Living Polymerization Methods

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Living polymerization techniques can be used to achieve a high degree of control over polymer chain architecture. Examples of the type of polymers that can be synthesized include block copolymers, comb-shaped polymers, multi-armed polymers, ladder polymers, and cyclic polymers. This control of structure, in turn, results in polymers with widely diverse physical properties, even though they are made from readily available low-cost monomers.

SYNTHETIC POLYMERS ARE LONG-CHAIN MOLECULES POSSESSING uniform repeat units (mers). The chains are not all the same length. These giant molecules are of interest because of their physical properties, in contrast to low molecular weight molecules, which are of interest due to their chemical properties. Possibly the most useful physical property of polymers is their low density versus strength. Dramatic uses of this property are demonstrated by the nonstop circumnavigation of the world by a "plastic" airplane on one tank of gas and by the construction of an airplane light enough to fly more than 110 km nonstop under human pedal power.

When synthetic polymers were first introduced, they were made by free radical initiation of single vinyl monomers or by chemical condensation of small difunctional molecules. The range of their properties was understandably meager. Random copolymers next entered the picture, greatly expanding the range of useful physical properties such as toughness, hardness, elasticity, compressibility, and strength. However, polymer chemists realized that their materials could not compare with the properties of natural polymers, such as wool, silk, cotton, rubber, tendons, and spider webbing. The natural polymers are generally condensation polymers made by addition of monomer units one at a time to the ends of growing polymer chains. Polymerization of all chains stops at identical molecular weights. For some time polymer chemists have realized that to approach nature's degree of sophistication, new synthetic techniques would be needed.

Conventional chain-growth polymerizations, for example, free radical synthesis, consist of four elementary steps: initiation, propagation, chain transfer, and termination. As early as 1936, Ziegler (*1*) proposed that anionic polymerization of styrene and butadiene by consecutive addition of monomer to an alkyl lithium initiator occurred without chain transfer or termination. During transferless polymerization, the number of polymer molecules remains constant. Since there is no termination, active anionic chain ends remain after all of the monomer has been polymerized. When fresh monomer is added, polymerization resumes. The name "living polymerization" was coined for the method by Szwarc (*2*) because the chain ends remain active until killed. (The term has nothing to do with living in the biological sense.) Before Szwarc's classic work, Flory (*3*) had described the properties associated with living polymerization of ethylene oxide initiated with alkoxides. Flory noted that since all of the chain ends grow at the same rate, the molecular weight is determined by the amount of initiator used versus monomer (Eq. 1).

$$\text{Degree of polymerization} = [\text{monomer}]/[\text{initiator}] \quad (1)$$

Another property of polymers produced by living polymerization is the very narrow molecular weight distribution (*3*). The polydispersity (D) has a Poisson distribution, $D = \overline{M}_w/\overline{M}_n = 1 + (1/dp)$; $\overline{M}_w$ is the average molecular weight determined by light scattering, $\overline{M}_n$ is the average molecular weight determined by osmometry, and dp is the degree of polymerization (the number of monomer units per chain). The values of $\overline{M}_w$ and $\overline{M}_n$ can also be determined by gel permeation chromatography (GPC). A living polymerization can be distinguished from free radical polymerization or from a condensation polymerization by plotting the molecular weight of the polymer versus conversion. In a living polymerization, the molecular weight is directly proportional to conversion (Fig. 1, line A). In a free radical or other nonliving polymerization, high molecular weight polymer is formed in the initial stages (Fig. 1, line B), and in a condensation polymerization, high molecular weight polymer is formed only as the conversion approaches 100% (Fig. 1, line C).

Some General Features of Living Polymerizations

Living polymerization techniques give the synthetic chemist two particularly powerful tools for polymer chain design: the synthesis of block copolymers by sequential addition of monomers and the synthesis of functional-ended polymers by selective termination of living ends with appropriate reagents. The main architectural features available starting with these two basic themes are listed in Table 1 along with applications for the various polymer types. Although living polymerization of only a few monomers is nearly perfect, a large number of other systems fit theory close enough to be useful for synthesis of the wide variety of different polymer chain structures shown in Table 1. In general, the well-behaved living systems need only an initiator and monomer, as occurs in the anionic polymerization of styrene, dienes, and ethylene oxide. For an increasing number of monomers, more complex processes are needed to retard chain transfer and termination. These systems use initiators, catalysts, and sometimes chain-end stabilizers. The initiator begins chain growth and in all systems is attached (or part of it, at least) to the nongrowing chain end. The catalyst is necessary for initiation and propagation but is not consumed. The chain-end sta-

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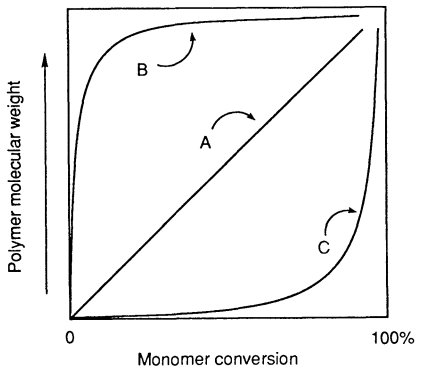


