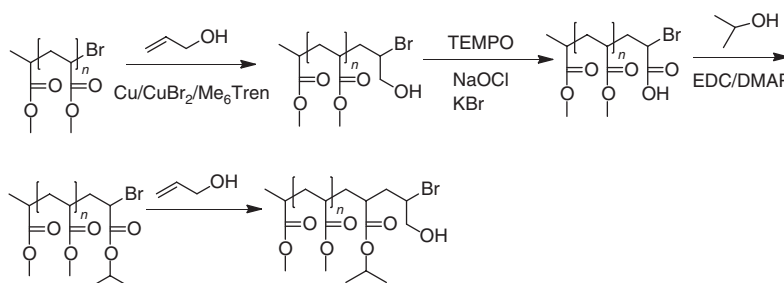
Scheme 1.9 Sequence-controlled vinyl copolymers. (Reprinted with permission from [12]. Copyright © 2011 Royal Society of Chemistry.)

at each esterification step (Scheme 1.9) [12]. Atom transfer radical addition also led to loss of bromo-end groups although oxidation and esterification were nearly quantitative.

1.4.7 Sequence-Regulated Polymerization Induced by Dual-Functional Template

By a suitable design of template having cationic and radical initiating sites, it was possible to polymerize, preferably, only the vinyl monomer that interacted with the template over the noninteracting vinyl monomer (Scheme 1.10) [13].

1.5 PROCESSING OF THERMOSET POLYMERS: DYNAMIC BOND FORMING PROCESSES AND SELF-HEALING MATERIALS

Temperature-induced flow is one of the distinguishing features of thermoplastics from thermosets. This behavior of thermoplastics makes them easily processable, thereby allowing thermoplastics to be extruded, injection molded, thermally formed into fibers, films, filaments, pellets, and so on. Thermosets have many interesting, useful, and unique characteristics that are as follows: superior dimensional
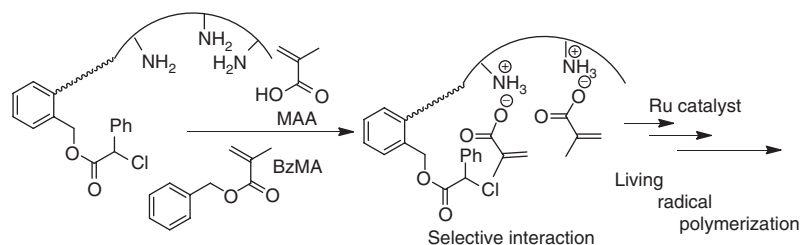
Scheme 1.10 Template-assisted sequence-regulated polymerization. (Reprinted with permission from [13]. Copyright © 2011 Wiley Periodicals Inc.)

stability, ability to perform at high temperatures, solvent resistance, creep resistance, high fracture strength, and high modulus. These properties make thermosets attractive for applications in a variety of fields such as adhesives, coatings, electrical insulation, printed circuit boards, and rubbers. Unlike thermoplastics that are reprocessable, thermoset formation is an irreversible process. However, some of the recently evolved concepts challenge this age-old phenomenon. There are instances, where, by making the covalent linkages reversible, concepts such as repairability and processability could be introduced into thermosets. For this purpose, it is necessary to form networks with chemical bonds that are labile, that is, bond breaking and bond making could be induced, for example, heat, catalysts, light, and reagents.

1.5.1 Plasticity of Networked Polymers Induced by Light

A photomediated reversible backbone cleavage in a networked structure without any degradation of mechanical properties was achieved by addition–fragmentation chain transfer process involving allyl sulfides. Initially, reaction of a radical with an in-chain functionality leads to the formation of an intermediate. This intermediate in turn fragments thereby reforming the initial functionality and the radical. As a result of the addition–fragmentation process, the topology of the network was changed; however, the nature of network remained unchanged. The network strands were unaffected, provided there were no side reactions or radical termination processes. Under such conditions, the number of allyl sulfide groups also remained unchanged. The fragmentation and reformation process facilitated the stress relaxation in each bond. It may be noted that cleavage and reformation reactions occurred in a facile manner because of the rubbery nature of network with very low T_g, $-25\,°C$ [14a]. Since these polymers were unsuitable as structural materials, thiol–yne networks were proposed as suitable alternatives [14b].

