

Chapter 11

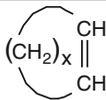
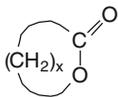
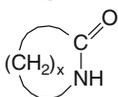
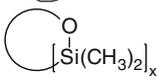
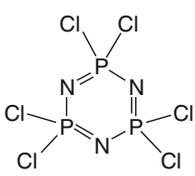
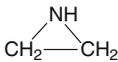
Ring-Opening Polymerization

Polymers can be synthesized by polymerizing monomers with ring structure as shown in Table 11.1. The polymerization of these compounds has some aspects of both chain and step polymerizations as far as kinetics and mechanisms are concerned. The ring-opening polymerization has been used in the polymerization of commercial important polymers such as curing of epoxy resin from 3-membered ring cyclic ethers (epoxides), polyesters from cyclic ester (lactones), polyamides from cyclic amides (lactams), polysiloxanes from cyclic siloxanes, and so on. We will discuss the reaction mechanisms and kinetics of ring-opening polymerization in depth using epoxide, lactam, and cyclic siloxane as examples.

11.1 Reactivity of Cyclic Monomers

The ease of polymerization of a cyclic monomer depends on both thermodynamic and kinetic factors [2]. The single most important factor that determines whether a cyclic monomer can be converted to linear polymer is the thermodynamic factor, i.e., the relative stabilities of the cyclic monomer and linear polymer structure. The thermodynamic stability of the monomer is dependent on the strain in the ring structure. The strain in cyclic structure is very high for the 3- and 4-membered rings, decreases sharply for 5-, 6-, and 7-membered rings, increases for 8–13 membered rings, and then decreases again for larger rings. There are two types of strain: angle strain and conformational strain. Ring structures of less than five atoms are highly strained due to the high degree of angle strain, i.e., the large distortion of their bond angles from the normal tetrahedral bond angle. Bond angle distortion is virtually absent in rings of five or more members. For rings larger than five atoms, the strain due to bond angle distortion becomes too excessive to have planar rings. Therefore, rings larger than five atoms exist in more stable, nonplanar forms. The differences in strain among 5-membered ring or larger are due to differences in conformational strain. The 5- and 7-membered rings are somewhat strained in comparison to the 6-membered ring because of the torsional strain arising from eclipsed conformations on adjacent atoms of the ring. Rings of 8 or

Table 11.1 Examples of polymers prepared by ring-opening polymerization [1]

Polymer type	Polymer repeating group	Monomer structure	Monomer type
Polyalkene	$\text{-(CH=CH(CH}_2\text{)}_x\text{)-}$		Cyclic alkene
Polyether	$\text{-(CH}_2\text{)}_x\text{O-}$		Cyclic ether ^a
Polyester ^b	$\text{-(CH}_2\text{)}_x\text{CO-}$		Lactone
Polyamide	$\text{-(CH}_2\text{)}_x\text{CNH-}$		Lactam
Polysiloxane	$\text{-(Si(CH}_3\text{)}_2\text{-O)-}$		Cyclic siloxane
Polyphosphazene	-(P=N)-		Hexachloro-cyclotriphosphazene ^c
Polyamine	$\text{-(CH}_2\text{CH}_2\text{NH)-}$		Aziridene ^d

^a Epoxide ($x = 2$); oxetane ($x = 3$)

^b Ring opening of cyclic oligomers has also been developed

^c Phosphonitrilic chloride trimer

^d Also called alkyleneimine

more members have transannular strain arising from repulsive interactions between hydrogens or other groups which are forced into crowd positions in the interior of the ring structure. Transannular strain nearly disappears for rings larger than 13 members, because the ring becomes sufficiently large to accommodate substituents without transannular repulsions. The general order of thermodynamic stability of different sized rings of cycloalkene is given by $3,4 \ll 5,7-13 < 6,14$ and larger. The same order is observed for a variety of ring structures such as ethers, lactones, or lactams. It has been observed that substituents on the ring generally increase its stability relative to the linear structure as repulsive interactions between substituents are less severe in the ring structure.