Fig. 1. Molecular weight conversion curves for various kinds of polymerization methods: (A) living polymerization; (B) free-radical polymerization; and (C) condensation polymerization.

bilizer usually decreases the polymerization rate. When the catalyst is a Lewis acid (electron-pair acceptor), the stabilizer will likely be a Lewis base (electron-pair donor), and vice versa. In all systems, the initiation step must be faster than or the same rate as chain propagation to obtain molecular weight control. If the initiation rate is slower than the propagation rate, the first chains formed will be longer than the last chains formed. If an initiator with a structure similar to that of the growing chain is chosen, the initiation rate is assured of being comparable to the propagation rate. A number of living systems operate better if excess monomer is present. A possible explanation is that the living end is stabilized by complexation with monomer (*4*). Large counterions tend to be more effective than small counterions in living polymerization systems even when the ionic center is only indirectly involved.

Anionic, cationic, covalent, and free radical processes for living polymerization are described below along with applicable monomers. The best conditions for polymerization of individual monomers are also described. Although many mechanistic questions have not been resolved, the most probable pathways for chain growth are given. Applications that appear to have high potential are pointed out.

Anionic Living Polymerizations

The major monomer classes that yield to anionic living polymerization techniques are styrenes, butadienes, methacrylates, acrylates, ethylene oxide, hexamethylcyclotrisiloxane, and lactones.

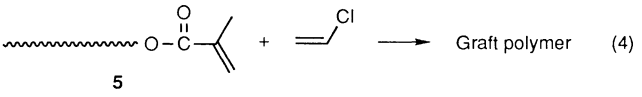
Styrene and substituted styrenes with non–base-sensitive groups have been the most studied monomers for living polymerization (*5*). Butyl lithium, **1**, and sodium napthalenide (*2*), **3**, are examples of excellent initiators (Eqs. 2 and 3). Butyl lithium gives polymer with

$$\underset{\mathbf{1}}{C_4H_9Li} + \text{Styrene} \longrightarrow \underset{\mathbf{2}}{C_4H_9\text{—polystyrene}^- Li^+} \quad (2)$$

$$\underset{\mathbf{3}}{\text{Sodium naphthalenide}} + \text{Styrene} \longrightarrow \underset{\mathbf{4}}{Na^+\ ^-\text{polystyrene}^-\ Na^+} + \text{Naphthalene} \quad (3)$$

one reactive end, **2**, and sodium naphthalenide gives polymer with two reactive ends, **4**. The use of **2** and **4** as initiators for other monomers results in AB (Table 1, no. 3) and ABA (Table 1, no. 4) block polymers. Treatment of **2** or **4** with ethylene oxide provides hydroxy-ended polymers (*6*) (Table 1, nos. 1 and 2).

A macromonomer, **5**, results from treatment of hydroxy-ended polymer with methacryl chloride (*7*). Copolymerization of **5** with another monomer such as vinyl chloride gives a graft polymer (Table 1, no. 5) (Eq. 4) (*8*). Linking **2** with polychlorosilanes produces star-branched polymers (Table 1, no. 7) with up to 56 arms (*9*). Similar star-branched polymers with a dispersity of arms can be made by addition of divinyl benzene to **2** (*10*).



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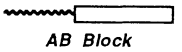
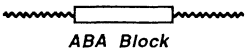
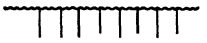
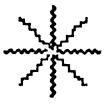
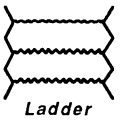
A cyclic polymer (Table 1, no. 9) results when one treats a dilute solution of **4** with a coupling agent such as dibromo-*p*-xylene or dimethyldichlorosilane (*11*).

Butadiene and isoprene also give living polymers on initiation with **1** or **3**. Considerable 1,2-polymerization results unless one uses alkyl lithium initiators in nonpolar solvents. Manufacture of styrene/butadiene/styrene block polymer, a thermoplastic elastomer, is at present the largest commercial use for living polymerizations. On cooling a polymer melt of this ABA block polymer, the hard styrene segments separate to form cross-links that are the basis for its rubberlike properties (Fig. 2).

Acrylate and methacrylate esters and amides plus acrylonitrile

Table 1. Architectural forms of polymers available by living polymerization techniques.

