Chapter 7

Chain-Reaction (Addition) Polymerization

I. INTRODUCTION

Unsaturated monomers are converted to polymers through chain reactions. In chain polymerization processes, the active center is retained at the end of a growing polymer chain and monomers are added to this center in rapid succession. The rate of addition of monomers to the active center relative to the overall conversion of the monomer to polymer is quite fast. This means that high-molecular-weight polymers are generated even while most of the monomers remain intact. Also, polymers formed at the initial stage of the reaction are little affected by the extent of reaction and are of comparable molecular weight with those formed later in the reaction. Thus in a partially polymerized mixture, only high-molecular-weight polymers and unchanged monomers are present with virtually no intermediates between these ends of the molecular weight spectrum.

II. VINYL MONOMERS

From elementary organic chemistry, we know that the positions and hence reactivities of the electrons in unsaturated molecules are influenced by the nature, number, and spatial arrangement of the substituents on the double bond. As a result of these influences, the double bond reacts well with a free radical for compounds of the types $CH_2 = CHY$ and $CH_2 = CXY$. These compounds constitute the so-called vinyl monomers where X and Y may be halogen, alkyl, ester, phenyl, or other groups. It must, however, be noted that not all vinyl monomers produce high polymers. In symmetrically disubstituted double bonds (e.g., 1, 2 disubstituted ethylenes) and sterically hindered compounds of the type $CH_2 = CXY$, polymerization, if it occurs at all, proceeds slowly.

The active centers that are responsible for the conversion of monomer to polymer are usually present in very low concentrations and may be free radicals, carbanions, carbonium ions, or coordination complexes among the growing chain, the catalyst surface, and the adding monomer. Based on the nature of the active center, chain-reaction polymerization may be subdivided into free-radical, ionic (anionic or cationic), or coordination polymerization. Whether or not the polymerization of a particular monomer proceeds through one or more of these active centers depends partly on the chemical nature of the substituent group(s). Monomers with an electron-withdrawing group can proceed by an anionic pathway; those with an electron-donating group by a cationic pathway. Some monomers with a resonance-stabilized substituent group — for example, styrene — can be polymerized by more than one mechanism. Table 7.1 summarizes the various polymerization mechanisms for several monomers.

III. MECHANISM OF CHAIN POLYMERIZATION

Irrespective of the character of the active center, chain-reaction polymerization, like all chain reactions, consists of three fundamental steps. These are *initiation*, which involves the acquisition of the active site by the monomer; *propagation*, which is the rapid and progressive addition of monomer to the growing chain without a change in the number of active centers; and *termination*, which involves the destruction of the growth activity of the chain leaving the polymer molecule(s). In addition to the above three processes, there is the possibility of another process known as *chain transfer* during which the growth activity is transferred from an active chain to a previously inactive species. We now discuss each of these steps in greater detail.

A. INITIATION

Initiation, as noted above, involves the generation of active species, which can be through free-radical, ionic, or coordination mechanism. This mechanism of chain initiation is the essential distinguishing feature between different polymerization processes. Quite expectedly, therefore, addition polymerization of vinyl

Table 7.1 *Initiation Mechanisms Suitable for the Polymerization of Olefin Monomers*

Olefin Monomer	Monomer Structure	Free Radical	Anionic	Cationic	Coordination
Ethylene	CH_2› CH_2	+	–	+	+
Propene	CH_2› CHMe	–	–	–	+
Butene-1	CH_2› CHEt	–	–	–	+
Isobutene	CH_2› Cme_2	–	–	+	–
Butadiene-1,3	CH_2› CH–CH› CH_2	+	+	–	+
Isoprene	CH_2› C(Me)–CH–CH_2	+	+	–	+
Styrene	CH_2–CHPh	+	+	+	+
Vinyl chloride	CH_2› CHCl	+	–	–	+
Vinylidene chloride	CH_2› CCl_2	+	+	–	–
Vinyl fluoride	CH_2› CHF	+	–	–	–
Tetrafluoroethylene	CF_2› CF_2	+	–	–	+
Vinyl ethers	CH_2› CHOR	–	–	+	+
Vinyl esters	CH_2› CHOCOR	+	–	–	–
Acrylic esters	CH_2› CHCOOR	+	+	–	+
Methacrylic esters	CH_2› C(Me)COOR	+	+	–	+
Arcrylonitrile	CH_2› CHCN	+	+	–	+

Note: +, monomer can be polymerized to high-molecular-weight polymer by this form of initiation; –, no polymerization reaction occurs or only low-molecular-weight polymers or oligomers are obtained with this type of initiator.

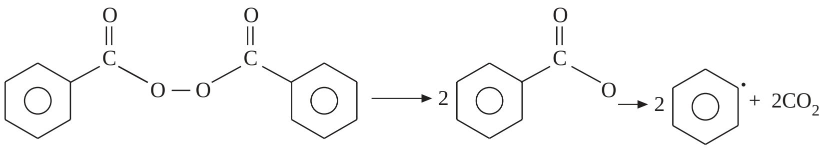
From Lenz, R.W., *Organic Chemistry of High Polymers,* Interscience, New York, 1967. © John Wiley & Sons. Reprinted with permission of John Wiley & Sons.

monomers differs from system to system, and a proper choice of the nature of the system vis-a-vis the monomer being polymerized is crucial to the degree of success of polymerization of vinyl monomers.

1. Generation of Free Radicals

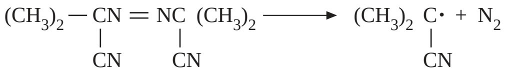
Free radicals can be generated by a number of ways, including thermal or photochemical decomposition of organic peroxides, hydroperoxides, or azo or diazo compounds. Other methods of generation of free radicals include dissociation of covalent bonds by high-energy irradiation and oxidation–reduction (redox) reactions. The active species produced by these processes are referred to as initiators. These species are frequently but erroneously also called catalysts. Initiators are consumed in the reaction while catalysts are regenerated after the reaction. Compounds usually used for free-radical generation include

- Benzoyl peroxide



(Str. 1)

- Azo-*bis*-isobutyronitrile (AIBN)

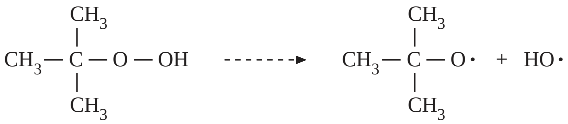


$$(CH_3)_2-\underset{|\atop CN}{C}N=N\underset{|\atop CN}{C}\ (CH_3)_2 \longrightarrow (CH_3)_2\ \underset{|\atop CN}{C}\cdot + N_2$$

- Potassium persulfate

$$K_2S_2O_8 \longrightarrow 2K^+ + 2SO_4^{-}\cdot$$

- *t*-Butylhydroperoxide



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O-OH \dashrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O\cdot + HO\cdot \qquad \text{(Str. 2)}$$

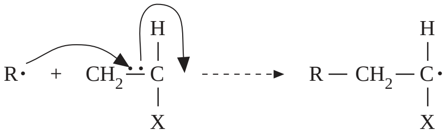
Peroxide-type initiators in aqueous system can be decomposed in redox reactions, particularly with reducing agents like ferrous ions, to produce free radicals.

$$\begin{aligned} &H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO\cdot \\ &S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\cdot \end{aligned} \qquad \text{(Str. 3)}$$

The initiation step in free-radical polymerization in the presence of thermal initiators is a two-step process: first is the homolysis of the relatively weak covalent bond in the initiator, designated here by R:R

$$R{:}R \rightarrow 2R\cdot \qquad (7.1)$$

Second, in the presence of a vinyl monomer, the free radical thus generated adds to one of the electrons of one of the bonds constituting the double bonds in the monomer. The remaining electron now becomes the new free radicals:

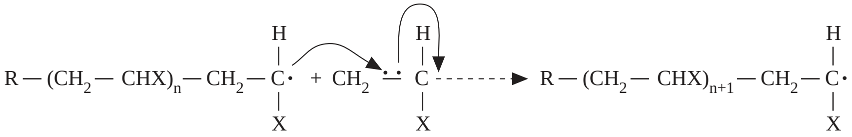


$$R\cdot + CH_2 \overset{\cdot\cdot}{=} \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}} \dashrightarrow R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot \qquad (7.2)$$

The first step is the rate-limiting step in the initiation process. That the above scheme represents that initiation mechanism, and is indeed partly evidence for the free-radical mechanism in addition polymerization of vinyl monomers, has been established by the presence of initiator fragments found to be covalently bound to polymer of molecules. The efficiency with which radicals initiate chains can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed.

B. PROPAGATION

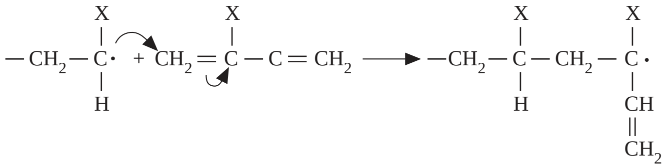
The free radical generated in the initiation step adds monomers in very rapid succession. Again, this consists of an attack of the free radical on one of the carbon atoms in the double bond. One of the electrons from the double bond pairs up with the free-radical electron forming a bond between the initiator fragment and the attacked carbon atom. The remaining electron shifts to the "unattacked" carbon atom of the double bond, which consequently becomes the free radical. In this way the active center is transferred uniquely to the newly added monomer. This process then continues until termination sets in.



$$R-(CH_2-CHX)_n-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot + CH_2 \overset{\cdot\cdot}{=} \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}} \dashrightarrow R-(CH_2-CHX)_{n+1}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot \qquad (7.3)$$

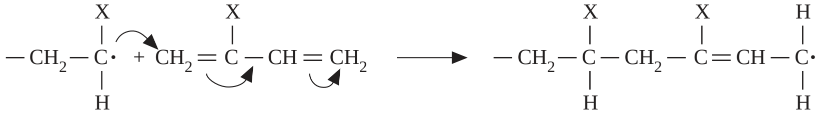
For diene monomers, the propagation mechanism is exactly the same as that of vinyl monomers. But the presence of two double bonds means either of two possible attacks can occur. Consequently, propagation of dienes may proceed in one of two ways: 1,4 (*trans* or *cis*) and 1,2:

1,2 addition



$$-CH_2-\overset{X}{\underset{H}{C}}\cdot + CH_2=\overset{X}{C}-C=CH_2 \longrightarrow -CH_2-\overset{X}{\underset{H}{C}}-CH_2-\overset{X}{\underset{\underset{CH_2}{\overset{\|}{CH}}}{C}}\cdot \qquad (7.4)$$

1,4 addition



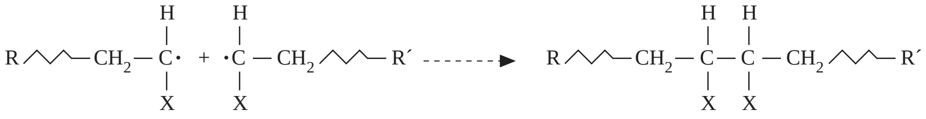
$$-CH_2-\overset{X}{\underset{H}{C}}\cdot + CH_2=\overset{X}{C}-CH=CH_2 \longrightarrow -CH_2-\overset{X}{\underset{H}{C}}-CH_2-\overset{X}{C}=CH-\overset{H}{\underset{H}{C}}\cdot \qquad (7.5)$$

In 1,2 addition, the unsaturation is part of the pendant group. In 1,4 addition, however, the unsaturation is part of the backbone. Two configurations are possible — *trans* or *cis*. These considerations have important consequences for the properties and hence end use of the resulting polymers.