Table 11.2 shows the semiempirical enthalpy, entropy, and free energy changes for the conversion of cycloalkanes to the corresponding linear polymer. The denoting liquid-crystal (lc) subscripts of ΔH , ΔS , and ΔG indicate that the values are those for the polymerization of liquid monomer to crystalline polymer. ΔH_{lc} is the major factor

Fig. 11.1 Determination of the equilibrium monomer concentration $[M]_c$ for the $(C_2H_5)_3O^+(BF_4)^-$ initiated polymerization of tetrahydrofuran in dichloroethane at $0^\circ C$ [2]

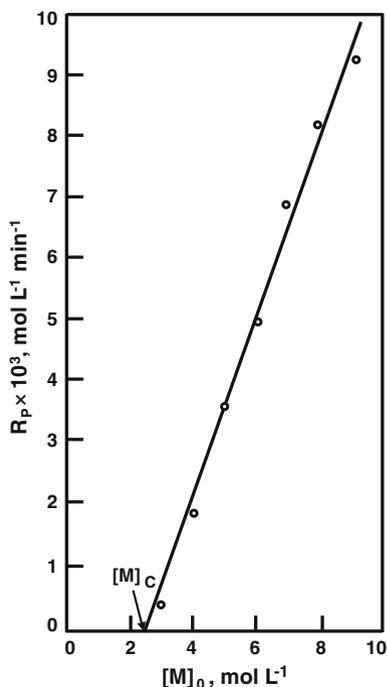


Table 11.2 Thermodynamics of polymerization of cycloalkanes at $25^\circ C$ [2]

$(CH_2)_n$	ΔH (KJ/mol)	ΔS (J/mol K)	ΔG (KJ/mol)
n			
3	-113.0	-69.1	-92.5
4	-105.1	-55.3	-90.0
5	-21.2	-42.7	-9.2
6	+2.9	-10.5	+5.9
7	-21.8	-15.9	-16.3
8	-34.8	-3.3	-34.3

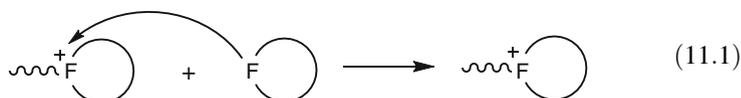
in determining ΔG_{1c} for 3- and 4-membered rings, while ΔS_{1c} is very important for the 5- and 6-membered rings. The enthalpy and entropy factors ΔH_{1c} and ΔS_{1c} contribute about equally for larger sized rings. Since both ΔH_{1c} and ΔS_{1c} are negative, ΔG_{1c} becomes less negative with increasing temperature. Above ceiling temperature, ΔG_{1c} becomes positive, and polymerization is no longer favorable. For all size rings, the presence of substituents decreases thermodynamic feasibility for polymerization. Interactions between substituents are more severe in the linear polymer than in the cyclic monomer, ΔH_{1c} is less negative, while ΔS_{1c} is more negative.

Although ring-opening polymerization is thermodynamically favored for all except the 6-membered cycloalkane, polymerization of cycloalkanes has been

achieved in very few cases, almost exclusively with cyclopropane derivatives, and only oligomers are obtained. This point out that thermodynamic feasibility does not guarantee the actual polymerization of a cyclic monomer. Polymerization requires that there is a kinetic pathway for the ring to open and undergo reaction. The cycloalkanes do not have a bond in the ring structure that is easily to be attacked by an initiator. On the other hand, the lactams, lactones, cyclic ethers and acetals, and other cyclic monomers can be polymerized. The presence of a heteroatom in the ring provides a site for nucleophilic or electrophilic attack by initiator species, resulting in initiation and subsequent propagation by ring opening. Thus, these type monomers are both kinetically and thermodynamically favored to be polymerized. In general, the polymerizability is higher for rings of 3, 4, and 7–11 members, lower for rings of 5 members, and much lower for rings of 6 members. However, there are exceptions. For instance, 6-membered rings with two or more heteroatoms in the ring undergo polymerization. The 6-membered lactam undergoes polymerization as well.