	Polymer	Application
1	OH *Functional ended*	Dispersing agents Synthesis of macromonomers
2	HO OH *α,ω-difunctional*	Elastomers synthesis Chain extension Cross-linking agents
3	 *AB Block*	Dispersing agents Compatibilizers for polymer blending
4	 *ABA Block*	Thermoplastic elastomers
5	 *Graft*	Elastomers Adhesives
6	 *Comb*	Elastomers Adhesives
7	 *Star*	Rheology control Strengthening agents
8	 *Ladder*	High-temperature plastics Membranes Elastomers
9	 *Cyclic*	Rheology control
10	 *Amphiphilic network*	Biocompatible polymers

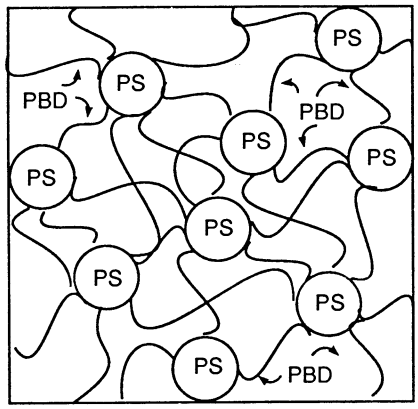
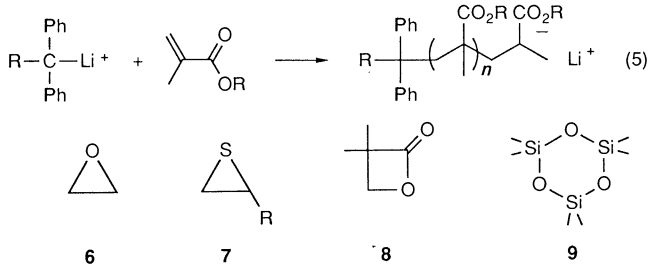


Fig. 2. Thermoplastic rubber from styrene butadienes block polymer (PS, polystyrene; PBD, polybutadiene).

represent a family of monomers called acrylics. Anionic living polymerization of acrylics presents several problems. Under the strongly basic conditions, initiators and anionic chain ends tend to attack the polar functional groups and α-protons. These side reactions kill living chain ends. If all of the chain ends are killed, polymerization stops. If only part of the chain ends are destroyed, the polymer molecular weight control will be lost and the molecular weight dispersity will rise. By working at −70°C or lower and initiating with a hindered initiator, for example, 1,1-diphenylhexyl lithium, one can prepare most of the architectural forms in Table 1 from methacrylates (Eq. 5; R is an alkyl group; Ph, phenyl) (*12*).



Acrylates do not polymerize well under comparable conditions. However, Teyssié *et al.* (*13*) showed that the addition of several equivalents of lithium chloride per chain end permits living polymerization at temperatures up to −20°C. In a more surprising result, Reetz and co-workers (*14*) have shown that a remarkable increase in chain and stability results by merely changing the counter ion from lithium to tetrabutylammonium. Poly(butyl acrylate), D = 1.14, was produced at room temperature and above. Reetz speculates that side reactions such as ketene formation and end cyclization to form a cyclohexanone that eliminate the highly reactive tetrabutylammonium alkoxides are less likely to occur than those that eliminate lithium alkoxides.

At present, no commercial products are based on living polymerization of acrylics, although dispersing agents based on AB block polymers look promising.

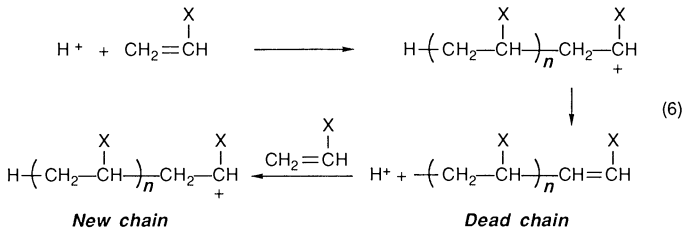
Ring-opening polymerization of strained heterocyclic compounds was one of the first types of living polymerization recognized (*3*). Sodium or potassium but not lithium alkoxides initiate ethylene oxide **6**. These polymers are water-soluble and are used in non-ionic detergents. Double-ended polymers can be chain-extended with isocyanates to give elastomers and urethane foams. Propylene oxide and other substituted oxides do not give good living polymers by anionic initiation. However, substituted sulfides **7** as well as ethylene sulfide give living polymers when initiated with sulfide anion (*15*).

Strained lactones, for example, **8**, form living polymers when initiated with tetraalkylammonium carboxylates (*16*). Ring cleavage occurs at the alkyl oxygen bond.

Living anionic polymerization of hexamethylcyclotrisiloxane, **9**, a strained ring compound, results on initiation with lithium trimethylsilanoate (*17*). The more readily available octamethylcyclotetrasiloxane, an unstrained ring compound, does not give living polymer under similar conditions.