1.5.2 Radically Exchangeable Covalent Bonds

Alkoxyamine units were utilized as thermodynamic covalent cross-linking system. Heating of a network polymer induced a state of equilibrium between dissociation

Styryl radical   TEMPO
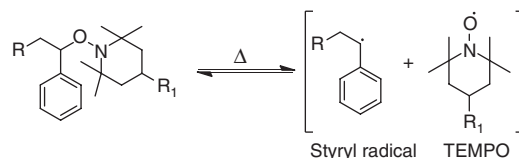
Scheme 1.11 Radical exchange reaction of an alkoxyamine derivative. (Reprinted with permission from [15]. Copyright © 2006 American Chemical Society.)

and association at the point of cross-linking. Poly(methacrylic ester)s possessing alkoxyamine as pendant groups underwent radical exchange reaction upon heating. The cross-linked structure was quantitatively decross-linked under stoichiometric control (Scheme 1.11) [15].

### 1.5.3   Self-Repairing Polyurethane Networks

Polyurethane networks exhibiting self-repairing characteristics when exposed to UV light were prepared by introducing chitosan substituted with oxetane groups in two component polyurethane. Any mechanical damage induced the ring-opening reaction of four-membered oxetanes, which resulted in two reactive ends. These reactive ends underwent cross-linking reaction with fragments formed from chitosan upon exposure to UV light thus repairing the network. These materials have been reported to self-repair in less than an hour and are proposed for applications as wide as transportation, packaging, fashion, and biomedical industries [16].

1.5.4   Temperature-Induced Self-Healing in Polymers

Polyketones with carbonyl groups in 1,4-arrangement were obtained by alternating co- or terpolymerization of carbon monoxide, ethylene, and propylene using homogeneous Pd-based catalysts. By Paul–Knorr reaction with furfurylamine, these 1,4-arranged polyketones were converted to furan derivatives that were subsequently subjected to Diels–Alder reaction with bismaleimide leading to the formation of cross-linked polymers. At elevated temperatures, these cross-linked polymers underwent retro Diels–Alder reaction. Thus, by making use of heat as external stimulus, these polymers could be subjected to many cycles of cross-linked–decross-linked structures. Dynamic mechanical analysis and three-point bonding tests demonstrated that this cycle is repeatable 100% for multiple times (Scheme 1.12) [17].

1.5.5   Diels–Alder Chemistry at Room Temperature

One of the interesting aspects of Diels–Alder reaction is that it is an addition process, and thus it is an atom economical process. Materials formed by Diels–Alder reactions have been termed as *dynamers*, which in turn is defined as a class
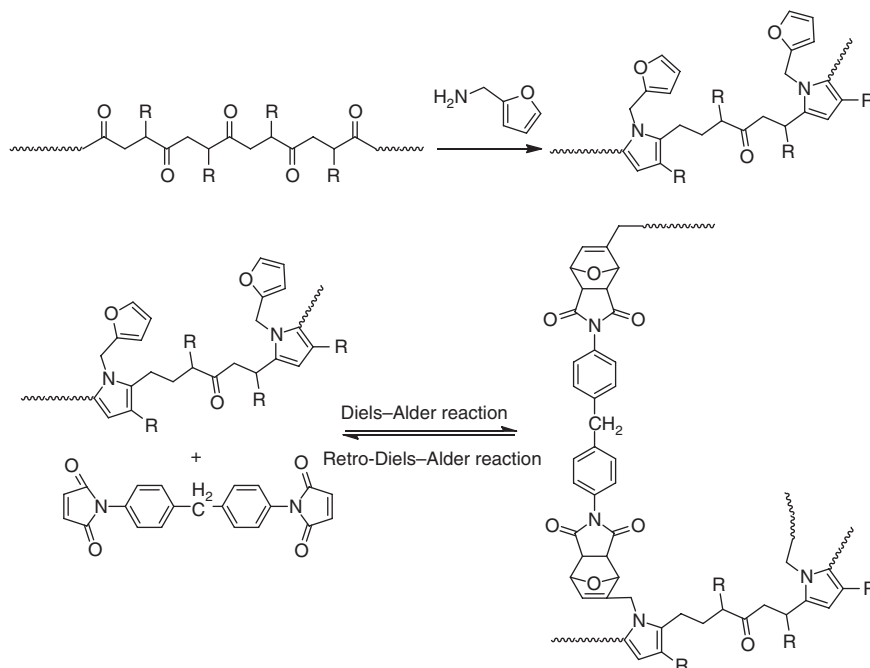
Scheme 1.12   Temperature-induced self-healing polymers. (Reprinted with permission from [17]. Copyright © 2009 American Chemical Society.)

of polymers that are formed by linking monomers in a reversible process. The reversible nature of the process allows continuous scrambling of polymer chain sequences. By employing bisfulvene dienes and bis(tricyanoethylene carboxylate) or bis(dicyanofumarate) as dienophile, a room temperature Diels–Alder process was reported (Scheme 1.13) [18].