11.2 General Aspects of Mechanisms and Kinetics

Ring-opening polymerization is generally initiated by the same types of ionic initiators used in the polymerization of monomers containing carbon–carbon and carbon–oxygen double bonds [2]. Most cationic ring-opening polymerization involves the formation and propagation of oxonium ion centers. Reaction involves the nucleophilic attack of monomer on the oxonium ion:



where F represents a functional group such as O, NH, Si–O, C(=O)–O, and C(=O)–NH in ethers, amines, siloxanes, esters, and amides, respectively. The typical anionic ring-opening polymerization involves the formation and propagation of anionic centers. Reaction proceeds by nucleophilic attack of the propagating anion on monomer:



where F^- represents an anionic propagating center, such as alkoxide or carboxylate, derived from the cyclic monomer. Ionic ring opening-polymerization exhibits similar behaviors as the ionic polymerization of carbon–carbon and carbon–oxygen double bonds discussed in [Chap. 8](#).

Some ring-opening polymerization proceeds by a different route called *activated monomer polymerization*. The reaction involves a cationic or anionic species

derived from the monomer. For example, cationic activated monomer polymerization does not proceed with monomer, but with protonated monomer that reacts with the neutral functional end group of the propagating polymer.



Ring-opening polymerization is like a chain polymerization, consisting of a sequence of initiation, propagation, and termination. On the other hand, only monomer adds to the growing chains of propagation that is similar to step polymerization. However, unlike step polymerization, monomer and larger sized species do not generally react themselves or with each other in ring-opening polymerization. Many ring-opening polymerizations proceed as living polymerization. Block copolymer can be synthesized by this way. The propagation rate constants of ring-opening polymerizations are generally similar to the rate constants in most step polymerizations which make them several orders of magnitude lower than those in typical chain polymerizations. Thus, the buildup of polymer molecular weight is slower for ring opening polymerization as compared to chain polymerizations.

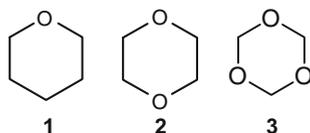
Polymerization–depolymerization equilibria are more often encountered in ring-opening polymerization than in the chain polymerizations. Ring-opening polymerization offers an alternate to step polymerization for the synthesis of many polymers. Thus, polyesters can be produced either by ring-opening polymerization of lactones as well as step polymerization of diacids with diols. The ring-opening polymerization has the advantage over step polymerization for high molecular weight polymer. The molecular weight of ring-opening polymerization depends on conversion and the monomer: initiator ratio. However, the monomers of ring-opening polymerization are not as readily available as the monomers of step polymerization. On the other hand, the molecular weight of step polymerization depends on the conversion and stoichiometric balance which is more difficult to control as compared with ring-opening polymerization.

11.3 Cyclic Ethers

The carbon–oxygen bond in ethers is a strong bond, and the ether oxygen is a Lewis base [2]. Thus, the ring-opening polymerization of cyclic ethers is initiated only by cationic species except for epoxides. The 3-membered ring of epoxide is highly strained which can be initiated by either cationic or anionic initiators.

The polymerization of simple cyclic ethers has been generally limited to those of 3, 4, and 5 ring members, although some works have been done with the 7-membered ring. The study of larger sized rings has been carried out mostly with cyclic acetals. The reactivity of different sized cyclic ethers follows the generally expected order. Cyclic ethers of less than 5 members or more than 6 members are relatively easily polymerized. The 5-membered cyclic ethers polymerize with more difficulty.

Substituted 5-membered cyclic ethers are usually unreactive, although some cyclic acetals undergo polymerization. The 6-membered cyclic ethers such as tetrahydropyran **1** and 1,4-dioxane **2** are unreactive under a wide range of reaction conditions, but the 6-membered cyclic acetal, trioxane **3**, undergoes polymerization.