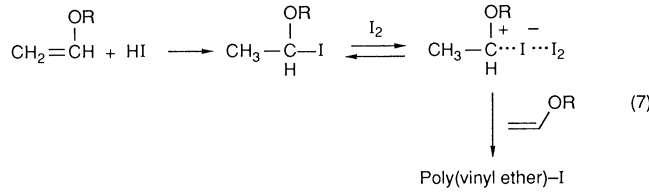
Cationic Living Polymerizations

Living cationic polymerization is more complex than its anionic counterpart. Carbenium ion chain ends generated by initiation of electron-rich monomers with strong protic acid readily transfer β-protons to start new chains (Eq. 6). The result is a lower



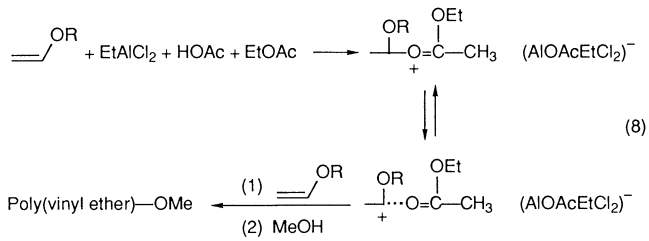
molecular weight than the theoretical value and many dead chain ends (*18*).

In 1984 Miyamoto, Sawamoto, and Higashimura reported a polymerization method for vinyl ethers that circumvented this problem (*19*). The chain ends were stored as a stable covalent iodide. This iodide was activated by Lewis acid (electron-pair acceptor) catalysts to generate small amounts of active complexed carbenium ions. The activated ends insert monomer without chain transfer or termination (Eq. 7). The exact nature of these activated species is



still being debated. Higashimura's group has synthesized examples of most of the structures listed in Table 1 using the new procedure.

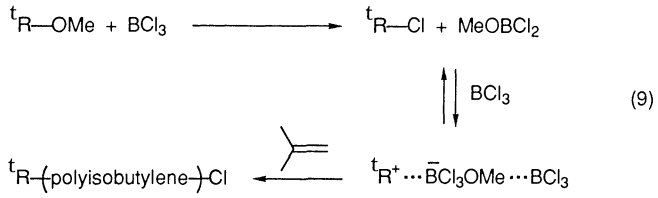
One disadvantage of the procedure is the light sensitivity of the iodo-ether end groups. In another breakthrough, Higashimura and co-workers (*20*) found a new way to stabilize the carbenium ion end groups. They used Lewis bases (electron-donor molecules) as additives. In this method, the carbenium-ion end groups are generated by the action of Lewis acid and a proton source on the monomer but are trapped by ethers or esters as onium salts (Eq. 8; Et, ethyl; Ac, acetyl). The exact nature of the end living group species needs to be



clarified further. To be effective, several equivalents of Lewis base are needed per equivalent of active end group. If dialkylsulfides are used as the donor molecules, the onium ion can be observed by nuclear magnetic resonance (NMR) (*21*). Kinetic studies show that donor molecules lower the rate of propagation, which indicates that monomer does not insert directly in the onium ion chain end.

Commercial polyvinyl ethers are made by nonliving cationic polymerization. A major use is the sticky part of fly paper and mending tapes.

Possibly the most studied cationic living polymerization is that of isobutylene (*18*). In early work, end-functional polymers and molecular weight control were obtained by quasi-living techniques involving chain transfer to initiator. At about the same time that Higashimura was solving the vinyl ether problem, Kennedy and co-workers discovered that similar techniques worked with isobutylene. Initiation by tertiary esters (*22*) or ethers (*23*) with excess BCl_3 as a catalyst gives "truly" living polymers. The use of excess Lewis acid gives the best results. Tertiary chloride initiators give living polymers if a small amount of external electron donor is added (*24*). Since mixtures of tertiary chloride and tertiary ester or ether give low polydispersity polymer and chloro-ended polymers are always isolated on quenching, Kennedy has recently concluded that the ester group or ether group comes off quickly and forms a large electron donor counterion (*24*). This counterion has a profound effect on the robustness of the system. In his latest mechanistic proposal, the chain ends are stored as tertiary chloride groups. These benign ends are in equilibrium with active, complexed carbenium ions that add monomer (*24*). Added electron donors lower the propagation rate. A simplified version of the new mechanism is shown in Eq. 9 (^tR, tertiary alkyl; Me, methyl).



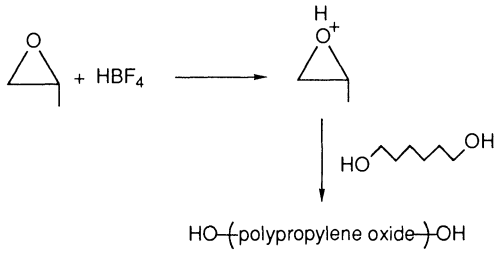
(9)

The main route to controlled polymer structure from living polyisobutene is through end functionalization (Table 1, nos. 1 and 2). The first formed tertiary chloride end group or α,ω-dichloro end groups are converted to functional groups such as –OH, $–NH_2$, $–SO_3^-$, $–CO_2H$, or epoxide (*18*). These in turn are converted to other end groups, for example, methacryl to give a macromonomer and α,ω-*bis*-methacryl to give a macro–cross-linking agent. On copolymerization with a small monomer, the macromonomer forms a graft polymer (Table 1, no. 5). The macro–cross-linking agent forms networks on copolymerization with small monomers. If the small monomers are hydrophilic, for example, *N,N*-dimethylacrylamide (*25*) or 2-hydroxyethyl methacrylate (*26*), amphiphilic networks result (Table 1, no. 10). These network polymers swell in both water and organic solvents and have excellent biocompatibility. When the network polymer surface is in contact with fatty tissue, the hydrophobic chains can migrate to the surface and interact. When in contact with hydrophilic tissue, the hydrophilic parts can migrate to the surface and interact. Amphiphilic block copolymers have been prepared from α,ω-substituted polyvinyl ethers (*27*).