C. TERMINATION

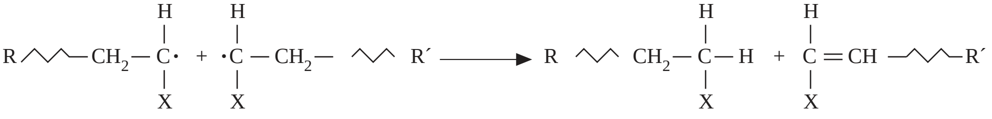
The propagation step would theoretically have continued until the consumption of all available monomers but for the tendency of pairs of free radicals to react and annihilate their mutual activities. The termination steps can occur by either of two mechanisms: combination (coupling) or disproportionation.

1. Combination or coupling — Two growing polymer chains yield a single polymer molecule terminated at each end by an initiator fragment.



$$R\sim\sim CH_2-\overset{H}{\underset{X}{C}}\cdot + \cdot\overset{H}{\underset{X}{C}}-CH_2\sim\sim R' \dashrightarrow R\sim\sim CH_2-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-CH_2\sim\sim R' \qquad (7.6)$$

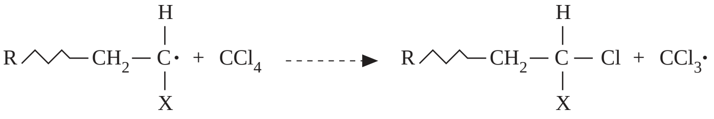
2. Disproportionation — This involves hydrogen transfer with the formation of two polymer molecules, one with a saturated end and the other with an unsaturated terminal olefin and each with an initiator fragment.



$$R\sim\sim CH_2-\overset{H}{\underset{X}{C}}\cdot + \cdot\overset{H}{\underset{X}{C}}-CH_2-\sim\sim R' \longrightarrow R\sim\sim CH_2-\overset{H}{\underset{X}{C}}-H + \overset{H}{\underset{X}{C}}=CH\sim\sim R' \qquad (7.7)$$

D. CHAIN TRANSFER

In addition to the three fundamental processes described above for chain-growth (addition) polymerization, another important process, chain transfer, may occur. Chain transfer involves the transfer of radical reactivity to another species, which may be a monomer, a polymer, a solvent, an initiator, or an impurity. This creates a new species that is capable of further propagation but terminates the growth of the original chain. The transfer reaction involves the transfer of an atom between the radical and the molecule. For a saturated molecule like a solvent an atom is transferred to the radical:



$$R\sim\sim CH_2-\overset{H}{\underset{X}{C}}\cdot + CCl_4 \dashrightarrow R\sim\sim CH_2-\overset{H}{\underset{X}{C}}-Cl + CCl_3\cdot \qquad (7.8)$$

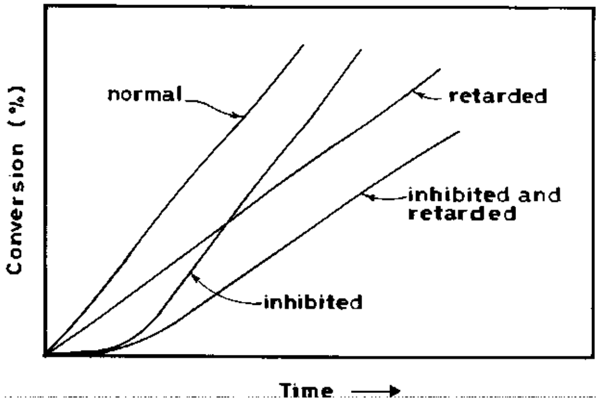
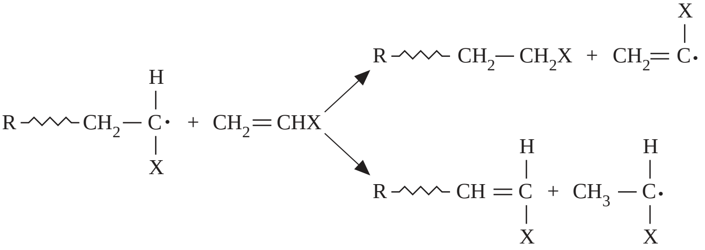


Figure 7.1 *The influence of retarders and inhibitors on conversion.*

On the other hand, if the molecule is unsaturated, like a monomer, the atom can be transferred to either the monomer or the chain radical:



$$\mathrm{R}\sim\sim\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot + \mathrm{CH_2}{=}\mathrm{CHX} \begin{array}{l} \nearrow \mathrm{R}\sim\sim\mathrm{CH_2}-\mathrm{CH_2X} + \mathrm{CH_2}{=}\overset{\mathrm{X}}{\mathrm{C}}\cdot \\ \searrow \mathrm{R}\sim\sim\mathrm{CH}{=}\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}} + \mathrm{CH_3}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot \end{array} \qquad (7.9)$$

It can be seen from this scheme that in chain transfer, radicals are neither created nor destroyed. Consequently, the overall polymerization rate is unaffected by chain-transfer processes. However, as we shall see presently, it does limit the obtainable molecular weight.

Chain transfer generally involves the cleavage of the weakest bond in the molecule. Consequently, molecules with active hydrogens play important roles in chain polymerization. A material deliberately added to the system to control molecular weight by chain transfer is called a *chain-transfer agent.* A substance that, if added to the monomer, reacts with chain radicals to produce either nonradical products or radicals with such low reactivity as to be incapable of adding monomer (and thus reducing the polymerization rate) is called a *retarder.* If a retarder is so effective as to completely suppress the rate and degree of polymerization, it is referred to as an *inhibitor.* Thus the distinction between the retarder and inhibitor is merely that of degree. If an inhibitor added to a system is consumed by the radicals generated within the system, an induction period during which no polymerization takes place ensues. Thereafter, normal polymerization occurs. In some cases, added substances first inhibit the polymerization process and then allow polymerization to occur at slower than normal rates. These phenomena are illustrated in Figure 7.1.

Retarders and inhibitors generally operate by chain-transfer mechanism. These substances may be impurities in the system or are formed by side reactions during polymerization. In some cases, they are added deliberately to the system to prevent inadvertent polymerization during transportation or storage. A typical example is hydroquinone, normally added to styrene must be subsequently stripped of the inhibitor before polymerization.

IV. STEADY-STATE KINETICS OF FREE-RADICAL POLYMERIZATION

The overall mechanism for the conversion of a monomer to a polymer via free-radical initiation may be described by rate equations according to the following scheme.

A. INITIATION

As noted earlier, this is a two-step process involving:

1. The decomposition of the initiator into primary radicals

$$I \xrightarrow{k_d} 2R\cdot \qquad (7.10)$$

2. The addition of a monomer to the primary free radical

$$R\cdot + M \xrightarrow{k_a} RM_i\cdot \qquad (7.11)$$

The constants k_d and k_a are the rate constants for initiator dissociation and monomer addition, respectively. Since initiator dissociation (eqn. 7.10) is much slower than monomer addition (eqn. 7.11), the first step of the initiation step (initiator dissociation) is the rate-limiting step. Some of the initiator radicals may undergo side (secondary) reactions, such as combination with another radical, that preclude monomer addition. Therefore only a fraction, f (an efficiency factor), of the initial initiator concentration is effective in the polymerization process. Also, decomposition of each initiator molecule produces a pair of free radicals, either or both of which can initiate polymerization. Based on these observations, the rate expression for initiation may be written as:

$$R_i = \frac{d[M.]}{dt} = 2\, fk_d [I] \qquad (7.12)$$

where $[I]$ represents the initiator concentration.

B. PROPAGATION

The successive addition of monomers during propagation may be represented as follows:

$$\begin{aligned} RM_1\cdot + M &\xrightarrow{k_p} RM_2\cdot \\ RM_2\cdot + M &\xrightarrow{k_p} RM_3\cdot \end{aligned} \qquad (7.13)$$

In general,

$$RM_x\cdot + M \xrightarrow{k_p} RM_{x+1}^{\Sigma} \qquad (7.14)$$

The above scheme is based on the assumption that radical reactivity is independent of chain length. Essentially, this means that all the propagation steps have the same rate constants k_p. In addition, propagation is a fast process. For example, under typical reaction conditions, a polymer of molecular weight of about 10^7 may be produced in 0.1 s. It may therefore be assumed that the number of monomer molecules reacting in the second initiation step is insignificant compared with that consumed in the propagation step. Thus the rate of polymerization equals essentially the rate of consumption of monomers in the propagation step. The rate expression for polymerization rate can therefore be written thus:

$$R_p = -\frac{d[M]}{dt} = k_p [M^*][M] \qquad (7.15)$$

where $[M^*] = \sum RM_x\bullet$ i.e., the sum of the concentrations of all chain radicals of type RM_x.

C. TERMINATION

Chain growth may be terminated at any point during polymerization by either or both of two mechanisms:

- Combination (coupling)

$$M_x\cdot + M_y\cdot \xrightarrow{k_{tc}} M_{x+y} \qquad (7.16)$$

- Disproportionation

$$M_x\cdot + M_y\cdot \xrightarrow{k_{td}} M_x + M_y \tag{7.17}$$

If there is no need to distinguish between the two types of termination, which in any case are kinetically equivalent, then termination may be represented as:

$$M_x\cdot + M_y\cdot \xrightarrow{k_t} P \tag{7.18}$$

where $k_t(k_{tc} + k_{td})$, k_{tc}, and k_{td} are the rate constants for overall termination process, termination by coupling, and termination by disproportionation, respectively. The termination rate is given by:

$$R_t = \frac{-d[M\cdot]}{dt} = 2k_t[M\cdot]^2 \tag{7.19}$$

The factor of 2 arises from the fact that at each incidence of termination reaction, two radicals disappear.