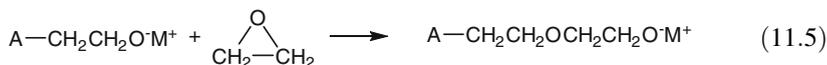
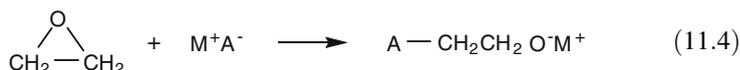


11.3.1 Anionic Polymerization of Epoxides

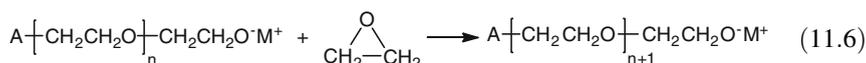
The anionic polymerization of epoxides such as ethylene and propylene oxides can be initiated by strong base such as metal hydroxide, alkoxide, oxide, amine, metal alkyls, and aryls (e.g., sodium naphthalene).

11.3.1.1 Reaction Mechanisms

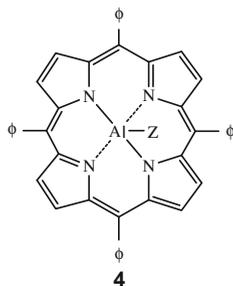
The reaction mechanisms of ethylene oxide initiated by M^+A^- can be shown in the following [2]:



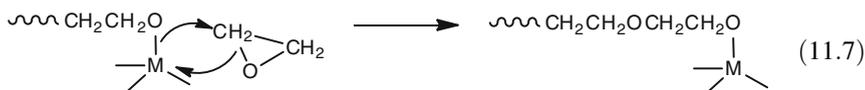
Equation 11.4 is the initiation reaction and Eq. 11.5 is the propagation reaction. The overall reaction can be expressed in the following:



Some initiators polymerize epoxides through an anionic coordination mechanism. Metalloporphyrin derivatives of aluminum and zinc (**4** with $Z = \text{Cl}, \text{OR}, \text{R}, \text{OOCR}, \text{SR}$) are commonly used as initiators.

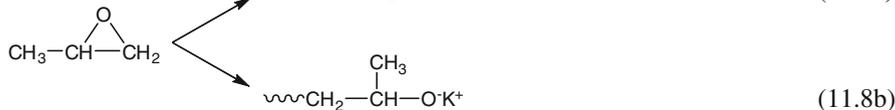
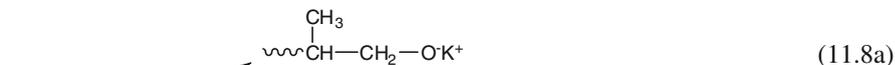


Propagation with the anionic coordination initiator **4**, involves covalent propagation in which the epoxide monomer is inserted into a metal–oxygen bond as shown in Eq. 11.7.



The propagation is a kind of anionic coordination process that involves the formation of an alkoxide anion on metal and then the cleavage of the metal–oxygen bond at the propagation center. The metalloporphyrin-initiated polymerizations are accelerated by sterically hindered Lewis acids. The Lewis acid coordinates with the oxygen of monomer that weakens the C–O bond for a facile nucleophilic attack. The Lewis acid must be sterically hindered to prevent the acid reacting with the propagating center attached to the porphyrin structure. Thus, aluminum ortho-substituted phenolates such as methyl aluminum bis (2,6-di-*t*-butyl-4-methyl phenolate) accelerate the polymerization very high in the order of 10^3 . The aluminum phenolates without ortho substituents and other less sterically hindered Lewis acids are much less effective.