1.5.6   Trithiocarbonate-Centered Responsive Gels

Trithiocarbonate units flanked between dimethacrylate terminal functionalities through linkers have been shown to exhibit dynamic covalent chemical characteristics. The network formed by this monomer undergoes reorganization either in the presence of CuBr/ligand or in the presence of radical initiators like AIBN (Scheme 1.14) [19].

1.5.7   Shuffling of Trithiocarbonate Units Induced by Light

The photoresponsive nature of trithiocarbonate units makes it undergo shuffling reaction when exposed to UV irradiation. Poly(*n*-butyl acrylate) cross-linked using trithiocarbonate was synthesized by radical addition–fragmentation chain transfer
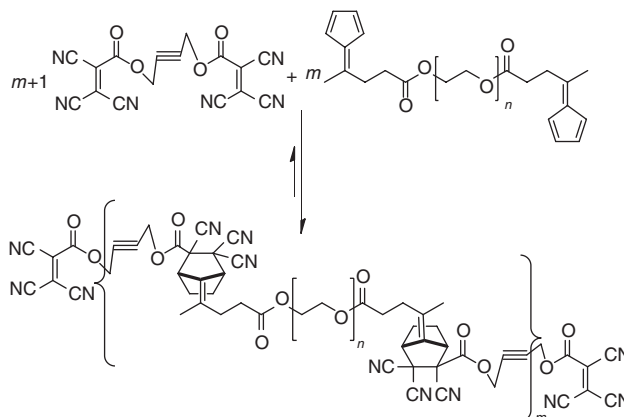
Scheme 1.13 Diels–Alder addition at room temperature. (Reprinted with permission from [18]. Copyright © 2009 Wiley Periodicals Inc.)

(RAFT) polymerization. Poly(*n*-butyl acrylate) was chosen as matrix due to its low T_g (−50 °C) because of which the chain mobility is high at room temperature. The tensile modulus of fresh sample was 69 ± 6 kPa and the same for self-healed polymers in the presence of solvent was 65 ± 11 kPa. The self-healing in bulk was incomplete due to the restricted chain mobility (Scheme 1.15) [20].

1.5.8 Processable Organic Networks

Networks formed by classical epoxy chemistry such as the reaction between diglycidyl ether of Bisphenol A and glutaric anhydride having epoxy/acyl ratio of 1 : 1 in the presence of 5 or 10 mol% zinc acetyl acetonate behave like processable glasses. Broken or ground samples of such networks, in spite of being cross-linked well above gel point, have been reported to be reprocessed by injection molding. These cross-linked networks behave like an elastomer at room temperature and are confirmed as networks by dissolution experiments since they display swelling tendency but do not dissolve even in good solvents upon prolonged immersion at high temperatures. The fact that these networked systems were able to relax stresses completely at high temperature and tend to flow was confirmed by rheology and birefringence studies [21].

1.6 MISCELLANEOUS DEVELOPMENTS

1.6.1 Atom Transfer Radical Polymerization (ATRP) Promoted by Unimolecular Ligand-Initiator Dual-Functional Systems (ULIS)