Over the course of polymerization (at steady state), the total radical concentration remains constant. This means that radicals are being produced and destroyed at equal rates (i.e., $R_i = R_t$). It follows from Equations 7.12 and 7.19 that

$$[M\cdot] = \left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2} \tag{7.20}$$

Since the overall polymerization rate is essentially the rate of monomer consumption during propagation, substitution of Equation 7.20 into Equation 7.15 yields:

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M] \tag{7.21}$$

Note that Equation 7.21 predicts that rate of polymer formation in free-radical polymerization is first order in monomer concentration and half order in initiator concentration. This assumes, of course, that the initiator efficiency is independent of monomer concentration. This is not strictly valid. In fact, in practice Equation 7.21 is valid only at the initial stage of reaction; its validity beyond 10 to 15% requires experimental verification. Abundant experimental evidence has confirmed the predicted proportionality between the rate of polymerization and the square root of initiator concentration at low extents of reaction (Figure 7.2). If the initiator efficiency, f, is independent of the monomer concentration, then Equation 7.21 predicts that the quantity $R_p/[I]^{1/2}[M]$ should be constant. In several instances, this ratio has indeed been found to show only a small decrease even over a wide range of dilution, indicating an initiator efficiency that is independent of dilution. This confirmation of first-order kinetics with respect to the monomer concentration suggests an efficiency of utilization of primary radicals, f, near unity. Even where the kinetics indicate a decrease in f with dilution, the decreases have been invariably small. For undiluted monomers, efficiencies near unity are not impossible.

Example 7.1: The following are data for the polymerization of styrene in benzene at 60°C with benzoyl peroxide as the initiator.

$[M] = 3.34 \times 10^3$ mol/m^3
$[I] = 4.0$ mol/m^3
$k_p^2/k_t = 0.95 \times 10^{-6}$ m^3/mol-s

If the spontaneous decomposition rate of benzoyl peroxide is 3.2×10^{-6} m^3/mol-s^{-1}, calculate the initial rate of polymerization.

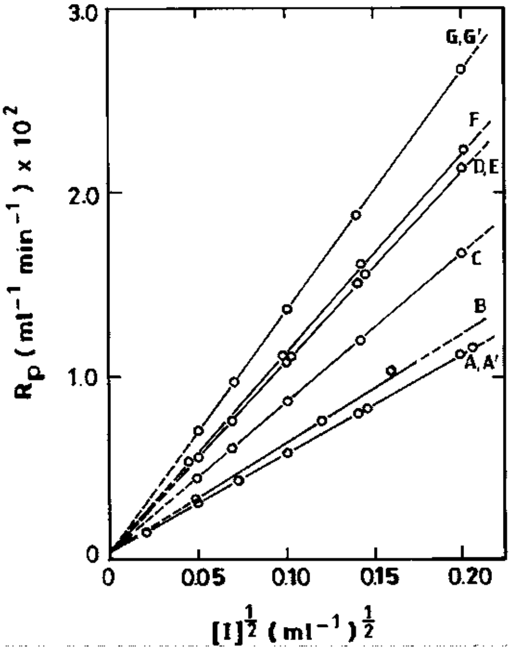


Figure 7.2 *Relationship between initiator concentration and polymerization rate for different initiators: A, bis(p-chlorobenzoyl)peroxide; B, benzoyl peroxide; C, acetyl peroxide in dimethylphthalate; D, lauroyl peroxide; E, myristoyl peroxide; F, caprylyl peroxide; G, bis(2,4 dichlorobenzoyl) peroxide. [A.I. Lowell and J.R. Price, J. Poly. Sci., 43, 1 (1996). With permission.]*

Solution: For the initial rate of polymerization, Equation 7.21 is valid. Assuming the initiator efficiency f = 1, then

$$R_p = k_p \left(k_d / k_t\right)^{1/2} [I]^{1/2} [M]$$

$$R_p^2 = k_d \left(k_p^2 / k_t\right) [I] [M]^2$$

$$\left(3.2 \times 10^{-6} \frac{m^3}{mol \cdot s}\right)\left(0.95 \times 10^{-6} \frac{m^3}{mol \cdot s}\right)\left(4.0 \frac{mol}{m^3}\left(3.34 \times 10^3 \frac{mol}{m^3}\right)^2\right.$$

$$R_p = 11.65 \times 10^{-3}\ mol/m^3 - s$$

$$R_p = 0.012\ mol/m^3 - s$$

Example 7.2: The data for the bulk polymerization of styrene at 60°C with benzoyl peroxide as initiator are

$[M] = 8.35 \times 10^3$ mol/m^3
$[I] = 4.0$ mol/m^3
$k_p^2/k_d = 1.2 \times 10^{-6}$ m^3/mol-s

If the initial rate of polymerization of styrene is 0.026 mol/m^3-s and the spontaneous decomposition of benzoyl peroxide in styrene is 2.8×10^{-6} s^{-1}, what is the efficiency of the initiator?

Solution:

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

$$R_p^2 = fk_d\left(\frac{k_p^2}{k_t}\right)[I][M]^2$$

$$fk_d = \frac{(0.026)^2}{1.26 \times 4 \times (8.35)^2}$$

$$= 1.92 \times 10^{-6}$$

$$f = \frac{1.92 \times 10^{-6}}{2.8 \times 10^{-6}} = 0.7$$

V. AUTOACCELERATION (TROMMSDORFF EFFECT)

Since the initiator concentration remains fairly unchanged in the course of vinyl polymerization, if the initiator efficiency is independent of monomer concentration, first-order kinetics with respect to the monomer is expected. This is indeed observed over a wide extent of reaction for the polymerization of styrene in toluene solution with benzoyl peroxide as initiator (Figure 7.3). The polymerization of certain monomers, either undiluted or in concentrated solution, shows a marked deviation from such first-order kinetics. At a certain stage in the polymerization process, there is a considerable increase in both the reaction rate and the molecular weight. This observation is referred to as *autoacceleration* or *gel effect* and is illustrated in Figure 7.4 for polymerization of methyl methacrylate at various concentrations of the monomer in benzene.

Observe that for monomer concentrations of up to 40%, plots show that first-order kinetics is followed. However, at higher initial monomer concentrations, a sharp increase in rate is observed at an advanced stage of polymerization. At the same time, high-molecular-weight polymers are produced. Autoacceleration is particularly pronounced with methyl methacrylate, methyl acrylate, and acrylic acid. It occurs independent of an initiator and is observed even under isothermal conditions. In fact, where there is no effective dissipation of heat, autoacceleration results in a large increase in temperature.

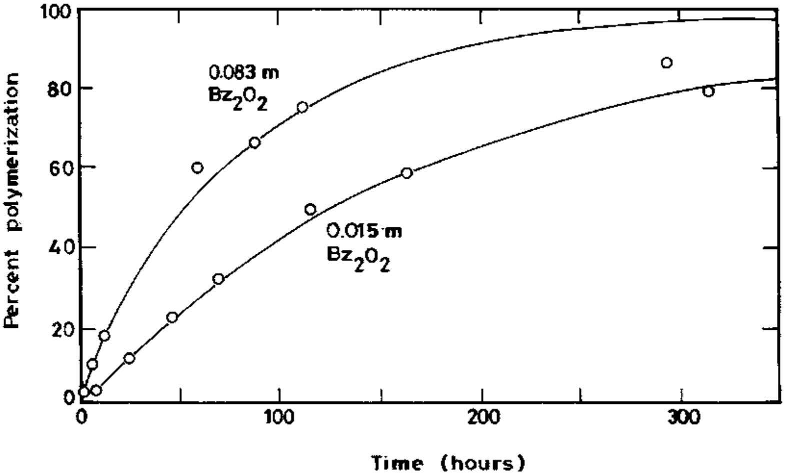


Figure 7.3 *Polymerization of 40 percent styrene in toluene at 50°C in the presence of the amounts of benzoyl peroxide shown. (G.V. Schulz and E. Husemann, Z. Physik Chem., B39, 246, 1938. With permission.)*

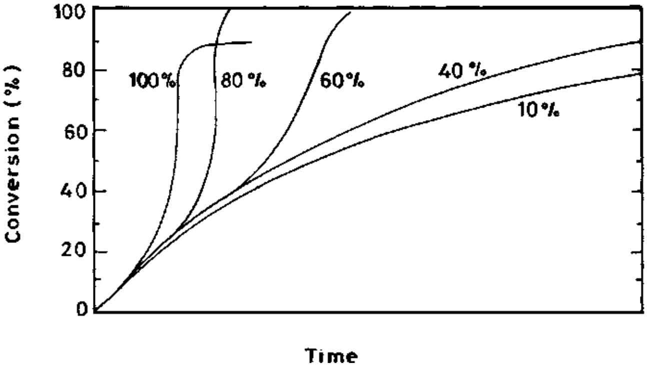


Figure 7.4 *The course of polymerization of methyl methacrylate at 50°C in the presence of benzoyl peroxide at different concentrations of monomer in benzene. (G.V. Schulz and G. Harboth, Macromol. Chem., 1, 106, 1947.)*

To understand the physical phenomena taking place during autoacceleration, let us look more carefully at the rate equation:

$$R_p \propto k_p \left(\frac{fk_d}{k_t} \right)^{1/2}$$

Since autoacceleration is not a function of the initiator, an increase in the factor fk_d does not provide an explanation for the observation. Consequently the phenomenon of autoacceleration could be due to an increase in the propagation rate constant k_p and/or a decrease in the termination rate constant k_t. Trommsdorff attributed autoacceleration to a decrease in the termination rate. As the concentration of polymer molecules generated builds up, the viscosity of the medium increases. This reduces the overall diffusion rate of growing radical-bearing polymer molecules even though the intrinsic reactivity of the radical remains unaffected. As a result, the bimolecular annihilation of radical reactivity becomes diffusion-controlled. This reduction in termination rate, in turn, increases the concentration of active radicals, and the rate of local consumption of monomers increases proportionately. The overall rate of propagation, however, remains relatively unaffected since the diffusion of monomers is hardly affected by the high medium viscosity. This reduction in termination rate with little or no change in the propagation rate leads to a rapid rise in the molecular weight.

A further reference to Figure 7.4 shows that autoacceleration does not result in complete polymerization of monomers. Also, the higher the dilution, the higher the extent of conversion. Pure poly(methyl methacrylate) has a glass transition temperature of about 90°C. It therefore follows that when the percentage of polymers formed reaches a certain high value, the reaction mixture is transformed into a glass at temperatures below 90°C. Propagation becomes monomer diffusion-controlled, and there is a virtual cessation of polymerization. There is ample experimental evidence to support the above explanation for the phenomenon of autoacceleration.