Endless ionomers result from α,ω-sulfonate–ended polyisobutylene (*28*). Salts of the sulfonate groups form ionic domains in the hydrophobic polyisobutylene which are, in effect, cross-links. Tough rubberlike resins result, especially with a three-armed star polyisobutylene terminated with $–SO_3^-$. The toughness that results from ionomer cross-linking is amply demonstrated by Du Pont's Surlyn, which is used to coat cut-proof golf balls.

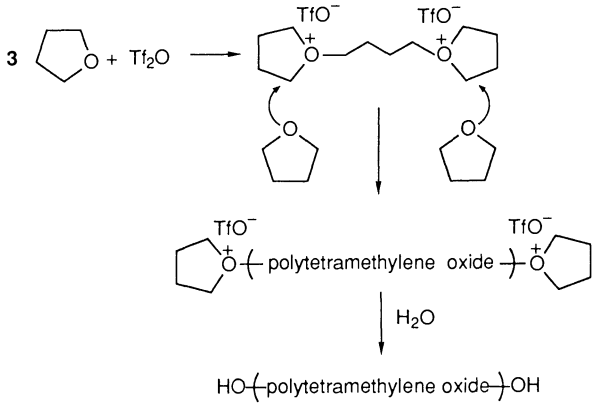
Styrenes substituted in the *para* position with electron-donating groups, for example, chloro (*29*), methyl (*30*), and methoxy (*30*), undergo living polymerization with initiators and catalysts similar to those used for vinyl esters and isobutylene. In another breakthrough that demonstrates the power of added Lewis base, Sawamoto, Higashimura, and Ishihama (*30, 31*) showed that styrene itself can be polymerized under living conditions. Initiation with CH_3SO_3H and $SnCl_4$ modified with tetrabutylammonium chloride gives polystyrenes with $\overline{M}_w\overline{M}_n = 1.2$. Five moles of Lewis acid are used per mole of initiator and 2.5 moles of the Lewis base. Substitution of 1-phenylethyl chloride for the methane sulfonic acid initiator gives polymer with even lower dispersity (*32*). Living polymer is not obtained in either case without the tetrabutylammonium chloride. Its critical role is now under intensive study. Although these same styrene monomers can be polymerized by living anionic polymerization, the living cationic polymerization allows block copolymers to be prepared with other electron-rich monomers without system switching.

Living cationic polymerization of propylene oxide and epichlorohydrin, but not ethylene oxide, is accomplished by initiation with an alcohol and a strong acid catalyst (*33*). Penczek calls this procedure activated monomer polymerization. If a glycol is used, α,ω-dihydroxy(polypropylene oxide) forms (Eq. 10).



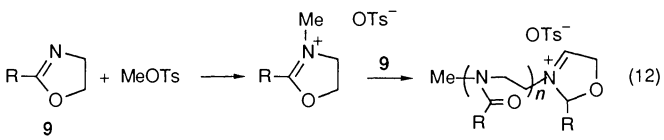
(10)

Low molecular weight diolpolymers based on tetrahydrofuran are important constituents of commercial polyurethanes and polyester elastomers. They are obtained by equilibrium polymerization with a strong acid, for example, FSO_3H. Although more costly, living polymerization of tetrahydrofuran provides much narrower molecular weight distributions and a variety of end groups. Initiation with trifluoromethanesulfonic anhydride (Tf_2O) gives *bis*-oxonium–ended polymer, which inserts monomer by attack on the α positions (*34*) (Eq. 11). In living polymerization of oxazolines, **9**, initiated by alkyl tosylates, attack occurs on a center three atoms away (Eq. 12).



(11)

The polymer backbone is a polyamide and thus hydrophilic. Removal of the acyl groups by hydrolysis gives linear poly(ethylene



(12)

$OTs^- = MeC_6H_4SO_3^-$

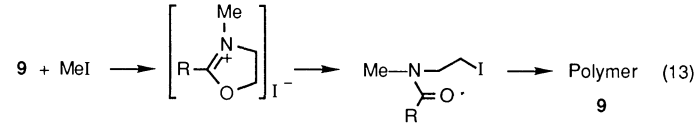
imine) (Ts, tosyl). By variation of the initiator and the R group on

the oxazoline, an incredible number of polymers with different backbone functionality and architecture have been synthesized by Saegusa's group (*35*).