The polymerization of an unsymmetric epoxide, propylene oxide, involves two possible reaction sites (at carbon 1 or carbon 2) on the epoxide ring for the nucleophilic ring-opening reaction. Thus, two different propagating species can be formed as below:



The propagation occurs almost exclusively by attacking at the carbon 2—less sterically hindered site, i.e., an S_N2 attack (Eq. 11.8b), so the polymer has a predominantly head-to-tail structure. As expected, more steric hindered propylene oxide and other substituted epoxides polymerize more slowly than does ethylene

oxide. Most anionic polymerizations of epoxides proceed as living polymerization, so the block copolymer can be formed by successive monomer addition.

11.3.1.2 Kinetics

The expressions for the rate and degree of polymerization of ring-opening polymerization are essentially the same as used to describe living chain polymerizations [2]. For instance, the polymerization rate of sodium methoxide initiated polymerization of ethylene oxide can be expressed in the following:

$$R_p = k_p^{app} [M^*][M] \quad (11.9)$$

where $[M^*]$ is the total concentration of free ion and ion pairs. The effect of reaction media on R_p are similar to the ionic polymerization discussed in Chap. 8. Changes in solvent and counterion affect reaction rates and the observed rate expressions by altering the relative amounts of free ion and ion-pair propagating species, and the extent of association of initiator and propagating species.

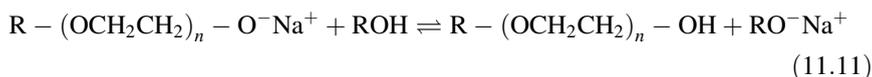
The degree of polymerization can be expressed by

$$\bar{X}_n = \frac{p[M]_0}{[I]_0} \quad (11.10)$$

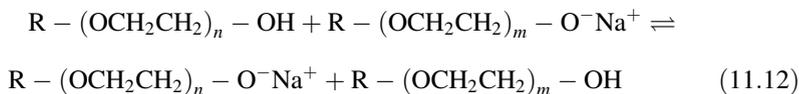
which is the same expressions for living radical and ionic polymerizations, p is the fractional conversion of monomer at a specific time of reaction. The total number of propagating chains per initiator molecule should be counted to determine $[I]_0$. For example, aluminum porphyrin initiator, $[I]_0$ is the concentration of the aluminum porphyrin since there is one propagating chain per aluminum atom. However, for aluminum isopropoxide, $[I]_0$ is three times the concentration of aluminum isopropoxide because each aluminum atom carries three propagating chains that is, each isopropoxide group is an initiator.

11.3.1.3 Exchange Reaction

Exchange side reactions are involved in the polymerization of epoxide which takes place in the presence of protonic substances such as water or alcohol [2]. For example, the polymerization initiated by metal alkoxides and hydroxides requires the presence of water or alcohol to produce a homogeneous system by solubilizing the initiator. In the presence of alcohol, the exchange reaction between a propagating chain and the alcohol can be expressed by



Similar exchange reaction is possible between the newly formed polymeric alcohol in Eq. 11.11 and other propagating chains:



These exchange reactions lower the polymer molecular weight. Thus, the number-average degree of polymerization is reduced by including the concentration of alcohol.

$$\bar{X}_n = \frac{p[M]_0}{[I]_0 + [ROH]_0} \quad (11.13)$$

Each alcohol molecule contributes equally with initiator to determine the size of propagating chains. The exchange reactions look like chain-transfer reactions, but they are not. The obtained polymeric alcohol via exchange is not dead but simply dormant. All alcohol and alkoxide molecules are in dynamic equilibrium in the reaction. Each polymer chain alternates between the active propagating alkoxide and dormant alcohol, so the exchange reaction places an upper limit on the polymer molecular weight. For example, ethylene oxide polymerizations initiated by alkoxides or hydroxides in alcohol, very few reports described the achievement of more than 10,000 molecular weight.

This alcohol exchange side reaction does not occur in the polymerizations initiated by alkoxides and hydroxides in aprotic polar solvents. This limitation also does not observe in the polymerizations initiated by the other initiators such as metal alkyls and aryls and various coordination initiators, since those initiators are soluble in benzene or tetrahydrofuran. Molecular weight as high as 10^5 – 10^6 has been achieved. However, the addition of alcohol or other protonic substance can serve to control polymer molecular weight. Equation 11.13 allows one to calculate the amount of alcohol or other substance required to be added to achieve the desired number-average molecular weight.