VI. KINETIC CHAIN LENGTH

The kinetic chain length, ν, is defined as the average number of monomers consumed by each primary radical. Obviously from this definition, the magnitude of the kinetic chain length will depend on the rate of the propagation relative to the termination rate, i.e.,

$$\nu = \frac{R_p}{R_t} \tag{7.22}$$

Since at steady state the rate of initiation equals the rate of termination, Equation 7.22 can also be written as

$$\nu = \frac{R_p}{R_t} = \frac{R_p}{R_i} \tag{7.23}$$

It follows on substitution for R_p and R_t from Equations 7.15 and 7.19, respectively, that

$$\nu = \left(\frac{k_p}{2k_t}\right)\frac{[M]}{[M\cdot]} \tag{7.24}$$

Substituting for [M·] from Equation 7.15 yields:

$$\nu = \left(\frac{k_p^2}{2k_t}\right)\frac{[M]^2}{R_p} \tag{7.25}$$

Equations 7.24 and 7.25 are quite general and do not depend on the nature of initiation. Notice the inverse relation between the kinetic chain length and the radical concentration. For reactions initiated by the decomposition of an initiator,

$$[M\cdot] = \left(\frac{dk_d}{k_t}\right)^{1/2}[I]^{1/2}$$

Thus

$$\nu = \frac{k_p}{2\left(fk_d\ k_t\right)^{1/2}}\frac{[M]}{[I]^{1/2}} \tag{7.26}$$

The kinetic chain length should be related to the number-average degree of polymerization. The degree of complexity of this relation will depend on the existence or otherwise of side (chain-transfer) reactions. We now consider first the case where there are no chain-transfer reactions. By definition

$$\overline{X}_n = \frac{M_o - M_t}{P_t} \tag{7.27}$$

where M_o = initial number of molecules of monomer present
M_t = number of monomer molecules at time t
P_t = number of polymer molecules at time t

On differentiating with respect to time, we obtain:

$$P(t)\frac{d\overline{X}_n(t)}{dt} + \overline{X}_n(t)\frac{dP(t)}{dt} = -\frac{dM(t)}{dt} \tag{7.28}$$

For a short interval, the instantaneous number-average degree of polymerization X_{ni} is constant, hence the above expression becomes

$$\overline{X}_{ni} = -\frac{dM(t)/dt}{dP(t)/dt} \tag{7.29}$$

Recall that the rate of consumption of monomers by an active center (disappearance of monomers) is, by definition, the rate of propagation, R_p. Now, in termination by combination, two growing chains undergo mutual annihilation to produce a single inactive polymer molecule, whereas for termination by disproportionation, a biomolecular annihilation of active polymer chains results in two polymers.

Consequently, $dP(t)/dt = H\ R_t$ for termination by combination, while $dP(t)/dt = R_t$ for termination by disproportionation. From these arguments, and since at steady state $R_t = R_i$,

$$\overline{X}_{ni} = 2R_p / R_t = 2R_p / R_i \qquad \text{for termination by combination} \tag{7.30}$$

while

$$X_{ni} = R_p / R_t = R_p / R_i \qquad \text{for termination by disproportionation} \tag{7.31}$$

But kinetic chain length is given by Equation 7.23. Hence

$$\overline{X}_{ni} = 2\nu \qquad \text{for termination by combination} \tag{7.32}$$

and

$$\overline{X}_{ni} = \nu \qquad \text{for termination by disproportionation} \tag{7.33}$$

Although experimental verifications are rare, the above expressions are valid for many systems, unless of course chain-transfer reactions occur. We consider the case of the occurrence of chain transfer in the next section.

Example 7.3: For pure styrene polymerized at 60°C, the value of the ratio k_p^2/k_t is 0.0012 1/mol-s. The corresponding value for pure vinyl acetate polymerized at 60°C is 0.125 l/mol-s.

a. Estimate their relative kinetic length chain lengths.
b. Calculate the kinetic chain length for polystyrene if the rate of polymerization is 10^{-4} mol/l-s and monomer concentration is 8.35 mol/l.

Solution:

a. $\nu = \left(k_p / 2k_t\right)^2 [M]^2 / R_p$

Assume the rates of polymerization and monomer concentrations are the same for styrene(s), and vinyl acetate (VA).

$$\nu_{VA} / \nu_s = \left(k_p^2 / k_t\right)_{VA} \Big/ \left(k_p^2 / k_t\right)_s = 0.125/0.0012 = 104$$

b. $\nu_s = (0.0012/2)\,(8.35)^2 / 10^{-4} = 400$

VII. CHAIN-TRANSFER REACTIONS

Very frequently, a discrepancy exists between the value of the number-average degree of polymerization, and the predicted value of the kinetic chain length ν. The number of polymer molecules is generally found to be more than would be expected to be produced by the primary radicals (i.e., X_n is always less than either 2 ν or ν). Obviously, other components of the reaction medium initiate chain growth. The existence of such polymer-producing extraneous reactions is attributable to chain-transfer reactions that consist essentially of the following sequence of steps:

$$\begin{gathered} M_x\cdot + TL \rightarrow M_xL + T\cdot \\ T\cdot + M \rightarrow TM\cdot, \text{ etc.} \end{gathered} \tag{7.34}$$

where TL = transfer agent, which may be a solvent, monomer, initiator, or polymer
L = a labile group such as hydrogen or chlorine atoms, etc.

Transfer to a polymer does not alter the number of polymer molecules produced, therefore we neglect this type of transfer reaction in the subsequent discussion.

In the presence of transfer reactions, the expression of the kinetic chain length has to be modified to include all possible sources of polymer molecules. Thus

$$\nu = \frac{R_p}{\text{Rate of All Reactions Leading to Polymer Molecule Production}} \tag{7.35}$$

From our discussion in the preceding section, termination mechanisms for generating polymer chains and assuming all transfer species are as reactive as the original (i.e., no inhibition), the expression for ν becomes:

$$\nu = \frac{R_p}{fk_d[I] + k_{tr,M}[M][M\cdot] + k_{tr,s}[S][M\cdot] = k_{tr,I}[I][M\cdot]} \tag{7.36}$$

where $k_{tr,M}$ $k_{tr,S}$ and $k_{tr,I}$ are velocity constants for chain transfer to monomer M, solvent S, and initiator I, respectively. To estimate the tendency for transfer quantitatively, we define transfer constants:

$$C_M = \frac{k_{tr,M}}{k_p};\ C_S = \frac{k_{tr,S}}{k_p};\ C_I = \frac{k_{tr,I}}{k_p} \tag{7.37}$$

Since $\overline{X}_n = \nu$ and substituting for [I] and [M·] Equation 7.36 becomes:

$$\frac{1}{\overline{X}_n} = \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + C_M + C_s\frac{[S]}{[M]} + C_I\left(\frac{k_t}{k_p^2\, fk_d}\right)\frac{R_p^2}{[M]^3} \tag{7.38}$$

$$\frac{1}{\overline{X}_n} = C_M + C_s\frac{[S]}{[M]} + \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + C_I\left(\frac{k_t}{k_p^2\, fk_d}\right)\frac{R_p^2}{[M]^3} \tag{7.39}$$

The complexity of this equation can be greatly reduced if, for example, polymerization of undiluted monomer is done (absence of a solvent) or conditions are chosen so as to minimize or even eliminate transfer to the initiator. In some cases substances exist whose transfer constants are equal to or exceed unity. These substances are useful in controlling the molecular weight of the polymer. With the addition of small quantities of such substances, known as *regulators* or *modifiers*, the molecular weight can be depressed to a desired level. In the preparation of synthetic rubbers from butadiene or diolefins, aliphatic mercaptans are frequently added to reduce the polymer chain length to a desired range required for subsequent processing. The effect of chain transfer on chain length and polymer structure is summarized in Table 7.2.

Table 7.2 *Effect of Chain Transfer on Chain Length and Structure*

Chain Transfer To	R_p	$\overline{M}_n$	$\overline{M}_w$	Molecular Architecture
Small molecule resulting in active radical	None	Decreases	Decreases	None
Small molecule resulting in retardation or inhibition	Decreases	May decrease or increase	May decrease or increase	None
Polymer (intermolecular)	None	None	Increases	Produces long branches
Polymer (intramolecular)	None	None	Increases	Produces short branches

---

Example 7.4: For the polymerization of pure (undiluted) styrene with benzoyl peroxide at 60°C, the number-average degree of polymerization, X_n, is given by the expression:

$$X_n = 0.6 \times 10^{-4} + 12.0\ R_p + 4.2 \times 10^{4}\ R_p^2$$

where R_p = rate of polymerization (mol/l-s).

a. What is the transfer constant to the monomer, C_M?
b. Calculate the transfer constant to the initiator if the monomer concentration [M] is 10 mol/l and $fk_d\ k_p^2/k_t = 2.29 \times 10^{-9}$.

Solution: a. Comparing the above equation with Equation 7.39, it is obvious that $C_M = 0.6 \times 10^{-4}$ and

$$C_I\left(\frac{k_t}{k_p^2\, fk_d}\right)\frac{R_p^2}{[M]^3} = 4.2 \times 10^{4}\ R_p^2$$

$$C_I = 4.2 \times 10^{4}\ [M]^3 \times 2.29 \times 10^{-9}$$

$$= 0.0962$$

A. TRANSFER TO UNDILUTED MONOMER

For bulk polymerization (i.e., polymerization in the absence of a solvent) Equation 7.39 reduces to:

$$\frac{1}{\bar{X}_n} = C_M + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} + C_I\left(\frac{k_t}{k_p^2\, fk_d}\right)\frac{R_p^2}{[M]^3} \qquad (7.40)$$

This expression is quadratic in R_p, and the predicted behavior has indeed been observed in polymerization of styrene at 60° with benzoyl peroxide as the initiator. The first term on the right-hand side of the equation represents the contribution of transfer to the monomer; it is constant and independent of the rate of polymerization. The second term corresponds to normal termination (i.e., H ν, transfer reactions), while the third term, which represents transfer to the initiator, increases with increasing rates since high rates require high concentrations of initiator.

B. TRANSFER TO SOLVENT

In the presence of a solvent and with a proper choice of reaction conditions so as to minimize other types of transfer, the general expression for transfer (i.e., Equation 7.39) becomes

$$1/X_n = 1/X_{no} + C_S\ [S]/[M] \qquad (7.41)$$

where $1/X_{no}$ combines the terms for normal polymerization with transfer to monomer and represents the reciprocal of the degree of polymerization in the absence of a solvent. Experimentally, in addition to the above precautions, the ratio $R_p/[M]^2$ is held constant while the concentration of the solvent is varied. The transfer constants to solvents for the peroxide initiation of the polymerization of some monomers are listed in Table 7.3.

Example 7.5: The transfer constant to the solvent for the polymerization of styrene in benzene at 100°C is 0.184×10^{-4}. How much dilution is required to halve the molecular weight given that $1/X_{no} = 2.5 \times 10^{-4}$?

Solution: For the molecular weight to be halved, then $1/X_n$ becomes $2/X_{no}$

$$\left(\frac{2}{\bar{X}_{no}}\right) - \frac{1}{X_{no}} = 0.184 \times 10^{-4}\ [S]/[M]$$

$$\left(\frac{1}{\overline{X}_{no}}\right)\frac{10^4}{0.184} = \frac{[S]}{[M]}$$

$$[S] = 13.6\,[M]$$

Dilution factor is about 14.

Table 7.3 *Transfer Constants to Solvents for the Peroxide Initiation of Monomer Polymerization at 60°C*

	Transfer Constant: $C_S \times 10^4$		
Solvent	**Methyl Methacrylate**	**Styrene**	**Vinyl Acetate**
Acetone	0.195	4.1	25.6 (70°C)
Benzene	0.83	0.028	2.4
Carbon tetrachloride	2.40	87.0	2023.0 (70°C)
Chloroform	1.77	3.4	554.0 (70°C)
Toluene	0.202	0.105	20.75

From Schulz, G.V. and Harborth, H., *Makromol. Chem.,* 1, 106, 1947. With permission.