Covalent Living Polymerizations

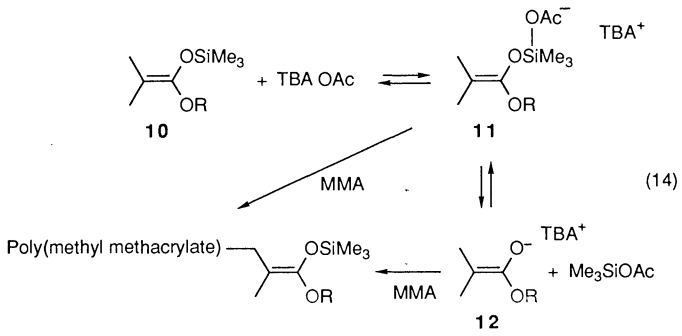
A number of living polymerizations, although nucleophilic or electrophilic in character, initiate and propagate by reaction of a reactive covalent end group with monomer. We have classified these as living covalent polymerizations. They include methyl iodide initiation of oxazolines, group transfer polymerization, immortal polymerization with aluminum porphyrins, metathesis polymerization, and coordination polymerization.

When an alkyl iodide rather than tosylate is used to polymerize oxazolines, the mechanism changes. The iodide ion is nucleopohilic enough to open the ring and regenerate an alkyl-iodide end group. Although a charged intermediate is involved, the propagation step involves two non-ionic species (*36*) (Eq. 13).



(13)

The living polymerization of methacrylates by sequential addition of monomer to a silyl ketene acetal **10** is an example of a covalent polymerization called group transfer polymerization (GTP) (*37*). The process is catalyzed by nucleophilic salts or Lewis acids (Eq. 14). The addition of Me_3SiOAc slows the rate of propagation but



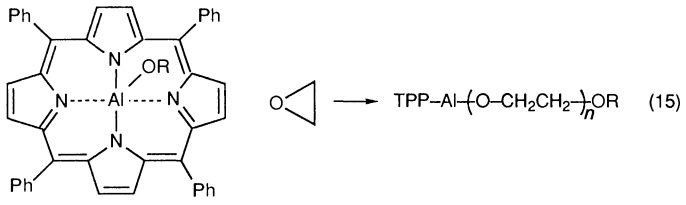
TBA = tetrabutylammonium
MMA = methyl methacrylate

better living conditions result. A controversy exists whether chain growth results directly from addition of intermediate **11** to monomer (*38*) or from formation of an equilibrium amount of enolate **12** (*39*). Although the same polymers are produced by anionic polymerization of methacrylates, GTP operates at more commercially attractive temperatures (~80°C).

The polymer structures shown in nos. 1 to 8, Table 1, have been made by GTP. Hydroxyl-terminated star polymers (Table 1, no. 7) show promise as polymer-strengthening agents (*40*). The ladder polymer (Table 1, no. 8) was produced by initiation of a difunctional monomer with a difunctional initiator in dilute solution (*41*). This is the first example of a ladder polymer made by living polymerization techniques.

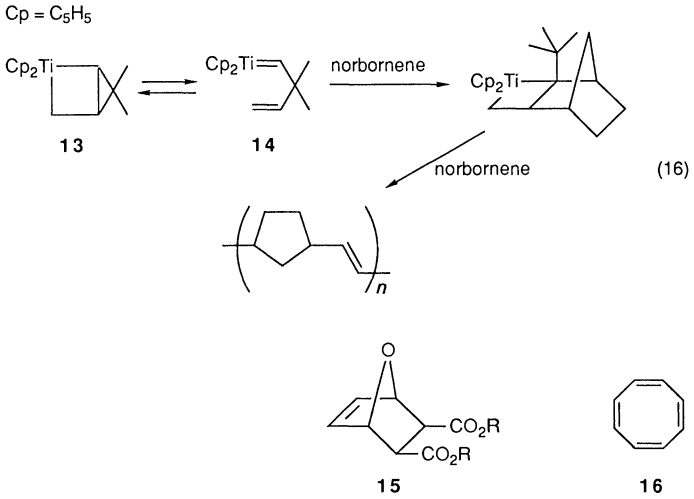
Block polymer dispersing agents and block polymer toners made by GTP are under commercial production.

In a process similar to GTP, Inoue and co-workers (*42*) have introduced immortal polymerization for living polymerizations of olefin oxides and lactones, as well as acrylates and methacrylates. An aluminum or zinc ion bound to tetraphenylporphyrin transfers from chain end to incoming monomer by a coordination process. The reaction is illustrated in Eq. 15 for ethylene oxide. The polymeriza-



tion is termed immortal polymerization since protoic substances do not kill the polymerization. Since alcohols rapidly exchange with the TPP–Al–OR, it is effectively the catalyst for living polymerization of olefin oxides initiated by alcohols (*43*).