Within the last few decades, three major developments took place in the free-radical polymerization of vinyl monomers, namely, nitroxide-mediated free-radical
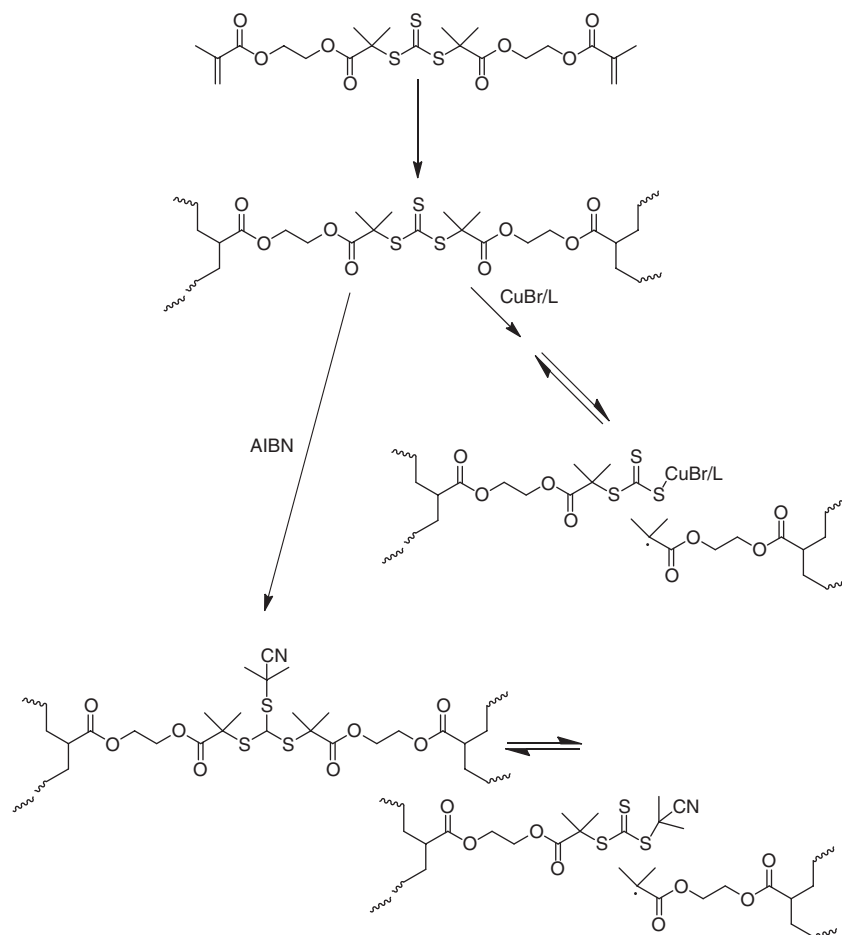
Scheme 1.14   Trithiocarbonate-centered responsive gels. (Reprinted with permission from [19]. Copyright © 2010 American Chemical Society.)
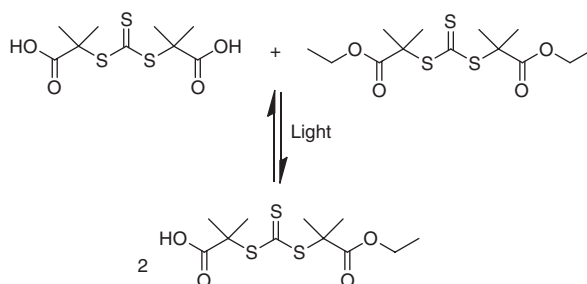
Scheme 1.15   Light-induced shuffling of trithiocarbonate units. (Reprinted with permission from [20]. Copyright © 2011 Wiley Periodicals Inc.)

polymerization (NMP) [22], RAFT polymerization [23], and ATRP [24]. Each of these techniques, in spite of many advantages, has inherent deficiencies that prevent it from becoming a major commercial process. Among these three techniques, ATRP is somewhat more convenient to practice. Two of the major problems associated with ATRP and worthy of mentioning are follows: presence of high residual metal impurities in the form of copper and its salts; and the inability to homo or copolymerize acidic monomers like acrylic and methacrylic acids in the free acid form. The residual metal impurity poses many challenges such as resulting in colored polymers such as black, blue, dark blue, brown and green. In this context, it may be noted that vinyl polymers such as polystyrene and poly(methyl methacrylate) are bright white solids, yielding highly transparent materials upon processing in the absence of any impurities. The presence of metal residue could affect the thermooxidative stability of polymers as well as pose health concerns because of the toxic nature of residual metals. Copolymers bearing acrylic and methacrylic acids are important for imparting variety of characteristics such as improved adhesion and stimuli responsive behavior, and for dispersing in aqueous media.

In ATRP, copper in lower oxidation state such as Cu(I)Br undergoes a redox transition during polymerization in cycles described as active and dormant, which represent chain growth and dead stages, respectively. Typically, tertiary amines are used for complexing the copper salt. Also, initiation process involves the abstraction of halogen atom such as bromine or chlorine from alkyl bromides or chlorides, which result in the formation of alkyl radical. The alkyl radical thus formed initiates polymerization by transferring the radical to vinyl monomer.