VIII. TEMPERATURE DEPENDENCE OF DEGREE OF POLYMERIZATION

The dependence of the polymerization rate and the number-average degree of polymerization on temperature can be demonstrated if the respective relation is expressed in the form of the Arrhenius equation.

$$k_b = A \exp\left(\frac{-E_b}{RT}\right) \tag{7.42}$$

$$\frac{d \ln R_p}{dT} = \frac{\left(E_p - \frac{E_t}{2}\right) + \frac{E_d}{2}}{RT^2} \tag{7.43}$$

$$\frac{d \ln \overline{X}_n}{dT} = \frac{\left(E_p - \frac{E_t}{2}\right) - \frac{E_d}{2}}{RT^2} \tag{7.44}$$

For radical polymerizations the activation energy of decomposition is of the order of 30 kcal/mol while $(E_p - E_t/2)$ is about 4 to 7 kcal/mol. Thus the temperature coefficients are, respectively,

$$dR_p/dT > 0 \tag{7.45}$$

$$dX_n/dT < 0 \tag{7.46}$$

These results predict that the rate of polymerization increases with increasing temperature while the molecular weight decreases. The same conclusion can be drawn for thermal polymerizations since $(E_p - E_t/2) - E_i/2$ is a negative quantity.

Example 7.6: The energies of activation for the polymerization of styrene with di-tertiary-butyl peroxide as initiator are

E_d = 33.5 kcal/mol
E_p = 7.0 kcal/mol
E_t = 3.0 kcal/mol

Calculate the relative (a) rates of propagation and (b) degree of polymerization (X_η) if the polymerization temperature is changed from 50°C to 60°C.

Solution:

a. $$\frac{d \ln R_p}{dT} = \frac{E}{RT^2}$$

where $E = E_p - \frac{E_t}{2} + \frac{E_d}{2}$.

$$\int_{R_{p/T_o}}^{R_{p/T}} d \ln R_p = \int_{T_o}^{T} \frac{E}{RT^2}\, dT$$

$$\ln \frac{R_{pT}}{R_{pT_o}} = \frac{E}{R}\left[\frac{1}{T_o} - \frac{1}{T}\right]$$

$$T_o = 50°\text{C} = 323\ \text{K};\ \ T = 333\ \text{K}$$

$$E = 7 - \frac{3}{2} + \frac{33.5}{2} = 22.25\ \text{kcal/mol}$$

$$\frac{E}{R} = \frac{22.25 \times 10^3\ \text{cal/mol}}{1.99\ \text{cal/mol} - \text{K}}$$

$$\frac{1}{T} - \frac{1}{T_o} = 0.0001\ \text{K}^{-1}$$

$$\ln \frac{R_{p60}}{R_{p50}} = 1.12$$

$$R_{p60}/R_{p50} = l^{1.12} = 3.06$$

$$\ln \overline{X}_{n60}/\overline{X}_{n50} = \frac{E}{RT}\left[\frac{1}{T_o} - \frac{1}{T}\right];\ E - E_p - \frac{E_t}{2} - \frac{E_d}{2}$$

$$= -11.25\ \text{kcal/mol}$$

$$E/RT = \left(-\frac{11.25 \times 10^3\ \text{cal/mol}}{1.99\ \text{cal/mol} - \text{K}}\right)\left(0.001\ \text{K}^{-1}\right)$$

$$= -0.57$$

$$\frac{\overline{X}_{\eta 60}}{\overline{X}_{\eta 50}} = l^{-0.57} = 0.57$$

IX. IONIC AND COORDINATION CHAIN POLYMERIZATION

A. NONRADICAL CHAIN POLYMERIZATION

In addition to the radical chain polymerization mechanisms discussed above, chain-reaction polymerization can also occur through other mechanisms. These include cationic polymerization in which the chain carriers are carbonium ions; anionic polymerization where the carriers are carbanions; and coordination polymerization, which is thought to involve the formation of a coordination compound between the catalyst, monomer, and growing chain. The polymerization mechanisms of these systems are complex and not as clearly understood as the mechanism of radical polymerization. This is because the reactions are generally heterogeneous, involving usually solid inorganic catalysts and organic monomers. In addition, ionic polymerizations are characterized by extremely high reaction rates. High-molecular-weight polymers are generated so fast that it is frequently neither possible to establish nor maintain uniform reaction conditions, thus making it difficult to obtain kinetic data or reproducible results. Two essential differences between free-radical and ionic polymerizations are apparent. First, in ionic polymerization, initiation involves the formation of an ion pair through the transfer of an ion or electron to or from the monomer. This contrasts with the generation and addition of a radical to the monomer in free-radical initiation reactions. Second, termination in ionic polymerization involves the unimolecular reaction of a chain with its counterion or a transfer reaction with the remnant species unable to undergo propagation. In contrast to radical chain polymerization, this termination process in ionic polymerization is strictly unimolecular — bimolecular annihilation of growth activity between two growing chains does not occur. The types of chain polymerization suitable for common monomers are shown in Table 7.1.

While many monomers can polymerize by more than one mechanism, it is evident that the polymerization mechanism best suited for each monomer is related to the polarity of the monomer and the Lewis acid–base strength of the ion formed. Monomers in which electron-donating groups are attached to the carbon atoms with the double bond (e.g., isobutylene) are capable of forming stable carbonium ions (i.e., they behave as Lewis bases). Such monomers are readily converted to polymers by cationic catalysts (Lewis acids). On the other hand, monomers with electron-withdrawing substituent (e.g., acrylonitrile) form stable carbanions and polymerize with anionic catalysts. Free-radical polymerization falls between these structural requirements, being favored by conjugation in the monomer and moderate electron withdrawal from the double bond. The structural requirements for coordination polymerization are less clearly delineated, and many monomers undergo coordination polymerization as well as ionic and radical polymerizations.

B. CATIONIC POLYMERIZATION

Typical catalysts that are effective for cationic polymerization include $AlCl_3$, $AlBr_3$, BF_3, $TiCl_4$, $SnCl_4$, and sometimes H_2SO_4. With the exception of H_2SO_4, these compounds are all Lewis acids with strong electron-acceptor capability. To be effective, these catalysts generally require the presence of a Lewis base such as water, alcohol, or acetic acid as a cocatalyst. As indicated in Table 7.1, monomers that polymerize readily with these catalysts include isobutylene, styrene, α-methylstyrene and vinyl alkyl ethers. All of these monomers have electron-donating substituents, which should enhance the electron-sharing ability of the double bonds in these monomers with electrophilic reagents.

Cationic polymerizations proceed at high rates at low temperatures. For example, the polymerization at –100°C of isobutylene with BF_3 or $AlCl_3$ as catalysts yields, within a few seconds, a polymer with molecular weight as high as 10^6. Both the rate of polymerization and the molecular weight of the polymer decrease with increasing temperature. The molecular weights of polyisobutylene obtained at room temperature and above are, however, lower than those obtained through radical polymerization.

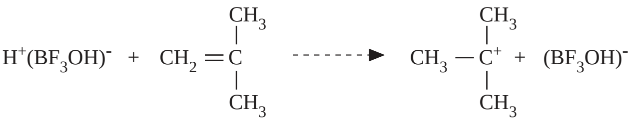
1. Mechanism

Based on available experimental evidence, the most likely mechanism for cationic polymerization involves carbonium ion chain carrier. For example, the polymerization of isobutylene with BF_3 as the catalyst can be represented thus:

First, the catalyst and cocatalyst (e.g., water) form a complex:

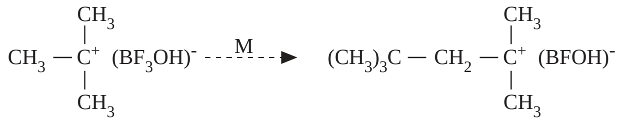
$$BF_3 + H_2O \longrightarrow H^+(BF_3OH)^- \tag{7.47}$$

The complex then donates a proton to an isobutylene molecule to form a carbonium ion:



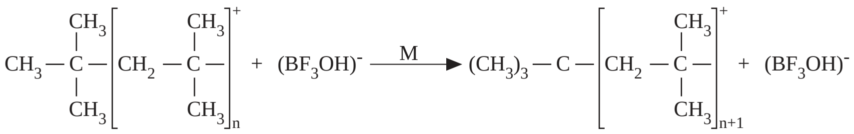
$$H^+(BF_3OH)^- + CH_2=\overset{CH_3}{\underset{CH_3}{C}} \dashrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + (BF_3OH)^- \tag{7.48}$$

The carbonium ion reacts with a monomer molecule in the propagation step.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}}\ (BF_3OH)^- \xrightarrow{M} (CH_3)_3C-CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}\ (BFOH)^- \qquad (7.49)$$

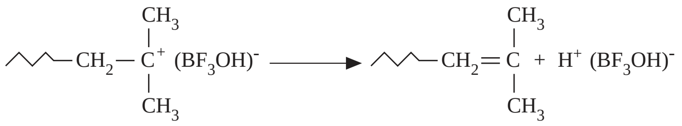
In general, the propagation reaction can be written as



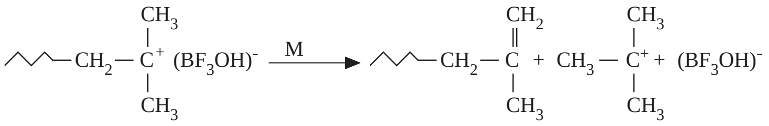
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\right]^+_n + (BF_3OH)^- \xrightarrow{M} (CH_3)_3-C-\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\right]^+_{n+1} + (BF_3OH)^- \qquad (7.50)$$

Since cationic polymerization is generally carried out in hydrocarbon solvents that have low dielectric constants, separation of the ions would require a large amount of energy. Consequently, the anion and cation remain in close proximity as an ion pair. It is therefore to be expected that the growth rate and subsequent reactions (e.g., termination and chain transfer) are affected by the nature of the ion pair.

Termination occurs either by rearrangement of the ion pair to yield a polymer molecule with an unsaturated terminal unit and the original complex or through transfer to a monomer.



$$\sim\!\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}\ (BF_3OH)^- \longrightarrow \sim\!\sim CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} + H^+\ (BF_3OH)^- \qquad (7.51)$$



$$\sim\!\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}\ (BF_3OH)^- \xrightarrow{M} \sim\!\sim CH_2-\overset{CH_2}{\underset{CH_3}{\overset{\|}{C}}} + CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + (BF_3OH)^- \qquad (7.52)$$

Unlike in free-radical polymerization, the catalyst is not attached to the resulting polymer molecule, and in principle many polymer molecules can be produced by each catalyst molecule.

