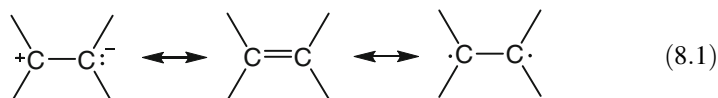


Chapter 8

Ionic Chain Polymerization

The carbon–carbon double bond can be polymerized either by free radical or ionic methods. The difference arises because the π -bond of a vinyl monomer can respond appropriately to the initiator species by either homolytic or heterolytic bond breakage as shown in Eq. 8.1.

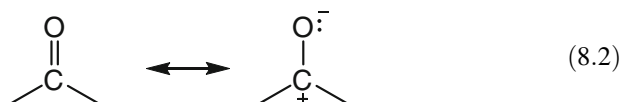


Although radical, cationic, and anionic initiators are used in chain polymerizations, they cannot be used indiscriminately, since all three types of initiation do not work for all monomers. Monomers show varying degrees of selectivity with regard to the type of reactive center that will cause their polymerization. Most monomers will undergo polymerization with a radical initiator, although at varying rates. However, monomers show high selectivity toward ionic initiators [1]. Some monomers may not polymerize with cationic initiators, while others may not polymerize with anionic initiators. The coordination polymerization requires coordination catalyst to synthesize polymers. It has been used extensively to polymerize high performance polyolefin but seldom used in the polymerization of polar monomer [2]. The detailed mechanisms of coordination polymerization will be discussed in Chap. 9. The various behaviors of monomers toward polymerization can be seen in Table 8.1. The types of initiation that bring about the polymerization of various monomers to high-molecular-weight polymer are indicated. Thus, although the polymerization of all monomers in Table 8.1 is thermodynamically feasible, kinetic feasibility is achieved in many cases only with a specific type of initiation.

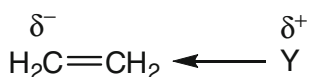
The carbon–carbon double bond in vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chain polymerization. The polymerization of the carbon–carbon double bond is by far the more important of the two types of monomers. The carbonyl group is not prone to polymerization by radical initiators because of its polarized nature:

Table 8.1 Types of chain polymerization suitable for unsaturated monomers [3]

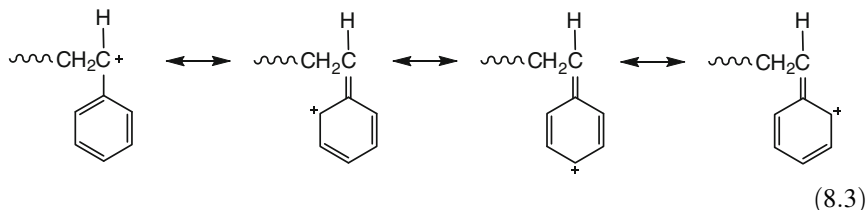
Monomer type	Radical	Cationic	Anionic	Coordination
Ethylene	+	-	-	+
1-Alkyl olefins (α -olefins)	-	-	-	+
1,1-Dialkyl olefins	-	+	-	+
1,3-Dienes	+	+	+	+
Styrene, α -methyl styrene	+	+	+	+
Halogenated olefins	+	-	-	-
Vinyl ethers	-	+	-	-
Vinyl esters	+	-	-	-
Acrylic and methacrylic esters	+	-	+	-
Acrylonitrile and methacrylonitrile	+	-	+	-
N-Vinyl carbazole	+	+	-	-
N-Vinyl pyrrolidone	+	+	-	-
Aldehydes, ketones	-	+	+	-



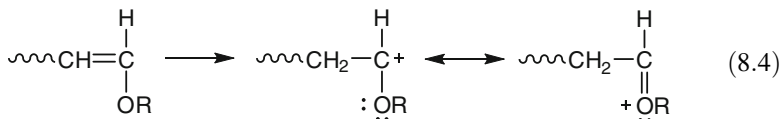
The type of substitute (Y) on the C=C double bond of monomer determines the ease of what kind of chain polymerization. If Y is an electron donating group, the electron density on the C=C double bond is shown as below:



The alkoxy substituent allows a delocalization of the positive charge. If the substituent was not present, the positive charge would be localized on the single α -carbon atom. The presence of the alkoxy group leads to stabilization of the carbocation by delocalization of the positive charge over two atoms—the carbon and the oxygen. Similar delocalization effects occur with phenyl, vinyl, and alkyl substituents, for example, for styrene polymerization:



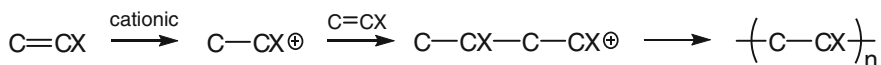
Certain vinyl compounds are best polymerized via cationic rather than free-radical intermediates. For instance,



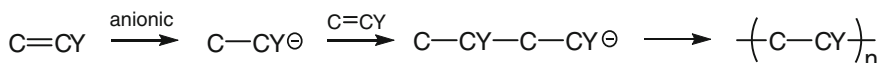
The most common commercial cationic polymerization is the polymerization of isobutylene ($\text{CH}_3\text{-C}(\text{CH}_3)=\text{CH}_2$) which can be polymerized with Friedel–Crafts catalysts in a reaction that involves tertiary carbocation intermediates. The reaction is sensitive to temperature, solvent, nucleophile impurities that are discussed later.

8.1 Characteristics of Ionic Chain Polymerization

Ionic polymerizations are highly selective. The cationic polymerization will undergo cationic intermediate as shown below:



The X has to be an electron donating group such as alkoxy, phenyl, vinyl, 1,1-dialkyl, and so on to stabilize the cationic intermediate. The anionic polymerization will undergo anionic intermediate as shown below:



The Y has to be an electron withdrawing group such as $-\text{CN}$, CO , phenyl, vinyl, and so on to stabilize the anionic intermediate.

Thus the selectivity of ionic polymerization is due to the very strict requirements for stabilization of anionic and cationic propagating species. The commercial utilization of cationic and anionic polymerizations is rather limited because of this high selectivity of ionic polymerizations compared to radical polymerizations.

Ionic polymerizations, especially cationic polymerizations, are not as well understood as radical polymerization because of experimental difficulties involved in their study. The nature of the reaction media in ionic polymerizations is often not clear since heterogeneous inorganic initiators are often involved. Further, it is extremely difficult in most instances to obtain reproducible kinetic data because ionic polymerizations proceed at very rapid rates and are extremely sensitive to the presence of small concentrations of impurities and other ionic reactive species. The rates of ionic polymerizations are usually faster than those of radical polymerizations. These comments generally apply more to cationic than anionic polymerizations. Anionic systems are more reproducible because the reaction components are better defined and more easily purified.

Table 8.2 Commercially important polymers prepared by ionic polymerization [4]

Polymer or copolymer	Major uses
<i>Cationic</i> ^a	
Polyisobutylene and polybutenes ^b (low and high molecular weight)	Adhesives, sealants, insulating oils, lubricating oil and grease additives, moisture barriers
Isobutylene-isoprene copolymer ^c (“butyl rubber”)	Inner tubes, engine mounts and springs, chemical tank linings, protective clothing, hoses, gaskets, electrical insulation
Isobutylene-cyclopentadiene copolymer	Ozone-resistant rubber
Hydrocarbon ^d and polyterpene resins	Inks, varnishes, paints, adhesives, sealants
Coumarone-indene resins ^e and poly(vinyl ether)s	Flooring, coatings, adhesives, polymer modifiers, tackifiers, adhesives
<i>Anionic</i> ^f	
<i>cis</i> -1,4-Polybutadiene	Tires
<i>cis</i> -1,4-Polyisoprene	Tires, footwear, adhesives, coated fabrics
Styrene-butadiene rubber(SBR) ^g	Tire treads, belting, hoses, shoe soles, flooring, coated fabrics
Styrene-butadiene block and star copolymers	Flooring, shoe soles, artificial leather, wire, and cable insulation
ABA block copolymers (A = styrene, B = butadiene or isoprene)	Thermoplastic elastomers
Polycyanoacrylate ^h	Adhesives

^a AlCl₃ and BF₃ most frequently used coinicators

^b “Polybutenes” are copolymers based on C₄ alkenes and lesser amounts of propylene and C₅ and higher alkenes from refinery streams

^c Terpolymers of isobutylene, isoprene, and divinylbenzene are also used in sealant and adhesive formulations

^d Aliphatic and aromatic refinery products

^e Coumarone (benzofuran) and indene (benzocyclopentadiene) are products of coal tar

^f *n*-Butyllithium most common initiator

^g Contains higher *cis* content than SBR prepared by free radical polymerization

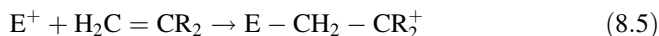
^h Monomer polymerized by trace amount of water

Cationic and anionic polymerizations have many similar characteristics. The formation of ions with sufficiently long lifetimes for propagation to yield high-molecular-weight products generally requires stabilization of the propagating centers by solvation. Relatively low or moderate temperatures are also needed to suppress termination, transfer, and other chain-breaking reactions which destroy propagating centers.

Although solvents of high polarity are desirable to solvate the ions, they cannot be employed for several reasons. The highly polar hydroxylic solvents (water, alcohols) react with and destroy most ionic initiators. Other polar solvents such as ketones prevent initiation of polymerization by forming highly stable complexes with the initiators. Ionic polymerizations are, therefore, usually carried out in solvents of low or moderate polarity. Table 8.2 summarizes some commercially important polymers prepared by ionic polymerization and their major usages. It is interesting to note that most products are rubber-based polymers which were established during the World War II period in search of man-made rubber.

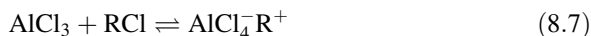
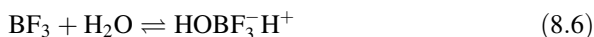
8.2 Cationic Polymerization

In cationic chain polymerization, the propagating species is a carbocation. Initiation is brought about by addition of an electrophile to a monomer molecule as shown in Eq. 8.5.