A modified ATRP process that overcomes the aforementioned deficiencies has been reported recently [25,26]. The ligand that coordinates with the metal salt and the alkyl halide were covalently linked to form ligand initiators (Figure 1.2) [25,27]. In this modified process, reducing the concentration of copper salt from 1000s of ppm to 10s of ppm did not have much influence on the rate of polymerization [26]. The polymerization was highly influenced by reaction conditions such as nature of solvent employed and polymerization temperature. Through this ULIS-promoted ATRP, very high molecular weight polymers as well as block copolymers were obtained [28]. The residual metal content of polymers obtained by ATRP promoted by ULIS was theoretically estimated to be two orders of magnitude lower. Analysis of polymers by techniques like inductively coupled plasma (ICP) also confirmed that the metal residue present in polymers precipitated in methanol without passing through alumina column to be 5 ppm or lower, well below than that present in purified polymers obtained by conventional ATRP [29]. It was also possible to homo- and copolymerize acrylic and methacrylic acids directly through the modified process [26,30,31]. Terpolymers derived by using acrylic acid as one of the comonomers have also been reported by ULIS-promoted ATRP [30]. The end group fidelity of polymers obtained by the modified process has been verified by chain extension reactions as well as by elemental analysis of macroinitiators [26,28,29,31]. This modified process potentially takes ATRP one step closer to downstream.
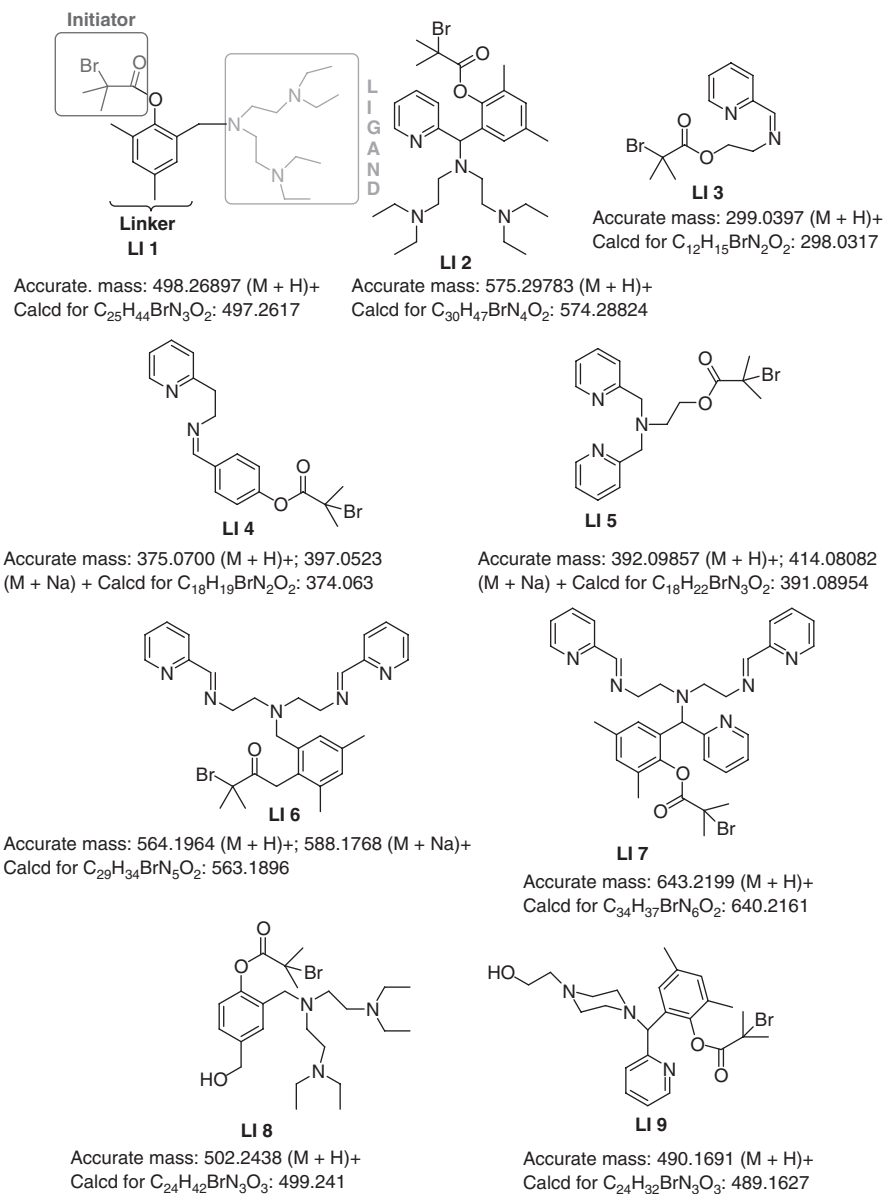
LI 1