2. Kinetics

For the purpose of establishing the kinetics of generalized cationic polymerization, let A represent the catalyst and RH the cocatalyst, M the monomer, and the catalyst–cocatalyst complex $H^+\ AR^-$. Then the individual reaction steps can be represented as follows:

$$\begin{aligned}
&A + RH \overset{K}{\rightleftharpoons} H^+\ AR^- \\
&H^+\ AR^- + M \xrightarrow{k_i} HM^+\ AR^- \\
&HM_n^+\ AR^- + M \xrightarrow{k_p} HM_{n+1}^+\ AR^- \\
&HM_n^+\ AR^- \xrightarrow{k_t} M_n + H^+\ AR^- \\
&HM_n^+\ AR^- + M \xrightarrow{k_{tr}} M_n + HM^+\ AR^-
\end{aligned} \qquad (7.53)$$

The rate of initiation R_i is given by

$$R_i = k_i\left[H^+\ AR^-\right][M] = k_i K[A][RH][M] \qquad (7.54)$$

As usual, the square brackets denote concentration. If the complex H^+AR^- is readily converted in the second step of Equation 7.48 (i.e., if the complex formation, step 1 Equation 7.48) is the rate-limiting step, then the rate of initiation is independent of the monomer concentration. Since AR^- remains in the close vicinity of the growing center, the termination step is first order

$$R_t = K_t \left[M^+\right] \tag{7.55}$$

where $[M^+]$ is the concentration of all the chain carriers $[HM_n^+AR^-]$. The retention of the terminating agent AR^- in the vicinity of the chain carrier is responsible for the primary difference between the kinetics of cationic polymerization and that of free-radical polymerization. Assuming that steady state holds, then $R_i = R_t$ and

$$\left[M^+\right] = \frac{K\,k_i}{k_t}[A][RH][M] \tag{7.56}$$

The overall rate of polymerization, R_p is given by

$$R_p = k_p\left[M^+\right][M] = K\,\frac{k_i\,k_p}{k_t}[A][RH][M]^2 \tag{7.57}$$

The number-average degree of polymerization, assuming predominance of termination over chain transfer, is

$$\bar{X}_n = \frac{R_p}{R_i} = \frac{k_p}{k_t}\,\frac{\left[M^+\right][M]}{\left[M^+\right]} = \frac{k_p}{k_t}[M] \tag{7.58}$$

If, on the other hand, chain transfer dominates, then

$$\bar{X}_n = \frac{R_p}{R_{tr}} = \frac{k_p\left[M^+\right][M]}{k_t\left[M^+\right][M]} = \frac{k_p}{k_{tr}} \tag{7.59}$$

In this case, the average degree of polymerization is independent of both the concentration of the monomer and the concentration of the catalyst. Available kinetic data tend to support the above mechanism.

Example 7.7: Explain why in the cationic polymerization of isobutylene, liquid ethylene or propylene at their boiling points are normally added to the reaction medium as a diluent. How will an increase in the dielectric constant of the reaction medium affect the rate and degree of polymerization?

Solution: Both the rate of polymerization and the molecular weight decrease with increasing temperature in cationic polymerization. These liquids help to prevent excessive temperature increases because part of the heat of polymerization is dissipated through the heat of evaporation of the liquids. In other words, the liquids act essentially as internal refrigerants.

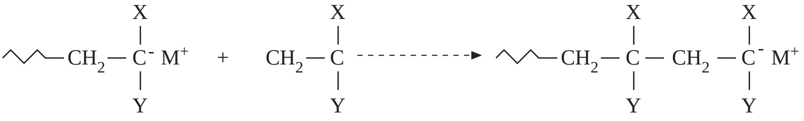
Using the general relation between the rate of reaction and activation energy ($k = Ae^{-E/RT}$), we note that a decrease in the activation energy, E, increases the rate of reaction while an increase in E has the opposite effect. An increase in dielectric constant increases the rate of initiation, k_i, by reducing the energy required for charge separation. On the other hand, an increase in the dielectric constant decreases k_t by increasing the energy required for the rearrangement and combination of the ion pair. Since both R_p and X_n are directly proportional to k_i/k_t, an increase in dielectric constant increases both quantities.

C. ANIONIC POLYMERIZATION

Monomers with electronegative substituents polymerize readily in the presence of active centers bearing whole or partial negative charges. For example, a high-molecular-weight polymer is formed when methacrylonitrile is added to a solution of sodium in liquid ammonia at –75°C. Typical electron-withdrawing substituents that permit the anionic polymerization of a monomer include –CN, –COOR, –C_6H_5, and –CH› CH_2. The electronegative group pulls electrons from the double bond and consequently renders the monomer susceptible to attack by an electron donor. Catalysts for anionic polymerization include Grignard reagents, organosodium compounds, alkali metal amides, alkoxide, and hydroxides.

1. Mechanism

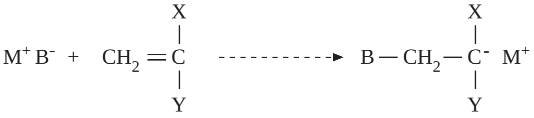
Propagation in anionic polymerization proceeds according to the following reactions:



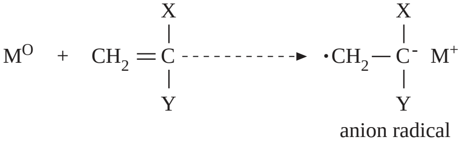
$$\sim\!\!\sim CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ + CH_2-\overset{X}{\underset{Y}{C}} \dashrightarrow \sim\!\!\sim CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ \qquad (7.60)$$

Here, M^+ represents a counterion that accompanies the growing chain. In most cases, M^+ is an alkali metal ion, whereas X and Y are either electron-withdrawing groups or unsaturated groups capable of resonance stabilization of the negative charge.

Initiation may occur in two ways: a direct attack of a base on the monomer to form a carbanion (Equation 7.61) or by transfer of an electron from a donor molecule to the monomer to form an anion radical (Equation 7.62).



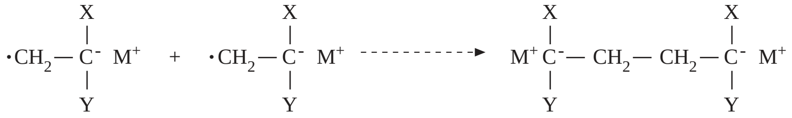
$$M^+B^- + CH_2=\overset{X}{\underset{Y}{C}} \dashrightarrow B-CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ \qquad (7.61)$$



$$M^O + CH_2=\overset{X}{\underset{Y}{C}} \dashrightarrow \underset{\text{anion radical}}{\cdot CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+} \qquad (7.62)$$

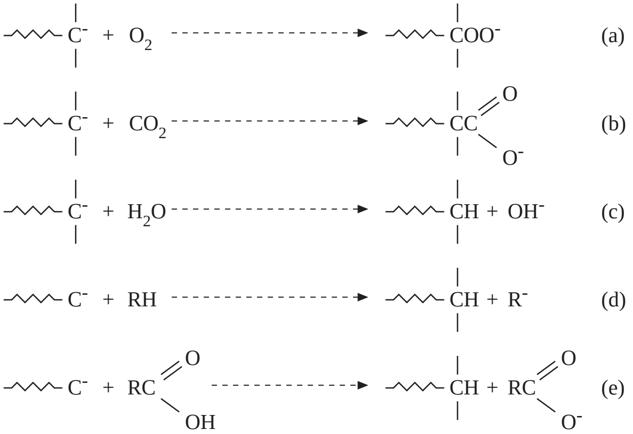
M^+B^- may be a metal amide, alkoxide, alkyl, aryl, and hydroxide depending on the nature of the monomer. The effectiveness of the catalyst in the initiation process depends on its basicity and the acidity of the monomer. For example, in the anionic polymerization of styrene, the ability to initiate reaction decreases in the order ⬡–CH_2^-–NH_2^- > NH_2^- @ OH^-. Indeed, OH^- will not initiate anionic polymerization of styrene. Where the anion is polyvalent, such as *tris*(sodium ethoxy) amine $N(CH_2CH_2O^-\ Na^+)_3$, an equivalent number of growing chains (in this case, three) can be initiated simultaneously.

The donor molecular in Equation 7.58 represents, in general, an alkali metal. In this case, transfer results in the formation of a positively charged alkali metal counterion and an anion radical. Pairs of anion radicals combine to form a dianion.



$$\cdot CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ + \cdot CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ \dashrightarrow M^+\,\overset{X}{\underset{Y}{C^-}}-CH_2-CH_2-\overset{X}{\underset{Y}{C^-}}\,M^+ \qquad (7.63)$$

In carefully controlled systems (pure reactants and inert solvents), anionic polymerizations do not exhibit termination reactions. As we shall see shortly, such systems are referred to as living polymers; however, because of the reactivity of carbanions with oxygen, carbon dioxide, and protonic compounds, termination occurs according to Equation 7.64.



$$\begin{aligned}
&\sim\!\mathrm{C^-} + \mathrm{O_2} \dashrightarrow \;\sim\!\mathrm{COO^-} && \text{(a)}\\
&\sim\!\mathrm{C^-} + \mathrm{CO_2} \dashrightarrow \;\sim\!\mathrm{C{-}C(=O)O^-} && \text{(b)}\\
&\sim\!\mathrm{C^-} + \mathrm{H_2O} \dashrightarrow \;\sim\!\mathrm{CH} + \mathrm{OH^-} && \text{(c)}\\
&\sim\!\mathrm{C^-} + \mathrm{RH} \dashrightarrow \;\sim\!\mathrm{CH} + \mathrm{R^-} && \text{(d)}\\
&\sim\!\mathrm{C^-} + \mathrm{RC(=O)OH} \dashrightarrow \;\sim\!\mathrm{CH} + \mathrm{RC(=O)O^-} && \text{(e)}
\end{aligned} \qquad (7.64)$$

The terminal groups in Equations 7.64a and 7.64b cannot propagate and, consequently, effectively terminate polymer growth. Equations 7.64c–7.64e involve proton transfer from the solvent to the growing chain resulting in a dead polymer. This is exemplified by the sodium-catalyzed polymerization of butadiene in toluene:

$$\sim\!\sim\!-\mathrm{CH_2-CH=CH-CH_2^-\ Na^+} \xrightarrow[(\text{toluene})]{\mathrm{CH_3C_6H_5}} \sim\!\sim\!-\mathrm{CH_2-CH=CH-CH_3 + C_6H_5CH_2^-\ Na^+}$$

Other possible termination reactions include (1) the transfer of a hydride ion leaving a residual terminal unsaturation (this, however, is a high-energy process and therefore unlikely); (2) isomerization of the carbanion to give an inactive anion; and (3) irreversible reaction of the carbanion with the solvent or monomer. In general, termination by transfer to the solvent predominates in anionic polymerization.