If the added alcohol ROH is more acidic than the polymeric alcohol, it will react with the first-formed propagating species as shown in below:



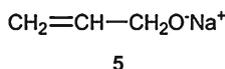
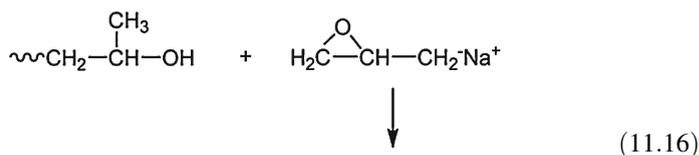
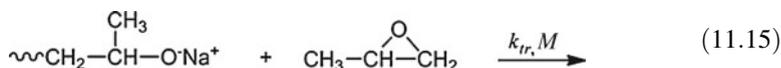
Reinitiation by $\text{RO}^- \text{Na}^+$ is slow, since ROH is relatively acidic. This results in a decreased polymerization rate and a broadening of the polymer molecular weight. The rate of polymerization will not be affected much if the ROH is less acidic than the polymeric alcohol. Exchange will occur in the later stages of reaction with a broadening of the molecular weight distribution. Other protonic compound such as HCl or RCOOH present in the reaction, the inhibition, or retardation will occur because the anion such as Cl^- or RCOO^- does not have nucleophilicity. Reinitiation cannot occur. The polymeric alcohols are no longer dormant but dead. In this case, both polymerization rate and polymer molecular weight decrease along with a broadening of the polymer molecular weight.

The above discussed initiators are not strong enough to open the ring of cyclic ethers larger than three. However, they can be polymerized in the presence of

Lewis acid. For example, the oxetane cannot be polymerized by porphyrin alone, but the reaction proceeds with the addition of Lewis acid. The tetrahydrofuran can be polymerized by the combination of aluminum alkoxide and Lewis acid. The Lewis acid complexes with the ether oxygen that results in weakened carbon-oxygen bond and enhanced nucleophilic attack.

11.3.1.4 Chain Transfer to Monomer

The molecular weight of propylene oxide polymerized by anionic polymerization is rather low (<6,000), because there are large amount of chain transfer to monomer. This involves proton abstraction from the methyl group on the epoxide ring then followed by rapid ring cleavage to form the allyl alkoxide anion **5**, which isomerizes partially to the enolate anion **6**. Species **5** and **6** reinitiate polymerization of propylene oxide. The monomer chain-transfer constant is larger by factors of 10^2 – 10^4 than the usual monomer transfer in ionic chain polymerization [3]. Equations 11.15–11.17 describe the chain-transfer reaction to monomer. Chain transfer to monomer is in the less extent for polymerizations using anionic coordination initiators and higher polymer molecular weight have been obtained [4].

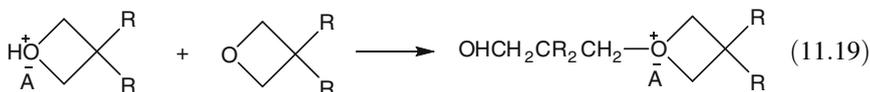


11.3.2 Cationic Polymerization of Epoxides

The epoxide is cationic polymerized through tertiary oxonium ion-propagating species using cationic initiators.