Accurate. mass: 498.26897 (M + H)+
Calcd for C$_{25}$H$_{44}$BrN$_3$O$_2$: 497.2617

LI 2

Accurate mass: 575.29783 (M + H)+
Calcd for C$_{30}$H$_{47}$BrN$_4$O$_2$: 574.28824

LI 3

Accurate mass: 299.0397 (M + H)+
Calcd for C$_{12}$H$_{15}$BrN$_2$O$_2$: 298.0317

LI 4

Accurate mass: 375.0700 (M + H)+; 397.0523
(M + Na) + Calcd for C$_{18}$H$_{19}$BrN$_2$O$_2$: 374.063

LI 5

Accurate mass: 392.09857 (M + H)+; 414.08082
(M + Na) + Calcd for C$_{18}$H$_{22}$BrN$_3$O$_2$: 391.08954

LI 6

Accurate mass: 564.1964 (M + H)+; 588.1768 (M + Na)+
Calcd for C$_{29}$H$_{34}$BrN$_5$O$_2$: 563.1896

LI 7

Accurate mass: 643.2199 (M + H)+
Calcd for C$_{34}$H$_{37}$BrN$_6$O$_2$: 640.2161

LI 8

Accurate mass: 502.2438 (M + H)+
Calcd for C$_{24}$H$_{42}$BrN$_3$O$_3$: 499.241

LI 9

Accurate mass: 490.1691 (M + H)+
Calcd for C$_{24}$H$_{32}$BrN$_3$O$_3$: 489.1627

Figure 1.2   Chemical structure of unimolecular ligand initiator systems [25,27].

1.6.2   Unsymmetrical Ion-Pair Comonomers and Polymers

Ion-pair comonomers are those, which as the name imply, composed of anionic and cationic vinyl monomers existing in pairs through the attraction of opposite charges. Symmetrical ion pairs are those where the vinyl functionality is

chemically similar, for example, ion-pair monomers derived from methacrylamides [32] and methcrylates [33]. Because of the chemical similarity of vinyl functionality, the reactivity toward polymerization is also similar. Polymers of this type where opposite charges prevail upon two adjacent monomeric units in the polymer chain are called as *polyampholytes* [34] contrary to zwitterions where the opposite charges are present within the same monomer. Unsymmetrical ion pairs (Figure 1.3) [35] are those where chemical nature of vinyl functionalities is different. Owing to this difference, the rate of polymerization of anionic and cationic components of ion-pair monomers could also vary. However, the mobility of monomers during polymerization would be governed by charge neutralization. Thus, even though the individual components of monomer pair may polymerize at different rates, the oppositely charged entities can be expected to be together whether polymerized or in the monomeric form. Indeed, this was found to be the case, when unsymmetrical ion pairs composed of *N*-alkyl-1-vinyl imidazole and styrene-4-sulfonate were polymerized under RAFT. Under conventional free-radical polymerization, this unsymmetrical ion-pair monomer yielded completely insoluble polymers. However, under RAFT-mediated polymerization process, soluble polymers were obtained. The nuclear magnetic resonance (NMR) analysis of this polymer indicated the presence of unreacted *N*-alkyl-1-vinyl imidazole monomer accompanying poly(styrene-4-sulfonate) even after dialysis in order to compensate the excess negative charge of polymer chain [35]. Such monomer pair has been found to be useful for making ionically cross-linked poly(methyl methacrylate) even at a concentration of about 5 mol% (Scheme 1.16) [35].