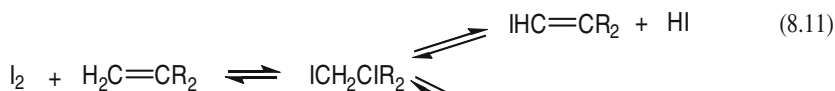
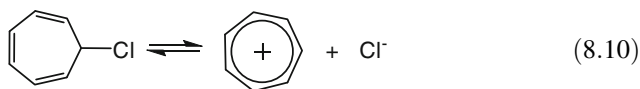
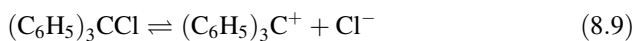


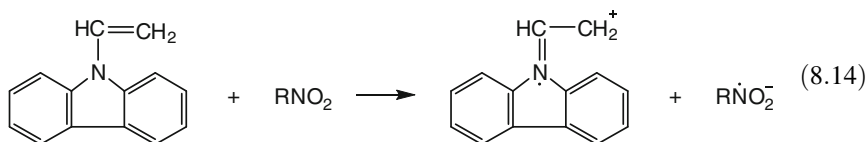
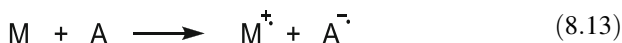
8.2.1 Initiators of Cationic Polymerization

Compounds used most frequently to initiate cationic polymerization are mineral acids, particularly H_2SO_4 and H_3PO_4 , and Lewis acids such as: $AlCl_3$, BF_3 , $TiCl_4$, and $SnCl_4$. Lewis acids need the presence of trace amounts of water (proton or cation source) which form the electrophilic species to initiate polymerization. Examples are the reactions of BF_3 with water (Eq. 8.6) and aluminum chloride with an alkyl chloride (Eq. 8.7). Water is called *initiator*, and the Lewis acid is called *coinitiator*. They form an *initiating system*. With certain very active Lewis acids, *autoionization* (Eq. 8.8) may occur.

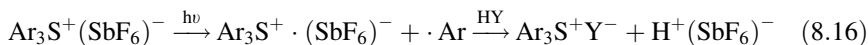
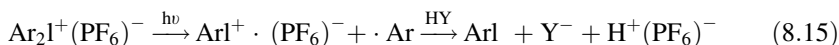


Other cationic initiators can be obtained from compounds that can easily form cations as shown in the following:





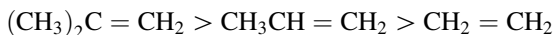
Cations can also be formed by photo initiation. Aryldiazonium salt (ArN_2^+Z^-), diaryliodonium salt (Ar_2^+IZ^-), and triarylsulfonium salt ($\text{Ar}_3\text{S}^+\text{Z}^-$) are effective photoinitiators of cationic polymerization, where Z^- is a nonnucleophilic and photostable anion such as tetrafluoroborate (BF_4^-), hexafluoroantimonate (SbF_6^-), and tetraeperfluorophenylborate [$(\text{C}_6\text{F}_5)_4\text{B}^-$], and hexafluorophosphate (PF_6^-). Diaryliodonium and triarylsulfonium salts act as photoinitiators of cationic polymerization. Photolytic cleavage of an $\text{Ar}-\text{I}$ or $\text{Ar}-\text{S}$ bond yields a radical—cation (Eq. 8.15) that reacts with HY to yield an initiator—coinitiator complex that acts as a proton donor to initiate cationic polymerization. HY may be solvent or some other deliberately added substance such as an alcohol with labile hydrogen. Overall, the process is a photolytically induced redox reaction between the cation—radical and HY . These initiators have been used in deep UV photo-resist applications.



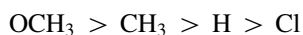
Not all initiating systems are equally effective. Relatively stable carbocations of the triphenylmethyl or tropylium type are only useful with very reactive monomers such as vinyl ethers. Mineral acid initiators seldom lead to very high molecular weight polymers.

8.2.2 Reaction Mechanisms of Cationic Polymerization

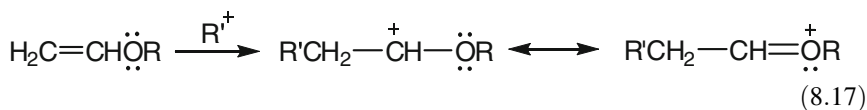
The cationic polymerization is a chain polymerization that involves three steps: (1) initiation, (2) propagation, and (3) termination. The feasibility of polymerization depends on the ease of cation formation from monomer. The reaction can occur with the addition of the electrophile (carbocation) to monomer and form more stable intermediate. The rate of addition to aliphatic monomers is of the order of



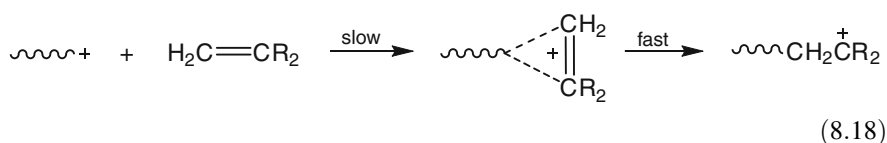
Only isobutylene provides the requisite carbocation stability for cationic polymerization. For a series of para-substituted styrene, the reactivity for substituent groups in cationic initiation is of the order of ring activation as



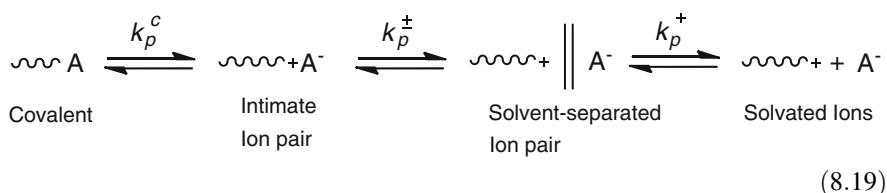
Ortho substituents retard the addition regardless of whether they are activating or deactivating. Vinyl ethers are particularly reactive toward cationic initiators because the unshared electron of oxygen can participate in the resonance stabilized intermediate structure as in the following:



The cationic polymerization is favored by increasing carbocation stability. The reaction mechanisms may involve two steps—a rate-limiting formation of a pi complex between the chain end and an approaching monomer molecule, followed by covalent bond formation (Eq. 8.18). In free radical polymerization, the covalent bond formation is a rate limiting step.



The solvent effects on the rate of cationic polymerization are more complicated than the free radical polymerization. Due to the formation of ionic species in the initiation step, one can expect that the polar solvent favors the initiation step. The opposite is expected in propagation because the charge is dispersed in the transition state. Another complicating factor is the degree of association between the cationic chain end and the anion (A^-). Between the extremes of pure covalent bonds and solvated ions are intimate ion pairs and solvent-separated ion pairs as the following:



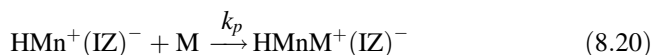
By increasing the solvent polarity of poor solvent, the propagating rate for poor solvents are increased by shifting the equilibrium away from intimate ion pairs to have more free ions. As the solvating power of the solvent increases, the shift will be in the opposite direction and propagation is retarded and cation is no longer labile. The cation is fully solvated by polar solvent.

Table 8.3 Effect of solvent on cationic polymerization of *p*-methoxystyrene by iodine at 30 °C [5]

Solvent	k_p (L/mol-s)
CH ₂ Cl ₂	17
CH ₂ Cl ₂ /CCl ₄ , 3/1	1.8
CH ₂ Cl ₂ /CCl ₄ , 1/1	0.31
CCl ₄	0.12

Polymerization rates and polymer molecular weights increase with increasing solvent polarity because there is a shift in concentrations from the unreactive (dormant) covalent species toward the ion pairs and free ions. For the perchloric acid polymerization of styrene, there is an increase in overall reaction rate by about three orders of magnitude when polymerization is carried out in 1,2-dichloroethane ($\epsilon = 9.72$) as compared with carbon tetrachloride ($\epsilon = 2.24$). Table 8.3 shows data for the polymerization of *p*-methoxystyrene by iodine in different solvents. The apparent propagation rate constant increases by more than two orders of magnitude by changing the solvent from nonpolar carbon tetrachloride ($\epsilon = 2.24$) to polar methylene chloride ($\epsilon = 9.08$).

The initiator ion pair (consisting of the carbocation and its negative counterion) produced in the initiation step proceeds to propagate by successive additions of monomer molecules as shown in Eq. 8.20.



where propagation rate constant: $k_p = k_p^+ + k_p^c + k_p^\pm$ decreases with increasing solvent polarity, and solvent stabilizes the reactant more than the transition state. The k_p^\pm increases with increasing solvent polarity when the transition state has a higher dipole moment than ion pair. However, the k_p^\pm decreases with increasing solvent polarity when the transition has a lower dipole moment than ion pair. The k_p^c is the rate constant for propagation by covalent species. The k_p^c has the opposite effect as k_p^\pm since the transition state involves the development of charged center from neutral reactants such as styrene polymerized by CH₃SO₃H, CF₃SO₃H, CH₃COOH. Table 8.4 summarizes the solvent effect on cationic polymerization by using the polar solvent in the first row and nonpolar solvent in the second row as the starting discussion point. The polarity of solvent is varied from solvent type by either increasing the polarity of the polar solvent or nonpolar solvent. The effect is quite different between polar solvent and nonpolar solvent.

Table 8.5 summarizes the solvent effect on the radiation cationic polymerization of isopropyl vinyl ether at 30 °C. When a nonpolar solvent benzene is used in the polymerization, the k_p^+ is decreased as compared with bulk polymerization of isopropyl vinyl ether. It is interesting to note that the k_p^+ is further decreased using polar solvent. The results clearly indicate that the transition state has a higher dipole moment than the reactants.