2. Kinetics

Available kinetic data for the polymerization of styrene by potassium amide in liquid ammonia support the following steps in the mechanism of anionic polymerization.

$$\begin{aligned}
&\mathrm{KNH_2} \overset{K}{\rightleftharpoons} \mathrm{K^+ + NH_2^-}\\
&\mathrm{NH_2^- + M} \xrightarrow{k_i} \mathrm{NH_2\,M^-}\\
&\mathrm{NH_2\,M_n^- + M} \xrightarrow{k_p} \mathrm{NH_2\,M_{n+1}^-}\\
&\mathrm{NH_2\,M_n^- + NH_3} \xrightarrow{k_{tr}} \mathrm{NH_2\,M_n\,H + NH_2^-}
\end{aligned} \qquad (7.65)$$

Considering the relatively high dielectric constant of the liquid ammonia medium, the counterion K^+ can be neglected. Assuming steady-state kinetics:

$$R_i = k_i\left[NH_2^-\right][M] \qquad (7.66)$$

$$R_t = k_{tr}\left[NH_2 - M_n^-\right]\left[NH_3\right] \qquad (7.67)$$

Thus from Equations 7.61 and 7.62

$$\left[NH_2 - M_n^-\right] = \frac{k_i}{k_{tr}}\,\frac{\left[NH_2^-\right][M]^2}{\left[NH_3\right]} \qquad (7.68)$$

The rate of polymerization becomes

$$R_p = k_p\left[NH_2 - M_n^-\right][M] \tag{7.69}$$

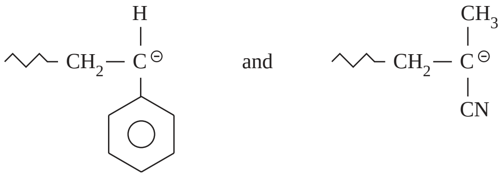
$$= k_p \frac{k_i}{k_{tr}} \frac{\left[NH_2^-\right][M]^2}{\left[NH_3\right]}$$

Given the predominance of transfer reactions, the degree of polymerization $\overline{X}_n$ is given by

$$\overline{X}_n = \frac{R_p}{R_t} = \frac{k_p}{k_{tr}} \frac{[M]}{\left[NH_3\right]} \tag{7.70}$$

Example 7.8: Polymerization of styrene in liquid ammonia gave high yield of low-molecular-weight polystyrene, whereas methacrylonitrile gave high conversion of high-molecular-weight polymethacrylonitrile. Explain.

Solution: Since the reaction is carried out in liquid ammonia, proton transfer from the solvent (ammonia) is the possible termination reaction. The relevant carbanions are



(Str. 4)

Since the –CN group is more electronegative than the phenyl group, the styrene carbanion will be more basic than the methacrylonitrile carbanion and as such more susceptible to proton transfer from ammonia. Transfer reactions generally lead to low-molecular-weight polymers.

D. LIVING POLYMERS

The absence of the termination step in anionic polymerizations with carefully purified reactants in inert reactions media results, as indicated above, in living polymers. In such systems, the growing species remain dormant in the absence of monomers but resume their growth activity with a fresh monomer supply. With adequate mixing, the monomer supplied to the system is distributed among the growing centers (living polymers). As a result, the number-average degree of polymerization is simply the ratio of the number of moles of monomer added to the total number of living polymers. That is,

$$\overline{X}_n = \frac{[\text{monomer}]}{[\text{catalyst}]}$$

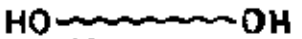
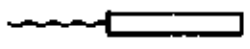
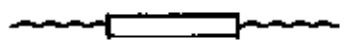
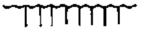
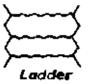
Unlike other chain reactions where the growing chains undergo spontaneous termination, the reactive end groups in living polymers may be annihilated (“killed”) by a choice of suitable reactants by the experimenter at a desired stage of the polymerization process. Thus living polymers offer fascinating potentials for the development of novel polymer systems. We discuss a few examples.

Spontaneous termination is governed by the laws of probability. Therefore, in polymerization involving spontaneous termination, the resulting polymers have a distribution of molecular weights since the lifetimes of the growing centers vary. But with living polymers where termination is lacking, a polymer with a nearly uniform molecular weight (monodisperse) can be obtained if the system is devoid of impurities and is well mixed.

The ability of living polymers to resume growth with the addition of fresh monomer provides an excellent opportunity for the preparation of block copolymers. For example, if a living polymer with one active end from monomer A can initiate the polymerization of monomer B, then an A–AB–B type copolymer can be obtained (e.g., styrene–isoprene copolymer). If, however, both ends of polymer A are active, a copolymer of the type B–BA–AB–B results. Examples are the thermoplastic rubbers polystyrene-polyisoprene-polystyrene and poly(ethylene oxide)-polystyrene-poly(ethylene oxide). In principle, for fixed amounts of two monomers that are capable of mutual formation of living polymers, a series of polymers with constant composition and molecular weight but of desired structural pattern can be produced by varying the fraction and order of addition of each monomer.

The potential versatility of living polymers in chemical synthesis is further demonstrated by the possibility of formation of polymers with complex shapes by employing polyfunctional initiators or terminating monodisperse living polymers with polyfunctional linking agents. For example, star-shaped poly(ethylene oxide) can be prepared with the trifunctional initiator trisodium salt of triethanol amine, $N(CH_2CH_2O^- Na^+)_3$. Another possible area of utilizing living polymers is in the introduction of specific end groups by terminating the living polymer with an appropriate agent. For example, termination of living polystyrene with CO_2 introduces terminal carboxylic groups, while reaction with ethylene oxide introduces hydroxy end groups. The utilization of these two approaches (synthesis of block copolymers or functional-ended polymers) provides the synthetic polymer chemist with a powerful tool for producing polymers with fascinating architectural features and properties (Table 7.4).

Table 7.4. Architectural forms of polymers available by living polymerization techniques (6)

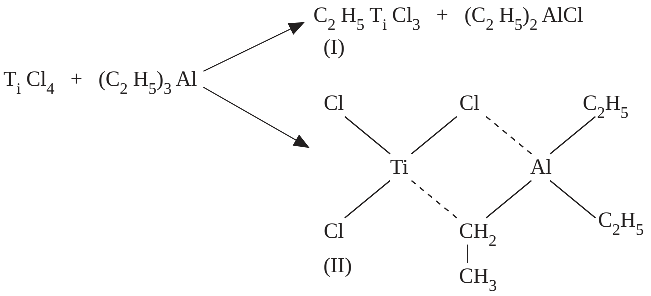
	Polymer	Application
1	 *Functional ended*	Dispersing agents Synthesis of macromonomers
2	 *α,ω difunctional*	Elastomer synthesis Chain extension Cross-linking agents
3	 *AB Block*	Dispersing agents Compatibilizers for polymer blending
4	 *ABA Block*	Thermoplastic elastomers
5	 *Graft*	Elastomers Adhesives
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

E. COORDINATION POLYMERIZATION

A major development in polymer chemistry was the development in 1953 of new catalysts leading to the formation of polymer with exceptional structural regularity. The first catalysts were described by Ziegler[7] for the low-pressure polymerization of ethylene. These were modified by Natta[8] and his associates and used for the highly stereospecific polymerization of α-olefins, diolefins, and other monomers. As indicated in Chapter 1, Ziegler and Natta were awarded the Nobel prize in chemistry in 1963 for their work in this area. These catalysts are usually referred to as Ziegler–Natta catalysts, and since polymerization processes utilizing these catalysts result in stereoregular structures, they are sometimes called stereospecific or stereoregular polymerization. However, the term *coordination polymerization* is used here to reflect the mechanism which, as we shall see presently, is believed to govern the reaction involving these catalysts.

1. Mechanisms

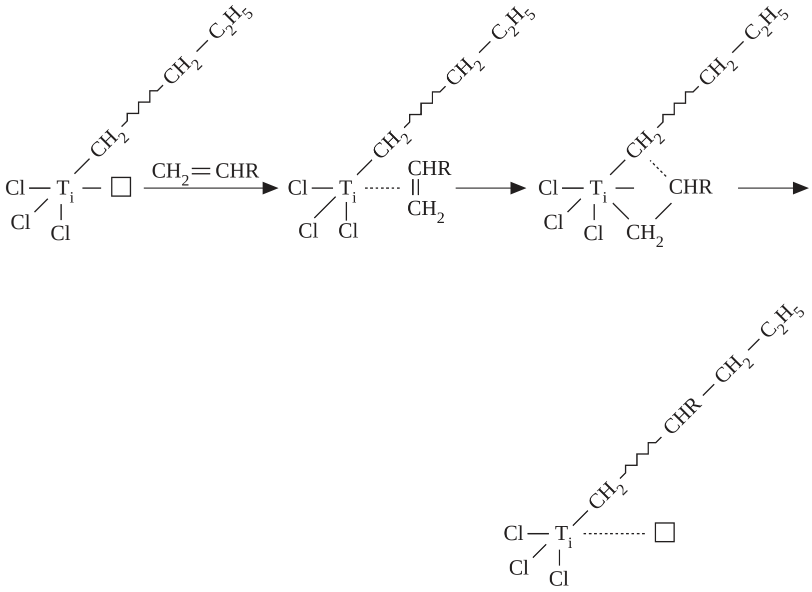
The metals that are more frequently found as components of Ziegler–Natta catalysts are some light elements of groups I–III of the periodic table (e.g., Li, Be, Mg, Al), present as organometallic compounds and halides, or other derivatives of transition metals of groups IV–VIII (e.g., Ti, V, Cr, Mo, Rh, Rn, Co, and Ni). A typical example is the product(s) of the reaction between triethylaluminum and titanium tetrachloride. The composition of the product is not well defined but is believed to be either an alkylated metal halide (monometallic I) or a bimetallic complex involving a bridge between the two metals (II).



(Str. 5)

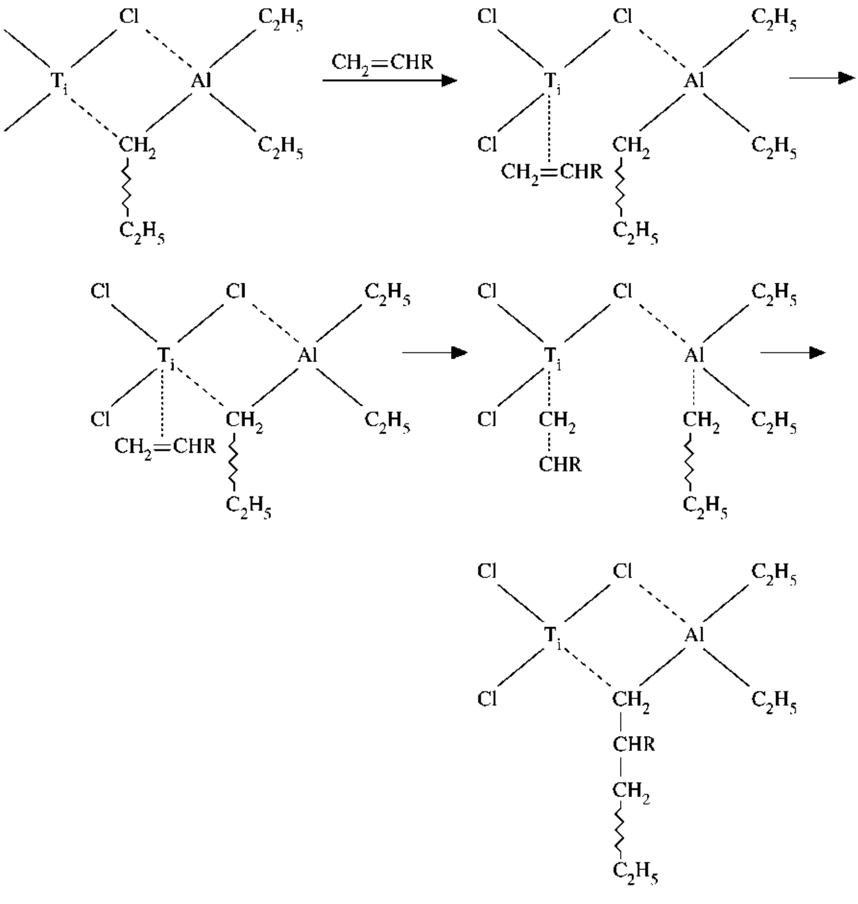
While coordination polymerization may be anionic or cationic, relatively fewer examples of cationic coordination polymerization leading to the formation of stereoregular polymers currently exist. These are limited almost exclusively to the polymerization of monomers containing heteroatoms with lone electron pairs such as oxygen or nitrogen. In any case, the growth reaction in coordination polymerization is considered to be controlled by the counterion of the catalysts, which first coordinates and orients the incoming monomer and then inserts the polarized double bond of the monomer in the polarized bond between the counterion and the end of the growing chain. Coordination involves the overlap of the electrons of the monomer with a vacant sp orbital in the case of groups I–III metals or a vacant d orbital in the case of transition metals. The proposed propagation mechanisms for both the monometallic and bimetallic catalyst are shown below.