In 1984, Grubbs and Gilliom reported the first living ring-opening metathesis polymerization (ROMP) of cyclic olefins (*44*). Nonliving metathesis polymerization had been known for many years. The breakthrough to obtaining living polymerization was in finding an organometallic catalyst with enough activity to metathesize a strained olefin but not enough activity to react with the unstrained double bonds inherent to the chain backbone. The titanium derivative **13** has just the right activity. At slightly above room temperature, the stable titanacyclobutane-ended polymer chains, **13**, are in equilibrium with alkylidene derivatives, **14**, which repeatedly add monomer (Eq. 16). A block polymer results when a



new strained monomer is added to dormant polymer and heat is again applied (*45*). Schrock and Murdzek (*46*) have developed a Mo-based catalyst that can polymerize functional monomers, for example, **15**.

Ring-opening metathesis "polymerization" of cyclooctatetraene **16** provides a route to polyacetylene which, when doped, conducts electricity (*47*). The titanium initiator must be kept dry and in an inert atmosphere. In recent work, Grubbs and co-workers (*48*) have discovered a Ru catalyst that can effect ROMP in water.

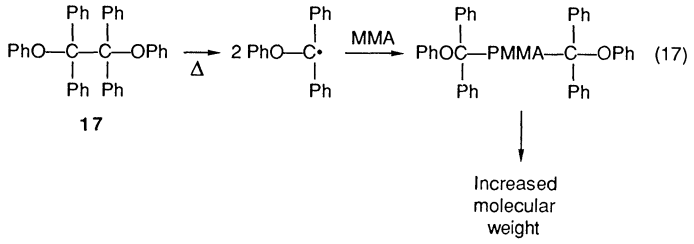
Doi *et al.* (*49*) have shown that coordination polymerization of propylene at −78°C with V(acetylacetonate)$_3$/$AlEt_2Cl$ catalyst is living. In a like manner, Bochmann *et al.* (*50*) have used *bis*(indenyl)$TiMe^+$ $^-BPh_4$ and Bercaw (*51*) has used $(C_5Me_5)_2ScR$ to obtain living polyethylene. In standard coordination polymerization of ethylene and propylene, extensive β-hydride elimination occurs. Teyssié and co-workers (*52*) have reported living polymerization of butadienes by *bis*[η^3-allyl) (trifluoroaceto)nickel.

The first living polymerization of an acetylene monomer was recently reported by Higashimura. 1-Chloro-1-octyne (ClC≡C–*n*-C_6H_{13}), as well as other chloroacetylenes, gave living polymer when treated with $MoCl_5$/*n*-Bu_4Sn/EtOH (*53*) or $MoOCl_4$/*n*-Bu_4Sn/EtOH (*54*). The ratios of moles propagating species produced to

moles Mo catalyst used were rather small (~0.02), although narrow molecular weight distributions (1.1 to 1.3) were obtained and polymer molecular weights increased in direct proportion to conversions. The true initiator, therefore, is not $MoCl_5$/*n*-Bu_4Sn/EtOH nor $MoOCl_4$/*n*-Bu_4Sn/EtOH, but some species formed from these mixtures or from an impurity.

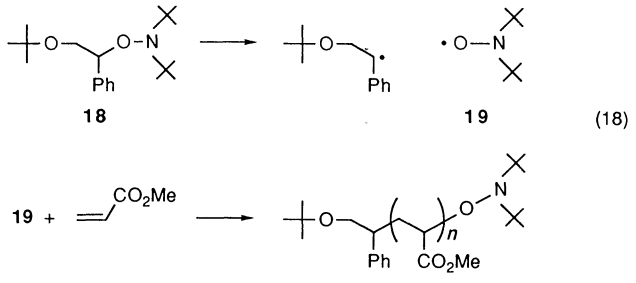
Free Radical Living Polymerizations

At present, no truly living, free radical polymerization exists. Extensive research on the problem by Otsu and co-workers (*55*) and Braun and co-workers (*56*) has provided usable techniques that give block and end-functional polymers. The goal is to find a free radical capping agent that will reversibly react with the free radical chain ends but that will not initiate new chains. Braun has used **17** to initiate and cap methyl methacrylate. On heating capped polymer with fresh monomer, polymerization resumes (Eq. 17). In



(17)

similar work, Otsu uses NMe_2CS_2– and also Ar_3C– as caps. These systems work well enough to provide routes to block and end-functionalized polymers. Possibly the best effort at living free radical polymerization has been reported by Solomon *et al.* in a patent (*57*). The capping radicals that he used were nitroxides, **19**. The process in which **18** is used as an initiator for methyl acrylate is shown in Eq. 18. On average, molecular weight dispersities were less than 2.



(18)

Conclusions

In the past decade a staggering number of different block polymers, macromonomers, macro–cross-linking agents, stars, and networks have become available through living polymerization techniques. The challenge now is to use these advanced materials to produce advanced products. The goal of this review has been to highlight what is available to the synthetic polymer chemist with the thought in mind that it is difficult to use something unless you know that it exists.