Table 8.4 Summary of solvent effect on cationic polymerization

Solvent	k_p^+	k_p^c	k_p^\pm
Polar	Decrease	Decrease for high dipole moment transition state	Increase for high dipole moment transition state
Nonpolar	Increase	Increase	Decrease

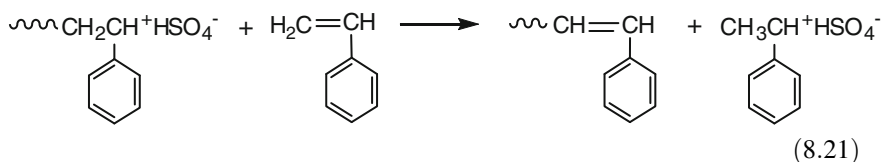
Table 8.5 Effect of solvent on k_p^+ in radiation polymerization of isopropyl vinyl ether at 30 °C [5]

Solvent	ϵ	k_p^+ (L/mol-s)
Benzene	2.7	57
None	3.0	130
(C ₂ H ₅) ₂ O	3.7	34
CH ₂ Cl ₂	6.0	1.5
CH ₃ NO ₂	19.5	0.02

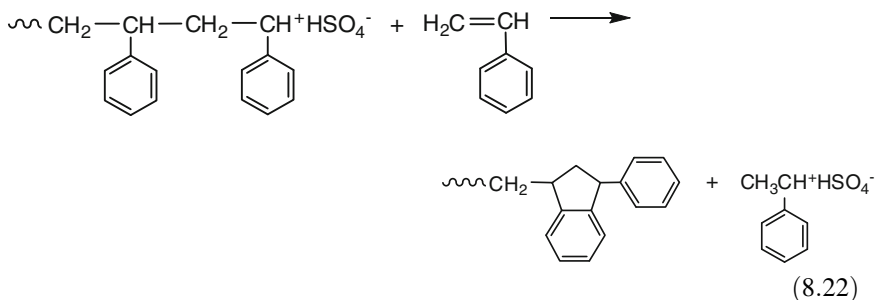
The need for solvation of ionic propagating species in cationic polymerization has been demonstrated in the reactions carried out in low dielectric constant media. In addition to lowering the polymerization rates in poor solvating media, one frequently encounters increased kinetic order in one of the reactants (monomer, initiator or coinitiator). The polymerization rate may show an increased order of dependence on the monomer, initiator, or coinitiator. For example, the polymerization of styrene by tin (IV) chloride initiator, its rate of polymerization depends on $[M]^2$ in benzene solution and $[M]^3$ in carbon tetrachloride solution. Carbon tetrachloride is a poor solvating agent compared to benzene, and the higher order in styrene concentration is due to styrene taking part in solvation of propagating species. At high concentrations of styrene or in neat styrene, the order in styrene decreases to two as the reaction medium becomes equivalent to the benzene system. The polymerization of styrene by trichloroacetic acid illustrates the situation where the initiator solvates ionic propagating species. The kinetic order in the concentration of trichloroacetic acid increases from one in the highly polar nitroethane to two in the less polar 1,2-dichloroethane, to three in neat styrene.

Chain transfer reactions are common in cationic polymerization. For example, in the polymerization of styrene with sulfuric acid, possible chain transfer reactions include:

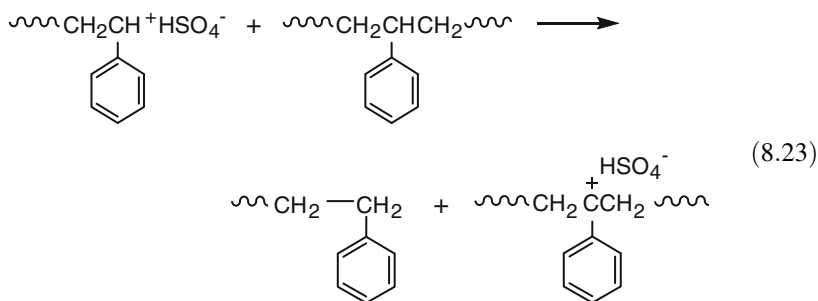
1. With monomer:



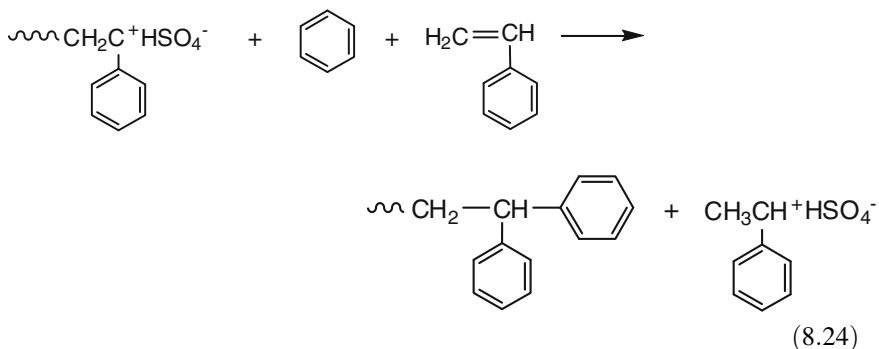
2. By ring alkylation:



3. By hydride abstraction from the chain to form a more stable ion:



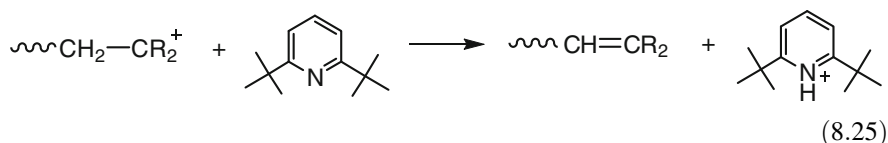
4. With solvent, for example, with benzene by electrophilic substitution:



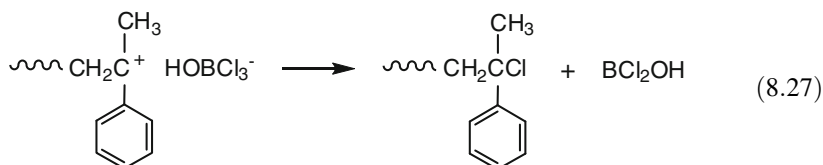
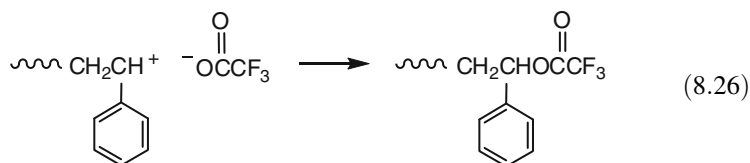
Chain branching occurs via reaction (Eq. 8.23) or by intermolecular ring alkylation (Eq. 8.24).

Chain transfer to monomer is so common in cationic polymerization that it is necessary to reduce the reaction by adding *proton trap*, such as 2,6-di-*t*-

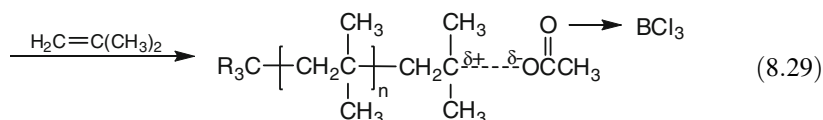
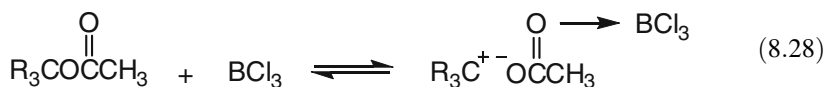
butylpyridine, which intercepts the proton before it transfers to monomer (Eq. 8.25). The result is a lower overall yield but higher molecular weight and lower polydispersity index. The bulky *t*-butyl groups prevent reaction with electrophiles larger than the proton.

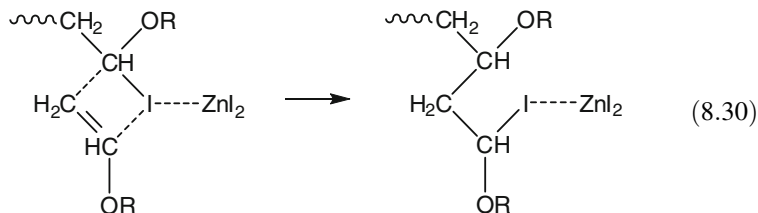


Termination reactions resulting from the combination of chain end with counterion (i.e., a change from ionic to covalent bonding) are observed in the polymerization of styrene, as in the trifluoroacetic acid initiated polymerization (Eq. 8.26), and chain end chlorination in the $\text{BCl}_3/\text{H}_2\text{O}$ initiated polymerization (Eq. 8.27)



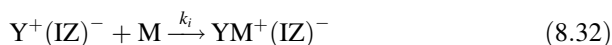
Living cationic polymerization is possible. Polymerization of isobutylene with a tertiary ester and BCl_3 , for example, involves formation of a tertiary carbocation initiating species (Eq. 8.28) and polymerization (Eq. 8.29) to yield polyisobutylene terminated with a very tightly bound but still active ion pair. A similar situation occurs when I_2/HI or I_2/ZnI_2 is used as the initiating system. In this case, the mechanism of propagation apparently involves insertion of vinyl ether into an activated carbon iodine bond (Eq. 8.30).



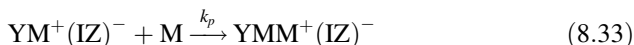


8.2.3 Kinetics of Cationic Polymerization

The initiation process of cationic polymerization can be generalized as



The propagation reaction is expressed in the following:



Termination occurs due to a combination of the propagating center with the counterion.