Monomettalic catalyst



(Str. 6)

Bimetallic catalyst



(Str. 7)

The dominant feature of the coordination polymerization mechanism is the presence of forces that orient and insert each incoming monomer into the growing polymer chain according to a particular steric configuration. The surface of the crystalline salts of the transition metals that constitute part of the catalyst system is thought to play a vital role in this function. With Ziegler–Natta catalysts, ethylene is polymerized to a highly linear chain compared with the branched products from the high-pressure process (radical polymerization). By a convenient choice of catalyst system, isotactic and syndiotactic polypropylene can be obtained. Higher α-olefins yield isotactic polymers with heterogeneous catalyst systems. The versatility and selectivity of Ziegler–Natta catalysts are demonstrated even more sharply in the polymerization of conjugated dienes. By a suitable choice of catalyst system and reaction conditions, conjugated dienes like butadiene and isoprene can be made to polymerize into any of their isomers almost exclusively: *trans*-1,4; *cis*-1,4; or isotactic or syndiotactic 1,2.

Example 7.9: Among the elements of the first group of the periodic table, only organometallic compounds of lithium show a considerable tendency to give stereospecific catalysts. Also, this tendency decreases with increasing atomic radius of the elements of this group. Explain this observation.

Solution: Two conditions that are essential for anionic coordination polymerization are (1) the monomer must form a complex with the metal atom of the catalyst before its insertion in the metal–carbon bond, and (2) the bond between the metal of the catalyst and the carbon atom of the polymer chain must be at least partially polarized. Now, the electropositive nature of the metals of the first group of the periodic table increases with increasing atomic radius. This means that among these elements lithium has the highest electron-withdrawing power (generates the highest electric field) and consequently has the highest ability to coordinate with the double bond of the monomer (condition 1). The ionization of the bond between the metal (M) and the polymer (P) may be represented as follows:

$$\underset{\substack{\text{covalent}\\ \text{(I)}}}{\mathrm{M} \text{ ——— } \mathrm{P}} \rightleftharpoons \underset{\substack{\text{polarized}\\ \text{(II)}}}{\mathrm{M}^{\delta+} \text{ ——— } \mathrm{P}^{\delta-}} \rightleftharpoons \underset{\substack{\text{free ions}\\ \text{(III)}}}{\mathrm{M}^{+} + \mathrm{P}^{-}} \qquad \text{(Str. 8)}$$

The degree of ionization of this bond depends partly but significantly on the electropositivity of the metal. Only the polarized metal–polymer bond of type II leads to the formation of sterically regular polymers. When a metal is very electropositive, it can be assumed that the growing polymer anion is essentially a free ion (III) and as such the positive counterion has negligible influence on the coordination, orientation, and insertion of the incoming monomer into the polymer chain and hence on the structural regularity of the polymer. Consequently, the tendency for stereospecificity decreases with increasing electropositivity (i.e., increasing atomic radius).

Example 7.10: Explain the observed variations in the stereoregularity of polymers when the metal of the catalyst or the reaction medium is varied.

Solution: The growth reaction in coordination polymerization first involves coordination of the monomer to the counterion of the catalyst and the insertion of the polarized double bond of the monomer in the polarized bond between the counterion and the end group of the growing chain. The nature of the coordinating metal in the catalyst determines the particular orientation imposed on the absorbed monomer. Consequently, stereoregularity of polymer may vary with different metals. The ability of the counterion to determine the orientation imposed on the incoming monomer is influenced by the extent of polarization of the bond between the counterion and the end group of the growing chain. The extent of polarization of this bond is itself a function of the solvating power of the reaction medium. Therefore, variation of the reaction medium causes a variation in polymer stereoregularity.

X. PROBLEMS

7.1. The following data were obtained by Arnett[12] for the polymerization of methyl methacrylate in benzene at 77°C with azo-*bis*-isobutyronitrile initiator. Assuming that the initiator efficiency is independent of monomer concentration, are the data consistent with the model for the rate of polymerization by free-radical mechanism?

[M] (kmol/m^3)	**[I] (mol/m^3)**	**–d[M]/dt (mol/m^3 · sec)**
9.04	0.235	0.193
8.63	0.206	0.170
7.19	0.255	0.165
6.13	0.228	0.129
4.96	0.313	0.122
4.75	0.192	0.0937
4.22	0.230	0.0867
4.17	0.581	0.130
3.26	0.245	0.0715
2.07	0.211	0.415

From Arnett, L.M., *J. Am. Chem. Soc.*,74, 2027, 1952. With permission.

7.2. A steady-state free-radical styrene polymerization process is being controlled such that the rate of polymerization is constant at 1.79 g of monomer/ml-min. The initiator concentration is 6.6×10^{-6} mol/ml.

a. What must be done to maintain the constant rate of polymerization?
b. If the rate constant for the first-order decomposition of the initiator, k_d, is 3.25×10^{-4} min^{-1}, what is the rate of free radical generation per second per milliliter? What is X_n?
c. What percentage of the original initiator concentration remains after a reaction time of 3 h?

7.3. Consider the isothermal solution polymerization of styrene at 60°C in the following formulation:

100 g styrene
400 g benzene
0.5 g benzoyl peroxide

Assume that the initiator is 100% efficient and has a half-life of 44 h. At 60°C, k_p = 145 l/mol-s, k_t = 0.130 l/mol-s. All ingredients have unit density.

a. Derive the rate expression for this polymerization reaction.
b. Calculate the rate of propagation at 50% conversion.
c. How long will it take to reach this conversion?

7.4. For the polymerization of pure (undiluted) styrene with benzoyl peroxide at 60°C, the number-average degree of polymerization, X_n, is given by the general expression:

$$\frac{1}{\bar{X}_n} = 0.60 \times 10^{-4} + 8.4 \times 10^{2} \frac{R_p}{[M]^2} + 2.4 \times 10^{7} \frac{R_p^2}{[M]^3}$$

For a rate of polymerization of 10^{-4} mol/l-s and monomer concentration of 8.35 mol/l calculate:

a. The value of the transfer constant to the monomer
b. Number-average degree of polymerization, X_n
c. X_n assuming there is no transfer (normal termination)

d. The kinetic chain length
e. The transfer constant to the initiator if $fk_dk_p^2/k_t = 2.29 \times 10^{-9}$
f. The efficiency of initiation of polymerization of styrene in benzoyl peroxide if $k_d = 3.2 \times 10^{-6}\ s^{-1}$

7.5. The bulk polymerization of styrene at 100°C with benzoyl peroxide as the initiator resulted in a polymer of molecular weight 4.16×10^5. End-use tests showed that this product would be adequate provided the variation in molecular weight did not exceed 20%. However, to ensure better temperature control of the reactor, it was decided that the polymerization should be carried out in a solvent at a dilution factor of 2. The following solvents are available:

Solvent	**Transfer Constant, C_S, for styrene at 100°C**
Cyclohexane	0.16×10^{-4}
Carbon tetrachloride	180.0×10^{-4}

Assuming that only transfer to the solvent is possible, show that cyclohexane is the better of the two solvents for the end use under calculation.

7.6. The transfer constants to the solvent for the polymerization of styrene, methyl methacrylate, and vinyl acetate in toluene at 80°C are given below:

Chain radical	$C_S \times 10^4$
Styrene	0.31
Methyl methacrylate	0.52
Vinyl acetate	92.00

Find the ratio of the dilution factors for the three monomers if the molecular weight of the resulting polymers is each reduced to one-fourth that from the solvent-free polymerization. Assume that the degree of polymerization X_n in the absence of the solvent for the monomers is the same [$X_{no} = 5.0 \times 10^3$].

7.7. Explain why molecular weight ($\overline{X}_n$) increases with decreasing reaction temperature in cationic polymerization. Assume that termination predominates over transfer.

7.8. The rate constant for propagation of (polystyrene)$^-$ Na$^+$ in tetrahydrofuran for 25°C was found to be 400 l-mol^{-1} s^{-1}. The rate constants for proton transfer to the anion from water and ethanol were 4000 l-mol^{-1} s^{-1} and 4 l-mol^{-1} s^{-1}, respectively. Which of these impurities (water or ethanol) is more likely to inhibit high polymer formation in sodium-catalyzed anionic polymerization of styrene in tetrahydrofuran?

7.9. If anionic coordination is carried out in ethers or amines, sterically regular structures are generally not obtained. Explain this observation.

7.10. One mole of styrene monomer and 1.0 × 10 mol of azo-*bis*-isobutyronitrile initiator are dissolved in 1 l benzene. Estimate the molecular weight of the resulting polymer if each initiator fragment starts a chain and

a. All chains start at the same time. Termination is by disproportionation (all chains are of equal length).
b. Same as in case (a) but termination is by coupling.
c. Same as in case (a) but 6.0×10^{-4} mol mercaptan are added and each mercaptan acts as a chain transfer agent once.

7.11. The following data are obtained for the polymerization of a new monomer. Determine

a. The time for 50% conversion in run D
b. The activation energy of the polymerization

Run	**Temperature (°C)**	**Conversion (%)**	**Time (min)**	**Initial Monomer Conc. (mol/l)**	**Initial Initiator Conc. (mol/l)**
A	60	50	50	1.0	0.0025
B	80	75	700	0.50	0.0010
C	60	40	60	0.80	0.0010
D	60	50	—	0.25	0.0100

7.12. Sketch, on the same plot, molecular weight conversion curves for

   a. Free-radical polymerization
   b. Living polymerization
   c. Condensation polymerization

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