Our synthetic tool box still needs methods for controlled polymerization of vinyl acetate, vinyl chloride, and fluorocarbon monomers. A truly living, free radical polymerization may be the answer. Most of the living polymerizations require low temperatures. For commercial production, processes that operate at above ambient temperatures are desirable. A breakthrough would be to find a way to synthesize polymer molecules one monomer unit at a time—like nature does. The Merifield synthesis (*58*) is not sufficient. A procedure like the one Tomalia (*59*) uses to synthesize dendritic polymer, in which the molecular weight is doubled as each shell is added, is an important step in the right direction.

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DNA: A Model Compound for Solution Studies of Macromolecules

R. PECORA

Well-defined, monodisperse, homologous series of oligonucleotides and DNA restriction fragments may now be produced and used as models of rigid and semirigid rodlike molecules in solution. Information from optical experiments on these model systems aids in the formulation and testing of theories of macromolecular dynamics in both dilute and concentrated solution.

THE PROPERTIES OF POLYMERIC SUBSTANCES ARE DETERMINED by their microscopic molecular structure and dynamics. Many of these properties, especially those that involve motion of the whole or large portions of a polymer chain, are strongly dependent on molecular weight. Most polymeric substances, whether they are solids or liquid dispersions, are polydisperse. They contain polymeric chains of varying degrees of polymerization (molecular weights). Such molecular weight dispersions make it difficult to test microscopic theories of polymer behavior that involve molecular weight–dependent properties. It is highly desirable for fundamental polymer science studies to have sets of well-defined, monodisperse, homologous series of model macromolecules (*1*).

It is generally very difficult to prepare such monodisperse series for synthetic macromolecules, although in some cases relatively narrow dispersions can be made by using "living polymerization" and other methods (*2, 3*). In many cases, fractionation of polydisperse materials can substantially reduce an initial polydispersity, but the resulting material is for many purposes usually still too polydisperse. Very narrowly disperse samples can be prepared of many biological macromolecules and particles (such as virus particles), but it is difficult in most cases to prepare homologous series.

Rigid and semirigid rodlike polymers are of great commercial and biological interest. Some of these polymers, especially the biological ones, are soluble in common solvents. However, even those that are not easily soluble normally must be characterized or processed in solution. For instance, many high-performance polymeric materials, such as Du Pont's Kevlar, are rigid rod polymers. These polymers, in addition to being highly polydisperse, are hard to prepare in high molecular weights and usually cannot be dissolved in noncorrosive solvents. Thus it is difficult to perform careful physicochemical experiments on these systems to characterize their properties (average molecular weights, polydispersity, and so forth) or to test molecular theories of their behavior in solution and in the melt. Their lack of easy solubility also creates problems in processing them into useful materials. Biological examples (usually water soluble) of semirigid rodlike molecules include the rodlike proteins such as collagen, myosin, actin, tubulin, rodlike viruses such as tobacco mosaic virus, fd-virus, and molecules such as the DNAs.

The DNAs present an exception to most of the difficulties of preparing a monodisperse, homologous series of molecules. Very short DNAs ranging from the monomer to about 100 base pairs (bp) in length ("oligonucleotides") may be relatively easily prepared with the aid of DNA synthesizers. Larger molecules may be made by using genetic engineering techniques to prepare appropriate bacterial plasmid DNAs from which monodisperse, blunt-ended fragments may be cut with restriction enzymes ("restriction fragments"). It is also likely that recently developed polymerase chain reaction (PCR) techniques may be used to produce oligonucleotides and fragments even more cheaply than has been previously done. The DNAs are, of course, soluble in water and can be dissolved in other solvents, such as alcohol-water mixtures, to study such phase phenomena as polymer collapse, polymer aggregation, and phase separation. The DNAs are also polyelectrolytes and so they may be used as models for the effects of small ions and the long-range Coulomb force on both the properties of a single polymer chain in solution and the interactions between polyions. The model polyelectrolyte that is most often studied is polystyrene sulfonate, whose polydispersity clouds much of the interpretation of the otherwise sophisticated experiments on it (*4*). Disadvantages of using the DNAs as model molecules include the labor and cost of producing the relatively large amounts needed for certain types of physiochemical measurements. There are also uncertainties expressed by several authors as to the complexity of DNA. For instance, it may be that proteins, either in the natural state or those introduced somewhere in the processing of the DNA, bind to the DNA and cause structural changes in it which affect the properties. Thus, it is possible that one may be studying different materials when ostensibly the same materials are prepared by different procedures (*5*).

In my laboratory a range of DNAs have been used as model systems for macromolecular dynamics in solution. The smaller oligonucleotides (less than about 30 bp in length) are used to test hydrodynamic theories of translational and rotational diffusion for rodlike molecules of relatively low length-to-diameter ratios as well as to extract information about DNA structure and dynamics.

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