The overall kinetics depends on the mode of termination in a particular system. If the termination is exclusively due to the combination of propagating center with counterion, one can follow the rate expression used in the radical polymerization basis on the steady-state conditions. The rates of initiation, propagation, and termination are given by

$$R_i = Kk_i[I][ZY][M] \quad (8.35)$$

$$R_p = k_p[YM^+(IZ)^-][M] \quad (8.36)$$

$$R_t = k_t[YM^+(IZ)^-] \quad (8.37)$$

At steady state $R_i = R_t$, then

$$[YM^+(IZ)^-] = \frac{Kk_i[I][ZY][M]}{k_t} \quad (8.38)$$

Combining Eq. 8.36 and Eq. 8.38 yields the rate of polymerization as

$$R_p = \frac{R_i k_p [M]}{k_t} = \frac{K k_i k_p [I][ZY][M]^2}{k_t} \quad (8.39)$$

The number-average degree of polymerization is obtained as the propagation rate divided by the termination rate:

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p [M]}{k_t} \quad (8.40)$$

Similar to radical polymerization, chain transfer reactions are also involved in cationic polymerization such as chain transfer to monomer, spontaneous termination, and chain transfer to chain transfer agent S. In addition to combination with the counterion, if there are chain transfer reactions present, the concentration of the propagating species remains unchanged, and the polymerization rate is again given by Eq. 8.39. However, the degree of polymerization is decreased by these chain transfer reactions and is given by the polymerization rate divided by the sum of all chain transfer reactions:

$$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,M} + R_{tr,S}} \quad (8.41)$$

The rate of spontaneous termination (R_{ts}) and the two transfer reactions ($R_{tr,M}$ and $R_{tr,S}$) are given by

$$R_{ts} = k_{ts} [YM^+(IZ)^-] \quad (8.42)$$

$$R_{tr,M} = k_{tr,M} [YM^+(IZ)^-][M] \quad (8.43)$$

$$R_{tr,S} = k_{tr,S} [YM^+(IZ)^-][S] \quad (8.44)$$

Combining Eq. 8.41 with Eqs. 8.36, 8.37, 8.42 to 8.44 yields

$$\bar{X}_n = \frac{k_p [M]}{k_t + k_{ts} + k_{tr,M} [M] + k_{tr,S} [S]} \quad (8.45)$$

or

$$\frac{1}{\bar{X}_n} = \frac{k_t}{k_p [M]} + \frac{k_{ts}}{k_p [M]} + C_M + C_S \frac{[S]}{[M]} \quad (8.46)$$

where C_M and C_S are the chain-transfer constants for monomer and chain-transfer agent S, which are defined by $k_{tr,M}/k_p$ and $k_{tr,S}/k_p$ respectively. Equation 8.46 is the same as the Mayo Equation for radical polymerization.

When chain transfer to S terminates the kinetic chain, the polymerization rate is decreased and is given by

$$R_p = \frac{K k_i k_p [I][ZY][M]^2}{k_t + k_{tr,S} [S]} \quad (8.47)$$

The above rate expressions are derived on the basis of R_i is a rate determination step as shown in Eq. 8.32. If Eq. 8.31 is the rate determination step, then R_i is independent of monomer concentration and is expressed by

$$R_i = k_1[I][ZY] \quad (8.48)$$

The polymerization rate expressions (Eq. 8.39) will then be modified by replacing Kk_t with k_t , and there will be one order lower dependence of R_p on $[M]$. The degree of polymerization is unchanged and still described by Eq. 8.45.

The expressions for R_p in cationic polymerization (Eq. 8.39) point out a very significant difference between cationic polymerization and radical polymerization. Radical polymerization shows a half-order dependence of R_p on R_i , while cationic polymerizations show a first-order dependence of R_p on R_i . The difference is a consequence of their different modes of termination. Termination is second order in the propagating species in radical polymerization but only first order in cationic polymerization.

In the absence of any chain transfer, the kinetic chain length \bar{v} , is equal to \overline{DP} and is expressed as

$$\bar{v} = \overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M][M^+]}{k_t[M^+]} = \frac{k_p[M]}{k_t}$$

If the chain transfer is the predominant mechanism for controlling chain growth, then

$$\bar{v} = \overline{DP} = \frac{R_p}{R_{tr}} = \frac{k_p[M][M^+]}{k_{tr}[M][M^+]} = \frac{k_p}{k_{tr}}$$

The molecular weight of cationic polymerization is independent of initiator concentration, unlike free radical polymerization, where \overline{DP} is inversely proportional to $[I]^{1/2}$ in the absence of chain transfer. The difference arises from radical disproportionation and combination reactions characteristic of free radical termination. By increasing initiator concentration, the probability of radical termination is increased, which is not the case in ionic polymerization.

Table 8.6 summarizes kinetic parameters of different monomers that undergo cationic polymerization. A comparison of the k_p^+ and k_p^\pm values for the styrene, *p*-methoxystyrene, and *N*-vinyl carbazole polymerizations shows the free ion propagation rate to be an order of magnitude higher than the ion pair propagation rate constant. The results indicate that the presence of counterion in the ion pair reduces the effective frequency factor in the cationic polymerization. Although there are relatively few reliable data of k_p^+ and k_p^\pm in other systems, it is generally agreed that the reactivity of free ions is no more than a factor of 5–20 greater than the reactivity of ion pairs. The counterion is typically quite large for cationic polymerization (e.g., SbCl_6^- , CF_3SO_3^-). The ion pair is a very loose ion pair, so the availability of the positive charge center for reaction has not much difference as compared to the free ion.

Table 8.6 Comparison of polymerization kinetic parameters of some monomers [5]

Parameter	Styrene	<i>i</i> -Butyl vinyl ether	<i>p</i> -Methoxy styrene	<i>N</i> -Vinyl carbazole
[Styrene], M	0.27–0.40	–	–	–
[CF ₃ SO ₃ H], M	3.8–7.1 × 10 ⁻³	–	–	–
[φ ₃ C ⁺ SbCl ₆], M	–	6.0 × 10 ⁻⁵	–	–
<i>k_i</i> , L/mol-s	10–23	5.4	–	–
<i>k_{ds}</i> , mol/L	4.2 × 10 ⁻⁷	–	–	–
<i>k_p⁺</i> , L/mol-s	1.2 × 10 ⁶	7.0 × 10 ³	3.6 × 10 ⁵	6.0 × 10 ⁵
<i>k_p[±]</i> , L/mol-s	1.0 × 10 ⁵	–	4.1 × 10 ⁴	5.0 × 10 ⁴
<i>k_{ts}</i> + <i>k_t</i> , s ⁻¹	170–280	0.2	–	–
<i>k_{tr}</i> , M, L/mol-s	1–4 × 10 ³	1.9 × 10 ²	–	–

A comparison of Table 8.6 with corresponding data for radical chain polymerization as shown in Table 8.7 allows us to understand why cationic polymerizations are generally faster than radical polymerizations. The propagation rate constants in cationic polymerization are similar to or greater than those for radical polymerization. However, the termination rate constants are considerably lower in cationic polymerization. The polymerization rate is determined by the ratio of rate constants k_p/k_t in cationic polymerization and $(k_p/k_t)^{1/2}$ in radical polymerization. The former ratio is larger than the latter by up to four orders of magnitude depending on the monomers being compared. Cationic polymerization is further favored, since the concentration of propagating species is usually much higher than in a radical polymerization. The concentration of propagating species of radical polymerization is typically 10⁻⁷–10⁻⁹ M, much lower than that in cationic polymerization.

Consider the situation where one polymer molecule is produced from each kinetic chain. This is the case for termination by disproportionation or chain transfer or a combination of the two, but without combination. The molecular weight distribution is similar to the linear step polymerization as shown in Eq. 8.49. One difference in the use of the equation for radical chain polymerizations compared to step polymerization is the redefinition of p as the probability that a propagating radical will continue to propagate instead of terminating. The value of p is given as the rate of propagation divided by the sum of the rates of all reactions that a propagating radical may undergo (Eq. 8.50).

$$\bar{X}_w/\bar{X}_n = (1 + p) \quad (8.49)$$

$$p = R_p / (R_p + R_i + R_{tr}) \quad (8.50)$$

For the cationic polymerization, the PDI can be determined by Eq. 8.49. It has a limit of 2 (at low conversion). For rapid initiation, PDI will be narrow. For very slow termination and transfer reaction, PDI will be close to 1. The existence of chain transfer reactions, PDI will be between 1 and 2, mostly larger than 2

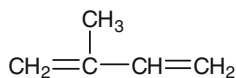
Table 8.7 Comparison of rate constants of cationic polymerization and free radical polymerization

Rate constant	Cationic	Free radical
k_t	Low	High
k_p	High	Low
R_p	k_p/k_t high	$(k_p/k_t)^{1/2}$ low

depending on the chain transfer reactions and their rates relative to propagation. At high conversion, the concentration of propagating centers, monomer, and transfer agent as well as rate constants change, and the PDI increases.

8.2.4 Commercial Cationic Polymerization

Cationic polymerizations are used extensively in the industry for the synthesis of rubbers [5]. Low molecular weight polyisobutylenes (up to \bar{M}_v , $5-10 \times 10^4$) ranged from viscous liquids to tacky semi-solids are synthesized by reacting isobutylene with AlCl_3 at -40 to 10 °C. High molecular weight polyisobutylenes ($\bar{M}_v > 10^5$) are rubbery solids and are obtained at considerably lower reaction temperatures (-100 to -90 °C) by using a process similar to that for butyl rubber. Butyl rubber (BR) is a copolymer of isobutylene and a small amount of isoprene **1** (0.5–2.5 %) produced by AlCl_3 in CH_2Cl_2 . The initiation system is produced by passing methyl chloride through beds of aluminum chloride at $30-45$ °C followed by dilution with methyl chloride and the addition of the initiator. The reaction is carried out at -100 to -90 °C.

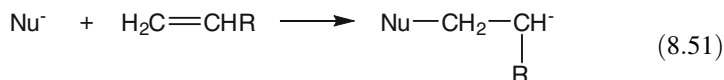


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The isoprene incorporates double bonds into the polymer chains, which is used for cross-linking (called curing in the rubber industry). Molecular weights of at least 200,000 are needed to obtain products that are non-tacky. The molecular weight is controlled by regulating the amount of transfer agent and terminating agent at low reaction temperature. The butyl rubber exhibits better chemical and physical properties than those of natural rubber due to the former having lower degree of unsaturation.

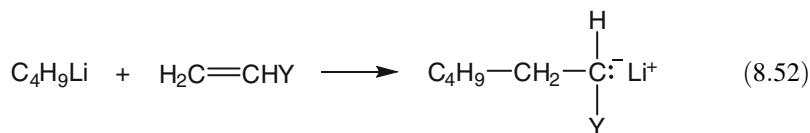
8.3 Anionic Polymerization

In anionic vinyl polymerization, the propagating chain is a carbanion which is formed by initiator undergoing nucleophilic addition to monomer (Eq. 8.51). Monomers having substituent groups capable of stabilizing a carbanion through resonance or induction are most susceptible to anionic polymerization. Examples of such groups are nitro, cyano, carboxyl, vinyl, and phenyl.