1.6.3 Imidazole-Derived Zwitterionic Polymers

Zwitterionic polymers are potentially useful in many applications such as antifouling membranes, enhanced oil recovery, and low temperature precipitation of proteins. Zwitterionic polymers are typically derived from metharylamides and methacrylates. Owing to the hydrolytic instability of amide and ester linkages, zwitterionic methacrylamides and methacrylates undergo hydrolysis to varying degrees even during polymerization. To avoid this hydrolysis, zwitterions free of hydrolytically unstable linkages such as vinylimidazole and benzimidazole based
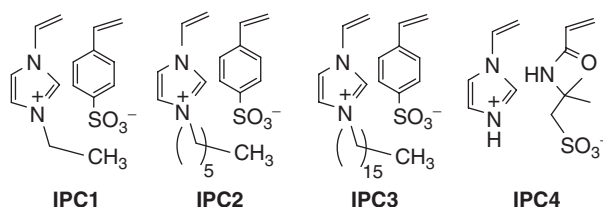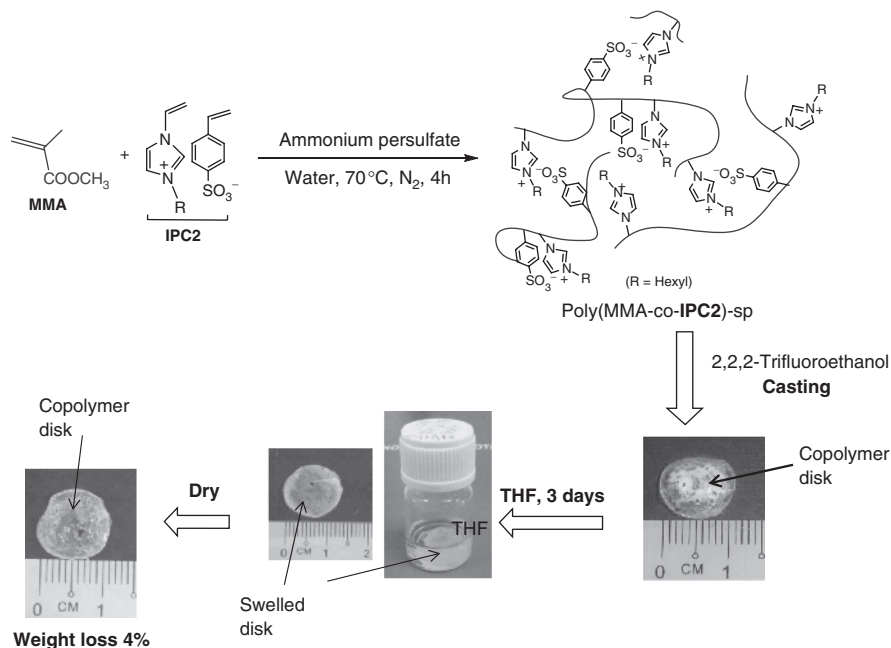

Figure 1.3 Chemical structure of unsymmetrical ion-pair comonomers. (Reprinted with permission from [35]. Copyright © 2013 Wiley Periodicals Inc.)

Scheme 1.16 Preparation of ionically cross-linked poly(methyl methacrylate) (PMMA) using unsymmetrical ion-pair comonomer. (Reprinted with permission from [35]. Copyright © 2013 Wiley Periodicals Inc.)

have been proposed recently (Scheme 1.17) [36]. These zwitterionic polymers showed very interesting solubility characteristics such as insoluble but swelling tendency in deionized water and solubility in concentrated brine solution. It also showed upper critical solution temperature (UCST) behavior as well as gel–sol behavior in brine solution. These zwitterionic polymers also showed non-Newtonian flow characteristics. Increased hydrophobicity with increased π–π interaction and intermolecular association between charged species are responsible for the aforementioned characteristics of these novel zwitterionic polymers. Owing to the unique solubility characteristics, these polymers are potentially useful in applications such as enhanced oil recovery and low temperature precipitation of proteins.