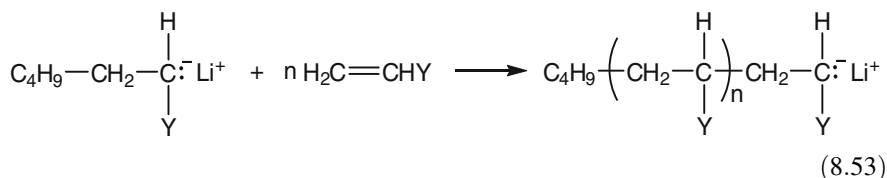


8.3.1 Reaction Mechanisms of Anionic Polymerization

The anionic polymerization is the same as other chain polymerizations which involve three reaction steps: (1) initiation, (2) propagation, and (3) termination, using the base or nucleophile as an initiator, e.g., NaNH_2 , $\text{LiN}(\text{C}_2\text{H}_5)_2$, alkoxides, hydroxides, cyanides, phosphines, amines, and organometallics compounds such as $n\text{-C}_4\text{H}_9\text{Li}$ and $\text{C}_6\text{H}_5\text{-MgBr}$. Alkyl lithium is the most useful initiator and used to initiate 1,3-butadiene and isoprene commercially. It is soluble in hydrocarbon solvents. Initiation proceeds by addition of the metal alkyl to monomer as



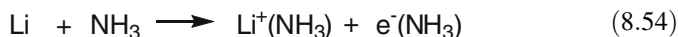
followed by propagation:



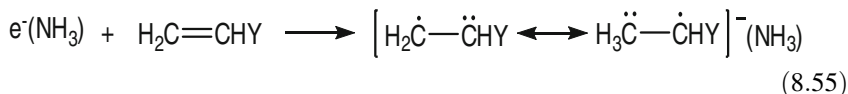
Monomer reactivity increases with increasing ability to stabilize the carbanion charge. Very strong nucleophiles such as amide ion or alkyl carbanion are needed to polymerize monomers, such as styrene, 1,3-butadiene with relatively weak electron withdrawing substituents. Weaker nucleophiles, such as alkoxide and hydroxide ions, can polymerize monomers with strongly electron withdrawing substituents, such as acrylonitrile, methyl methacrylate, and methyl vinyl ketone. Methyl- α -cyanoacrylate $\text{C}=\text{C}(\text{CN})-\text{CO}-\text{OMe}$, containing two electron-withdrawing groups,

can be polymerized by a very weak nucleophile such as Br^- , CN^- , amines, and phosphines. This monomer is used to make “superglue” or magic glue, and can be polymerized by water, which was used as wound repair agent during the Vietnam War.

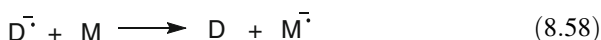
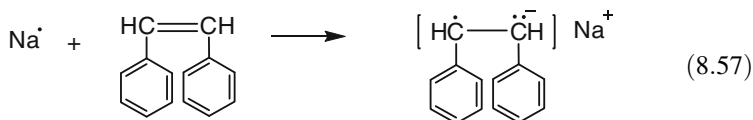
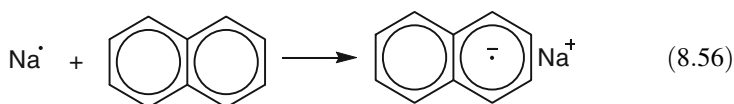
Electron-transfer initiation from other radical-anions, such as those formed by reactions of sodium with nonenolizable ketones, azomethines, nitriles, azo, and azoxy compounds, has also been studied. In addition to radical-anions, initiation by electron transfer has been observed when one uses certain alkali metals in liquid ammonia. Polymerization initiated by alkali metals in liquid ammonia proceeds by two different mechanisms. The mechanism of polymerization is considered to involve the formation of a *solvated electron*:



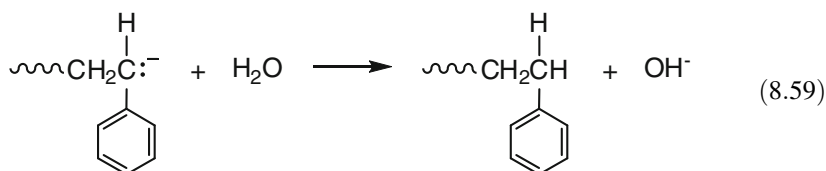
Such ammonia solutions are noted by their characteristic deep blue color. The solvated electron is then transferred to the monomer to form a radical-anion,



Stable addition complexes of alkali metals that initiate polymerization by electron transfer are formed by reaction of metal and compound in an inert solvent. Examples are the reactions of sodium with naphthalene (Eq. 8.56) or stilbene (Eq. 8.57). A general equation for the reaction of this type of donor D^- with monomer M may be written as Eq. 8.58.



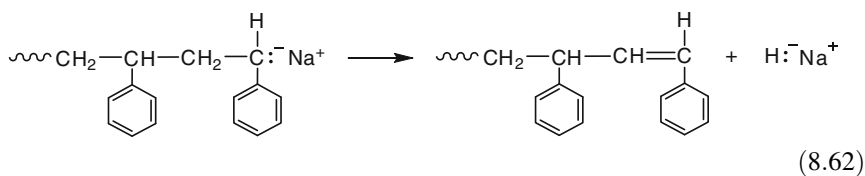
Many anionic polymerizations, such as styrene, 1,3-butadiene, nonpolar monomer have no termination reaction (reacts with counterion). By adding proton donor such as water or alcohol to the living polymers, the living chain can be terminated as shown in Eq. 8.59. The hydroxide ion is usually not sufficiently nucleophilic to reinitiate polymerization.

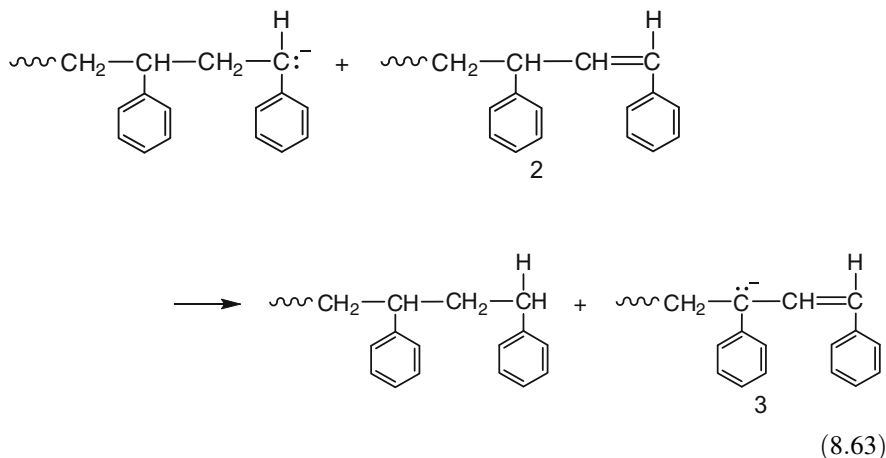


Most anionic polymerization is carried out in an inert atmosphere with rigorously purified reagents and cleaned glassware. Oxygen and carbon dioxide add to propagating carbanion to form peroxy (Eq. 8.60) and carboxyl anions (Eq. 8.61). They are not reactive enough to continue propagation.

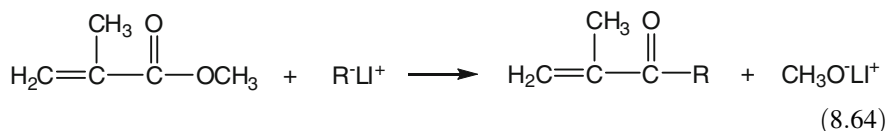


Living polymers do not live forever. In the absence of terminating agents, the concentration of carbanion centers decays with time. Polystyrol carbanions are the most stable of living anionic systems; they are stable for weeks in hydrocarbon solvents. Stability is enhanced by storage below 0 °C. The mechanism for the decay of polystyryl carbanions, referred to as *spontaneous termination*, is based on spectroscopy of the reaction system and final polymer after treatment with water. The reaction consists of *hydride elimination* (Eq. 8.62) followed by abstraction of an allylic hydrogen from **2** and by a carbanion center to yield the unreactive 1,3-diphenyl allyl anion **3**.





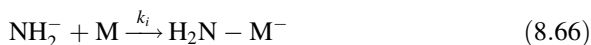
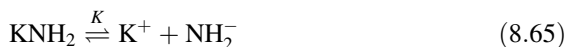
Several different nucleophilic substitution reactions have been observed in the polymerization of methyl methacrylate (MMA). Attack of initiator on monomer converts the active alkyl lithium to the less active alkoxide initiator. Furthermore, MMA can be converted to isopropenyl alkyl ketone as shown in Eq. 8.64.



The resulting polymerization is a copolymerization between these two monomers, not a homopolymerization of MMA. More importantly, this results in a slower reaction since the carbanion derived from the ketone is not as reactive as the carbanion from MMA. To avoid this side reaction, one can use bulky anionic initiator such as diphenyl ethylene *s*-Bu lithium and carry out the reaction at -78°C in tetrahydrofuran [6].

8.3.2 Kinetics of Anionic Polymerization with Termination

The kinetic and mechanistic aspects of anionic polymerization are better understood than those of cationic polymerization. In the case of the potassium amide-initiated polymerization in liquid ammonia, initiation involves dissociation (Eq. 8.65) followed by addition of amide ion to monomer (Eq. 8.66).



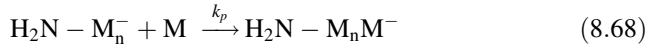
Because the second step is slow relative to the first step,

$$R_i = k_i[\text{H}_2\text{N}^-][\text{M}] \quad (8.67a)$$

or

$$R_i = k_i K [\text{M}][\text{KNH}_2]/[\text{K}^+] \quad (8.67b)$$

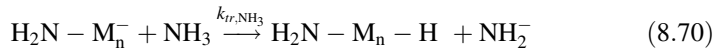
Propagation proceeds according to



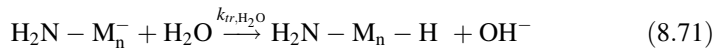
Rate expressions for propagation may be written in the conventional way:

$$R_p = k_p [\text{M}][\text{M}^-] \quad (8.69)$$

The chain transfers to solvent (NH_3) results that an anion produces without termination.



However, the chain transfers to impurities, such as H_2O , results in a termination.



The transfer rates for solvent and impurities can be expressed as Eqs. 8.72 and 8.73

$$R_{tr,\text{NH}_3} = k_{tr,\text{NH}_3} [\text{M}^-][\text{NH}_3] \quad (8.72)$$

$$R_{tr,\text{H}_2\text{O}} = k_{tr,\text{H}_2\text{O}} [\text{M}^-][\text{H}_2\text{O}] \quad (8.73)$$

Assuming a steady state whereby $R_i = R_p$, and combining Eqs. 8.67b, 8.69, and 8.73, one obtains

$$R_p = K k_i k_p [\text{M}]^2 [\text{KNH}_2]/k_{tr,\text{H}_2\text{O}} [\text{K}^+][\text{H}_2\text{O}] \quad (8.74)$$

Therefore, the inverse average kinetic chain length is expressed as

$$1/\bar{X}_n = C_{\text{NH}_3} [\text{NH}_3]/[\text{M}] + C_{\text{H}_2\text{O}} [\text{H}_2\text{O}]/[\text{M}] \quad (8.75)$$

where the C_{NH_3} and $C_{\text{H}_2\text{O}}$ are defined as follows:

$$C_{\text{NH}_3} = k_{tr,\text{NH}_3}/k_p; C_{\text{H}_2\text{O}} = k_{tr,\text{H}_2\text{O}}/k_p \quad (8.76)$$

The propagation rate constant and the polymerization rate of anionic polymerization are affected by solvent and counterion. Table 8.8 shows the effect of solvent on the polymerization of styrene by sodium naphthalene. Polar solvents (tetrahydrofuran and 1,2-dimethoxy ethane) have higher k_p^{app} than nonpolar solvent

Table 8.8 Effect of solvent on anionic polymerization of styrene [5]

Solvent	Dielectric constant	k_p^{app} L/mol-s
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxy ethane	5.5	3,800

(benzene and dioxane). The reaction has a higher k_p in 1,2-dimethoxy ethane than in tetrahydrofuran (THF), due to the solvation effect of dimethoxy ethane. The increase in k_p^{app} with increased solvating power of the reaction medium is due mainly to the increased fraction of free ions present relative to ion pairs.

The rate of polymerization is the sum of the rates for the free propagating anion P^- and the ion pair $P^-(C^+)$.

$$R_p = k_p^- [P^-][M] + k_p^\mp [P^-(C^+)] [M] \quad (8.77)$$

Where k_p^- and k_p^\mp are the propagation rate constants for the free ion and ion pair, respectively, $[P^-]$ and $[P^-(C^+)]$ are the concentrations of the free ion and ion pair, and $[M]$ is the monomer concentration. C^+ is the positive counterion.

$$R_p = k_p^{app} [M^-][M] \quad (8.78)$$

Comparison of Eqs. 8.77 and 8.78 yields the apparent k_p as

$$k_p^{app} = \frac{k_p^- [P^-] + k_p^\mp [P^-(C^+)]}{[M^-]} \quad (8.79)$$

The two propagating species are in equilibrium according to



governed by the dissociation constant K that is given by

$$K = \frac{[P^-][C^+]}{[P^-(C^+)]} \quad (8.81)$$

When $[P^-] = [C^+]$, the concentration of free ions is

$$[P^-] = (K[P^-(C^+)])^{1/2} \quad (8.82)$$

The extent of dissociation is small under most conditions, the concentration of ion pairs is close to the total concentration of free ions and Eq. 8.81 can be rewritten as

$$[P^-] = (K[M^-])^{1/2} \quad (8.83)$$

The concentration of ion pairs is given by

$$[\text{P}^-(\text{C}^+)] = [\text{M}^-] - (K[\text{M}^-])^{1/2} \quad (8.84)$$

Combination of Eqs. 8.79, 8.83, and 8.84 yields k_p^{app} as a function of $[\text{M}^-]$:

$$k_p^{app} = k_p^\mp + \frac{(k_p^- - k_p^\mp)K^{1/2}}{[\text{M}^-]^{1/2}} \quad (8.85)$$

When polymerization is carried out in the presence of excess counterion by adding a strongly dissociating salt, the concentration of free ions, depressed by the common ion effect, is given by

$$[\text{P}^-] = \frac{K[\text{M}^-]}{[\text{C}^+]} \quad (8.86)$$

When the added salt is strongly dissociated and the ion pairs slightly dissociated, the counterion concentration is very close to that of the added salt $[\text{CZ}]$:

$$[\text{C}^+] \simeq [\text{CZ}] \quad (8.87)$$

The concentrations of free anions and ion pairs are given by

$$[\text{P}^-] = \frac{K[\text{M}^-]}{[\text{CZ}]} \quad (8.88)$$

$$[\text{P}^-(\text{C}^+)] = [\text{M}^-] - \frac{K[\text{M}^-]}{[\text{CZ}]} \quad (8.89)$$

which are combined with Eq. 8.79 to yield

$$k_p^{app} = k_p^\mp + \frac{(k_p^- - k_p^\mp)K}{[\text{CZ}]} \quad (8.90)$$

Equations 8.79 and 8.90 allow one to obtain k_p^- , k_p^\mp and K from k_p^{app} values obtained in the absence and presence of added common ion. A plot of k_p^{app} obtained in the absence of added common ion versus $[\text{M}^-]^{-1/2}$ yields a straight line whose slope and intercept are $(k_p^- - k_p^\mp)K^{1/2}$ and k_p^\mp , respectively. A plot of k_p^{app} obtained in the presence of added common ion versus $[\text{CZ}]^{-1}$ yields a straight line whose slope and intercept are $(k_p^- - k_p^\mp)K$ and k_p^\mp , respectively. The combination of the two slopes and two intercepts allows the individual calculation of k_p^- , k_p^\mp and K . (Note: K , $[\text{P}^-]$ and $[\text{P}^-(\text{C}^+)]$ can also be independently determined from conductivity measurements.)

The polydispersity (PDI) of living anionic polymerized polymer can be expressed by the following depending on the mode of termination:

$$\bar{X}_n = 2p[\text{M}]_0/[\text{I}]_0 \quad (8.91)$$

or

$$\bar{X}_n = p[M]_0/[I]_0 \quad (8.92)$$

where the $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator, respectively, and the p is the fractional conversion of monomer at any time in the reaction. Low PDI can be obtained for system that has fast initiation, efficient mixing, in the absence of de-propagation, termination, and transfer reaction. The PDI is around 1.1–1.2 for many living polymerizations. The presence of termination, transfer, or side reaction will broaden the PDI. Although the bulk of propagation is carried by a small fraction of the propagating species (i.e. the free ions), this does not significantly broaden the molecular weight of polymer. Since the free ions and ion pairs are in rapid equilibrium, each polymer chain propagates as both free ion and ion pair over its lifetime and the average fractions of its lifetime spent as free ion and ion pair are not too different from any other propagating chain.

Table 8.9 shows the K and the propagation rate constants for free ions and ion pairs in styrene polymerization in THF at 25°C with various alkali metal counterions. The corresponding k_p^\mp values in dioxane are also presented. The value of K and k_p^- in dioxane could not be obtained as conductivity measurements indicated no detectable dissociation of ion pairs to free ions in dioxane. The reactivity of the free ion is greater compared to any of the ion pairs as expected. The K values indicate that the increased solvating power affects the reaction rate primarily through an increase in the concentration of free ions. Since free ions are so much more reactive than ion pairs, their small concentration has a very large effect on the observed polymerization rate. The table shows that the dissociation constant for the ion pair decreases in going from lithium to cesium as the counterion. The order of increasing K is the order of increasing solvation of the counterion. The smaller Li^+ is solvated to the greater extent and the larger Cs^+ is the least solvated. The decrease in K has a significant effect on the overall polymerization, since there is a very significant change in the concentration of the highly reactive free ions. Thus, the free-ion concentration for polystyryl cesium is less than that of polystyryl lithium. The reactivities of the various ion pairs also increase in the same order as the K values: $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$. The fraction of the ion pairs that are of the solvent-separated type increases with increasing solvation of the counterion. Solvent-separated ion pairs are much more reactive than contact ion pairs. The order of reactivity for the different ion pairs in dioxane is the reverse of that in tetrahydrofuran. Solvation is not important in dioxane. The ion pair with the highest reactivity is that with the weakest bond between the carbanion center and counterion.

The effect of counterion on ion-pair reactivity is different for methyl methacrylate (MMA) compared to styrene as shown in Table 8.10. The absence of solvent effect by THF for MMA polymerization is due to the presence of intramolecular solvation. The additional binding of the counterion to the polymer accounts for the low dissociation constant ($K < 10^{-9}$, MMA; compared to 10^{-7} , styrene). Smaller

Table 8.9 Effect of counterion on anionic polymerization of styrene* [3]

Polymerization in tetrahydrofuran				
Counterion	k_p^\mp	$K \times 10^7$	k_p^-	k_p^\mp for dioxane
Li ⁺	160	2.2	6.5×10^4	0.94
Na ⁺	80	1.5	6.5×10^4	3.4
K ⁺	60–80	0.8	6.5×10^4	19.8
Rb ⁺	50–80	0.1	6.5×10^4	21.5
Cs ⁺	22	0.02	6.5×10^4	24.5

*Units of K are mole L⁻¹; rate constants are L mol⁻¹ s⁻¹

counterions “fit better” into the intramolecular solvation sphere. Table 8.11 shows a comparison between anionic polymerization and cationic polymerization. The behaviors of these two polymerizations are quite different although both of them belong to ionic polymerization.

8.4 Group Transfer Polymerization

Unlike conventional anionic polymerization, group transfer polymerization (GTP) affords low-polydispersity living polymers at room temperature or above. Typically, an organosilicon compound is used to initiate the polymerization in solution in the presence of an anionic or Lewis acid catalyst. Examples of each type of compounds are given in Table 8.12.