1.6.4 Post-Modification of Polymers Bearing Reactive Pendant Groups

Polymers bearing reactive pendant groups are useful for post-polymerization modification reactions. Such modifications can be used for improving many of the properties of polymers such as compatibility, solubility, thermal stability, and processability. A copolymer of maleic anhydride was converted to water and organosoluble through one such modification reaction (Scheme 1.18) [37]. The copolymer that was water insoluble became amphiphilic upon modification
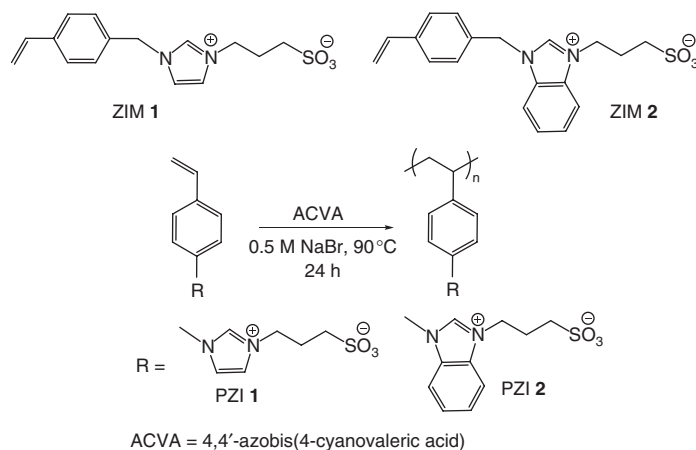
Scheme 1.17 Zwitterionic polymers free of hydrolyzable linkages. (Reprinted with permission from [36]. Copyright © 2013 Royal Society of Chemistry.)
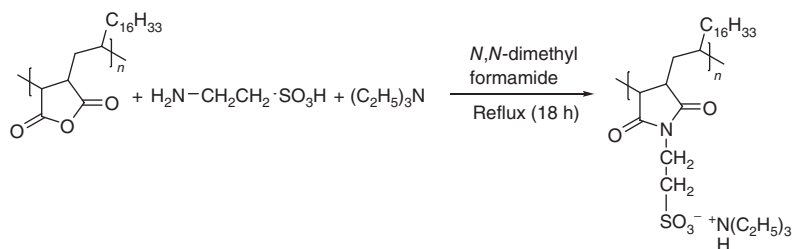
Scheme 1.18 Preparation of amphiphilic polymer by post-polymerization modification reaction involving reactive pendant group [37].

whereby it turned soluble in deionized water as well as in organic solvents. The modification reaction also enhanced the thermal stability of starting polymer (Figure 1.4) [37]. The aqueous solution of modified, amphiphilic polymer was clear and low in viscosity as compared to aqueous solutions of polymers like polyvinyl alcohol. These polymers are potentially useful as elastic coatings for protecting glass, metal, and plastic during transport, in cosmetics, and as flocculants in water purification.

1.7   CONCLUSION

It may be noted that the field of polymer science is applied in nature. As discussed earlier, even though, new developments in published literature abound, not many of these developments have been translated into commercial processes. As there has been a tremendous increase in the number of people involved in research particularly so in applied research fields like polymer science, any new development
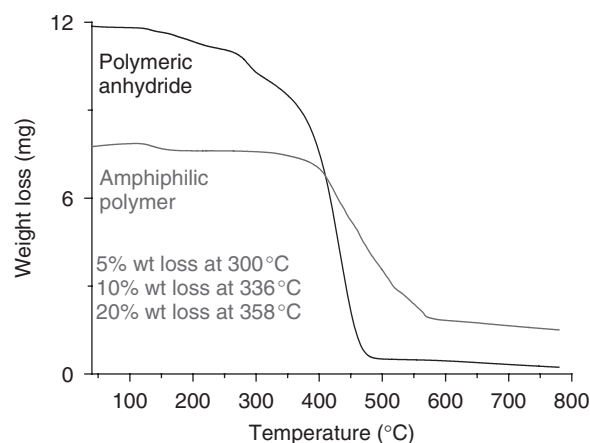
Figure 1.4 Comparison of thermal stability of unmodified and modified polymers by thermogravimetric analysis [37].

attracts the attention of vast array of researchers resulting in the generation of enormous body of published literature within a very short span of time. One good example, in the recent past, for this trend, is the development in controlled radical polymerization processes. Each one of these processes has inherent weaknesses that prevent these processes from being practiced as large-scale industrial process. In the history of chemical research, such occurrences are not uncommon. It is common for challenges to arise from many fronts in any new development. Successful outcome relies on overcoming these challenges. Opportunity for newer developments constantly arises due to many factors like legislation-induced banning of products on account of environment and health concerns, development of new processes particularly from bio-based renewable processes and products, demanding applications, and increasing environmental awareness and concerns of general public on chemicals. Nowadays, the economic cycles also are a major determining factor.

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