Equation 8.93 shows an example of chemical reactions involved in the group transfer polymerization. In each propagation step, the SiR₃ group is transferred to the carbonyl oxygen of the incoming monomer, hence the name of GTP is obtained [4]. If a difunctional initiator is used, the chain propagates from each end (Eq. 8.94):

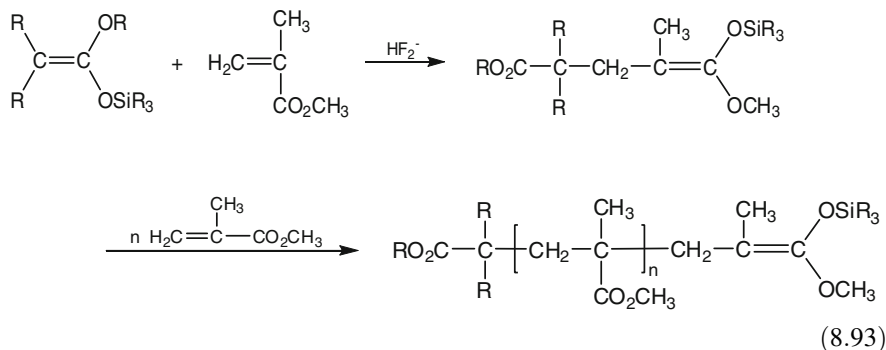
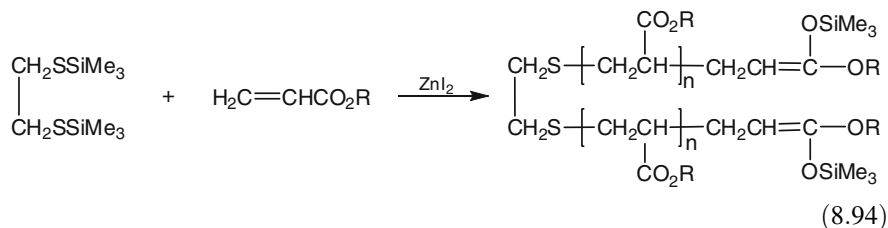


Table 8.10 Comparison of effect of counterion on anionic polymerization between styrene and methyl methacrylate

Cation	Styrene	Methyl methacrylate
Li ⁺	160	1
Na ⁺	80	~ 30–33
K ⁺	60–80	~ 30–33
Rb ⁺	50–80	~ 30–33
Cs ⁺	22	~ 30–33

Table 8.11 Comparison between cationic polymerization and anionic polymerization

Factor	Anionic	Cationic
Propagating species	Anionic ion pair/free ions	Cationic ion pair/free ions
Difference in ion pair/free ion reactivity	Large	Small
Temperature sensitivity	Relative small	Large
$E_R = E_i + E_p - E_t$	Positive	Negative (mostly $E_t > E_i + E_p$)
Solvent	Aliphatic/aromatic hydrocarbon and ether	Prefer polar solvent
Halogenated solvent	No (facile nucleophilic substitution Rx)	Yes
Living polymerization	Most	Seldom



Once the monomer is consumed, a different monomer may be added, or the chain can be terminated by removal of catalyst or by protonation (Eq. 8.95) or alkylation (Eq. 8.95)

Table 8.12 Representative compounds used in group transfer polymerization [4]

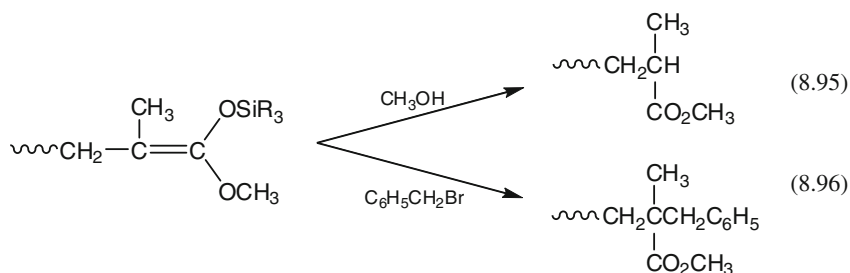
Monomers ^a	Initiators ^a	Catalysts ^a	Solvents
$\text{H}_2\text{C}=\text{CHCO}_2\text{R}$	$\text{Me}_2\text{C}=\text{C}\begin{matrix} \text{OMe} \\ \text{OSiMe}_3 \end{matrix}$	Anionic ^b HF_2^- CN^-	Acetonitrile 1,2-Dichloroethane ^d Dichloromethane ^d
$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{Me} \\ \text{CO}_2\text{R} \end{matrix}$	$\text{Me}_3\text{SiCH}_2\text{CO}_2\text{Me}$	N_3^- Me_3SiF_2	N,N-Dimethylacetamide N,N-Dimethylacetamide
$\text{H}_2\text{C}=\text{CHCONR}_2$	Me_3SiCN	Lewis acid ^c	Ethyl acetate
$\text{H}_2\text{C}=\text{CHCN}$	RSSiMe_3	ZnX_2 R_2AlCl	Propylene carbonate Tetrahydrofuran
$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{Me} \\ \text{CCN} \end{matrix}$	ArSSiMe_3	$(\text{R}_2\text{Al})_2\text{O}$	Toluene ^d
$\text{H}_2\text{C}=\text{CH}\overset{\text{O}}{\parallel}\text{CR}$			

^a R = alkyl, Ar = aryl, Me = methyl, X = halogen

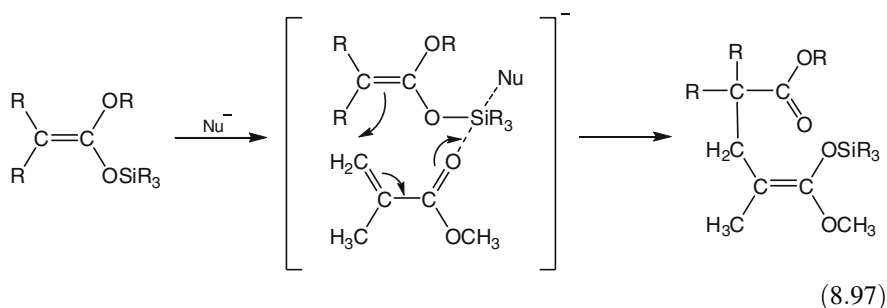
^b 0.1 mol % relative to initiator

^c 10–20 mol % relative to monomer

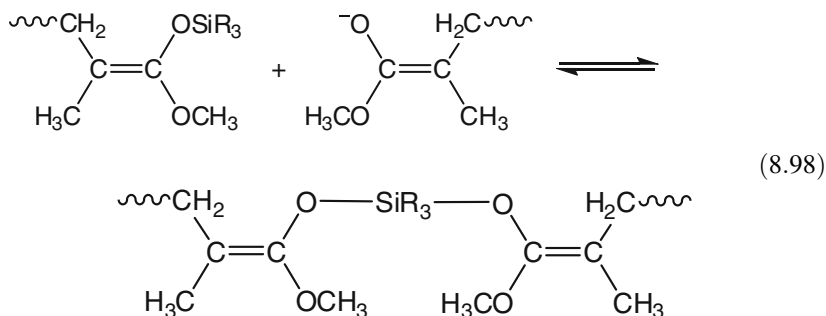
^d Preferred with Lewis acid catalysts



There are two reaction mechanisms proposed for the GTP. Equation 8.97 shows the propagating chain is completely covalent, and a hypervalent silicon intermediate is formed by activation with the nucleophilic catalyst (Nu^-). The silyl group is then transferred to the carbonyl group of an incoming monomer molecule via an eight-membered ring transition state. If Lewis acid catalysts are used, the catalyst coordinates with the carbonyl oxygen of monomer, then the monomer becomes more susceptible to nucleophilic attack by the initiator.



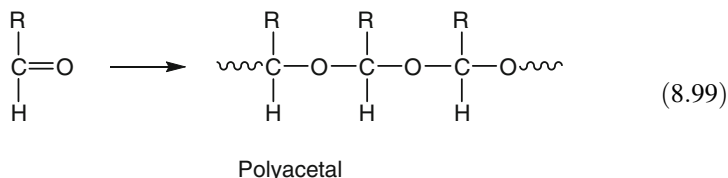
Equation 8.98 shows enolate anions and silyl ketene acetal chain ends are in rapid equilibrium with a hypervalent silicon complex. The complex thus provides a low equilibrium concentration of enolate anions for propagation and maintaining living chain ends.



Group transfer polymerization (GTP) requires the absence of materials such as H_2O with active hydrogen, but O_2 does not interface with the reaction. Solvent types are wider than anionic polymerization. In anionic polymerization, dimethylformamide reacts with nucleophilic catalyst; chlorinated hydrocarbons, acetonitrile reacts with Lewis acid catalyst; ether, tetrahydrofuran and toluene are the most common solvents. The GTP lacks anionic propagation center, thus more polar solvent can be used. The concerted reaction mechanism of group transfer polymerization can reduce the side reaction problems of anionic polymerization. However, the GTP has a lower rate of propagation than that of anionic polymerization. It remains to be seen whether or not the GTP is used commercially in the near future.

8.5 Chain Polymerization of Carbonyl Monomer

The polymerization of the carbonyl group in aldehydes yields polymers, referred to as *polyacetals*, since they contain the acetal repeating structure (Eq. 8.99).

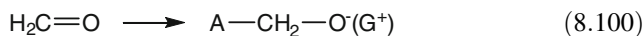


They have to be synthesized by either cationic or anionic polymerization at low temperatures, because they exhibit low ceiling temperature except formaldehyde as shown in Table 8.13.

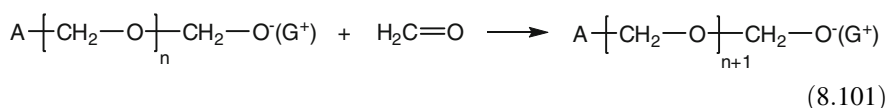
8.5.1 Anionic Polymerization of Carbonyl Monomer

Formaldehyde can be polymerized by any base. Metal alkyls, alkoxides, phenolate, carboxylates, hydrated alumina, amine, phosphine, pyridine are effective in polymerizing formaldehyde. The polymerization proceeds as follows:

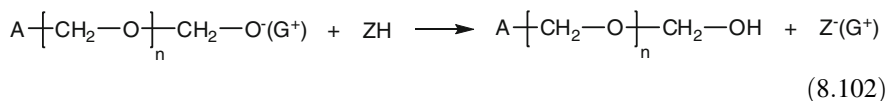
Initiation



Propagation



Termination by chain transfer



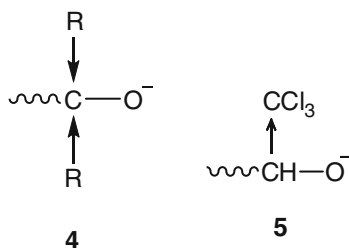
The aldehyde is initiated by anionic species A^- to form an alkoxide anion with nearby counterion G^+ . Propagation proceeds in a like manner and termination occurs by transfer of a proton from ZH. The chain-transfer agent ZH can transfer a proton to the propagating alkoxide anion, such as water or alcohol. The chain-

Table 8.13 Ceiling temperatures [5]

Monomer	T _c (°C)
Formaldehyde	119
Trifluoroacetaldehyde	81
Propanol	-31
Acetaldehyde	-39
Pentanal	-42

transfer agent can have an effect on the polymerization rate if Z^- is not as effective as A^- in reinitiating polymerization.

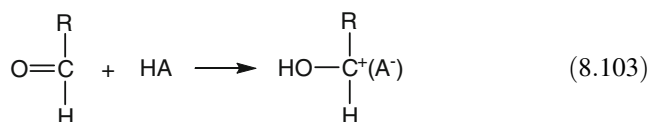
Strong bases are required to initiate aliphatic aldehydes such as acetaldehyde and high aldehyde. The inductive effect of an alkyl substituent destabilizes the propagating anion **4** by increasing the negative charge density on oxygen. The alkyl group also decreases reactivity for steric reasons. Steric considerations are probably also responsible for low ceiling temperature as compared to formaldehyde. Alkali metal alkyls and alkoxides are required to initiate the polymerization. The presence of trace amount of water is detrimental, since the initiator reacts to form hydroxide ion, which is too weak to initiate polymerization. Ketones **4** are unreactive toward polymerization because of the steric and inductive effects of two alkyl groups. A side reaction of aldol condensation occurs with acetaldehyde and higher aldehydes containing α -hydrogens. The Aldol reaction can be extensive at ambient temperatures or higher but it can be avoided by polymerization at low temperature. The substitution of halogens on the alkyl group of an aliphatic aldehyde greatly enhances its polymerizability. Trichloroacetaldehyde (chloral) is easily polymerized by weak bases: pyridine, alkali thiocyanates, and even chloride ion. Furthermore, the polymerization of chloral by *n*-butyl lithium at -78°C can be completed in less than a second. The electron-withdrawing inductive effect of the halogens acts to stabilize the propagating anion **5** by decreasing the charge density on the negative oxygen.



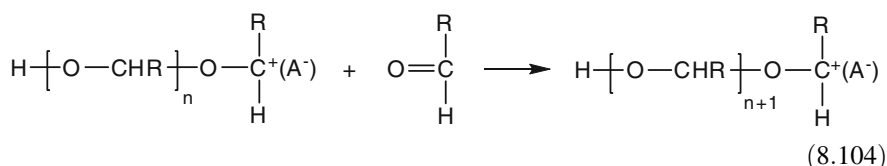
8.5.2 Cationic Polymerization of Carbonyl Monomer

Acidic initiators can be used to polymerize carbonyl monomers, although their reactivity is lower than that in anionic polymerization. Hydrochloric acid, acetic acid, Lewis acid can be used as cationic initiator. The initiation and propagation steps are shown in the following:

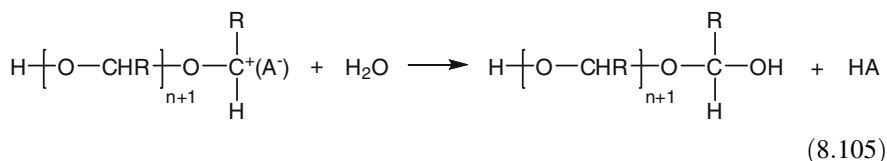
Initiation



Propagation



Termination



Competing side reactions in cationic polymerization of carbonyl monomers include cyclotrimerization, acetyl interchange. Acetaldehyde and higher aldehyde are reasonably reactive in cationic polymerization as compared to formaldehyde. Haloaldehydes are lower in reactivity as compared to their non-halogen counterparts due to the electron withdrawing of halogen.

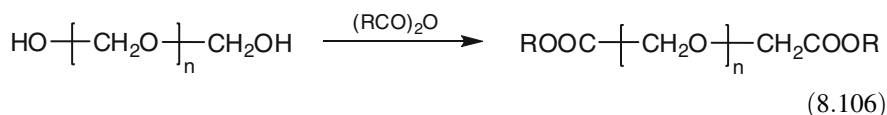
8.5.3 Radical Polymerization of Carbonyl Monomer

The carbonyl double bond is difficult to be polymerized by radical initiators because of the carbonyl group being highly polarized and not prone to be attached by radical; most radicals are produced at temperatures above the ceiling temperature of carbonyl monomers [5]. There are, however, a few isolated cases of carbonyl polymerizations by radical initiators. Trifluoroacetaldehyde has been

polymerized using benzoyl peroxide at 22°C. The polymerization is slow, with 18 h required to obtain 90 % conversion. However, fluorothiocarbonyl monomers such as thiocarbonyl fluoride have been polymerized at high rates by using a trialkyl boron-oxygen redox system at -78°C. Thioacetone is also polymerized by this redox system. Radical polymerizations are observed with these monomers because the electron-withdrawing substituents on the carbonyl and thiocarbonyl group decrease its polarity. The greater susceptibility of the thiocarbonyl double bond to radical polymerization is due to the lower electronegativity of sulfur compared to oxygen.

8.5.4 End-Capping Polymerization

The low ceiling temperature of polyacetal can be end capped to increase its stability. Depolymerization occurs on heating of polyoxymethylene (POM) when reactive carbanion or carbocation centers are formed by thermal bond scission at the hydroxyl end groups. The stability of POM can be improved by converting the less stable hydroxyl end groups into more stable ester groups by reaction with an anhydride [5]:

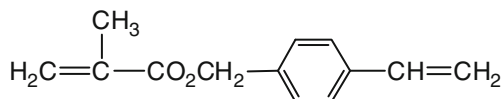


This reaction is referred to as *end capping* or *end blocking*. The result is that reactive carbanion or carbocation centers do not form and depolymerization does not occur at the ceiling temperature of the polymer. The polymer chains are end blocked from depolymerization. The effective ceiling temperature is increased considerably above the ceiling temperature. Acetic anhydride is the usual capping reagent.

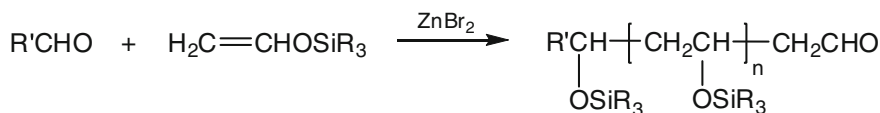
The anionic polymerization formaldehyde to POM followed by end capping is carried out commercially with a trade name of *Delrin*. The POM is highly crystalline (60–77 %) because of the ease of packing of single, polar polymer chain ($T_m = 175^\circ\text{C}$). The commercial products have number-average molecular weights of 20,000–70,000 (PDI ~ 2). The POM has a good combination of properties—high strength, toughness, resistant to creep, fatigue, and abrasion; low coefficient of friction; low moisture absorption.

8.6 Problems

- Give clear explanations for the following facts:
 - Polymerization rate and polymer stereochemistry are more sensitive to solvent effects in ionic polymerization than in free radical polymerization.
 - $\overline{DP} = \bar{v}$ in cationic polymerization, but this is not always the case in free radical or anionic polymerization.
 - Ethyl vinyl ether undergoes cationic polymerization faster than β -chloroethyl vinyl ether under the same conditions.
- Predict the order of reactivity (and justify your prediction): (a) in cationic polymerization: styrene, *p*-methoxystyrene, *p*-chlorostyrene, *p*-methylstyrene; (b) in anionic polymerization: styrene, 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine.
- Write reactions illustrating transfer to monomer and transfer to polymer in the cationic polymerization of propylene and isobutylene. Which type of transfer would you expect to predominate in each case? Suggest a reason why propylene does not form high-molecular-weight polymer under cationic conditions. (*Note*: The order of stability of carbocations is tertiary > allylic > secondary > primary).
- If trifluoroacetic acid is added dropwise to styrene, no polymerization occurs. On the other hand, styrene is added to the acid, however, high-molecular-weight polymer forms rapidly. Please explain.
- What number-average molecular weight of polystyrene will be formed by polymerization of 2.0 M styrene using 1.0×10^{-3} M of sodium naphthalene in tetrahydrofuran using appropriate data from Table 8.9? If the reaction is run at 25°C, how long will it take to reach 90 % conversion?
- Predict the structure of the soluble polymer formed from 2,6-diphenyl-1,6-heptadiene under anionic conditions. Write a mechanism for its formation.
- Predict the structure of the polymer formed by (a) group transfer, (b) cationic, and (c) free radical polymerization of *p*-vinylbenzyl methacrylate (C. Pugh and V. Percec, *Polym. Bull.*, **14**, 109 (1985)).



- Silyl vinyl ethers are polymerized in the presence of aldehyde initiators and Lewis acid catalysts to give silylated poly (vinyl alcohol):



Propose a mechanism for the polymerization (D. Y. Sogah and O.W. Webster, *Macromolecules*, 19, 1775, 1986).

9. Please propose experimental approaches to determine whether the polymerization of a particular monomer is by a radical or ionic mechanism.
10. The sodium naphthalene polymerization of methyl methacrylate is carried out in benzene and tetrahydrofuran solutions. Which solution will yield the highest polymerization rate? Please discuss the effect of solvent on the relative concentrations of the different types of propagating centers.

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