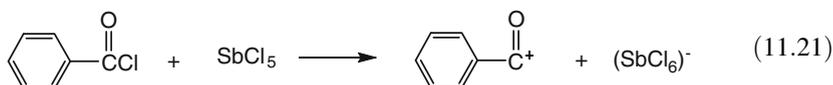
11.3.2.1 Initiation

A variety of cationic initiator systems used in polymerization of alkene can be used for cyclic ether to generate tertiary oxonium ion-propagating species [2]. Strong protonic acids such as trifluoroacetic, fluorosulfonic, and trifluoromethanesulfonic (triflic) acids initiate polymerization by the formation of a secondary oxonium ion initially (Eq. 11.18) which then reacts with a second monomer molecule to form the tertiary oxonium ion (Eq. 11.19) as shown below. This type of initiation is limited by the nucleophilicity of the anion A^- derived from the acid. For acids other than the very strong acids such as fluorosulfonic and triflic acids, the anion is sufficiently nucleophilic to react with monomer, secondary and tertiary oxonium ions. Thus, only very low molecular weight products are produced. The presence of water can also directly disrupt the polymerization, since its nucleophilicity allows it to react with monomer rather than the formation of the propagating oxonium ions.

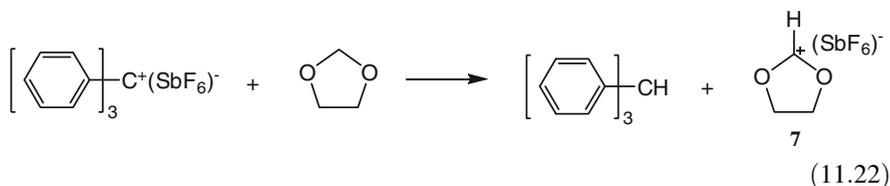


Lewis acids, such as BF_3 and $SbCl_5$ need in conjunction with water or some other protogen, initiate polymerization of cyclic ethers. The initiator and cointiator form an initiator–cointiator complexes [e.g., $BF_3 \cdot H_2O$, $H^+(SbCl_6)^-$] to act as a proton donor. Cationic photopolymerizations are achieved when similar proton donors are formed by the photolysis of diaryliodonium or triarylsulfonium salts.

The use of cationogen such as an alkyl or acyl halide with a Lewis acid generates carbocations and acylium ions, either in situ or as isolate salts, which can initiate polymerization as shown below:



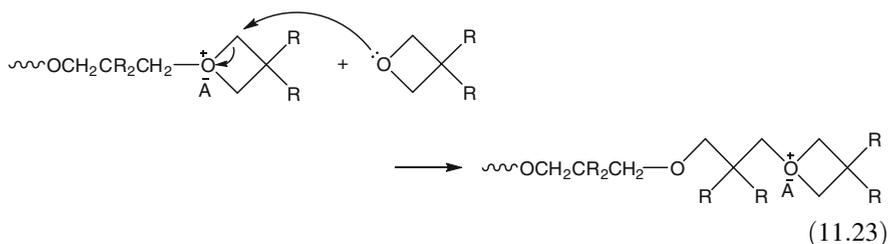
The initiation with some carbocations, especially trityl, does not involve direct addition to monomer. The carbocation abstracts a hydride ion from the alpha carbon of monomer and the newly formed carbocation initiates polymerization. The hydride ion abstraction is very facile with 1,3-dioxolane, so it can be used to produce stable 1,3-dioxolan-2-ylum salts (**7**), then used subsequently as initiators as shown below:



A more reactive cyclic ether such as oxirane or oxetane has been used in combination with Lewis acid, protogen, or cationogen to initiate the polymerization of less reactive cyclic ethers such as tetrahydrofuran. The formation of the secondary and tertiary oxonium ions of the more reactive cyclic ether can act as initiators for polymerization of the less reactive cyclic ether. The reactive cyclic ethers are called promoter which is used in relative small amounts to the cyclic ether being polymerized. The promoter increases the ability of the less reactive cyclic ether to form the tertiary oxonium ion.

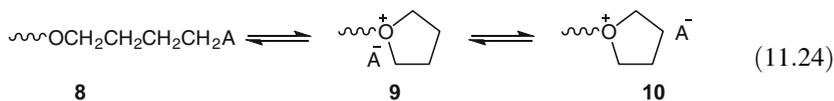
11.3.2.2 Propagation

The propagation of cationic polymerization of cyclic ethers is proceeded by a tertiary oxonium ion, as shown below, where A^- is counter ion [2].



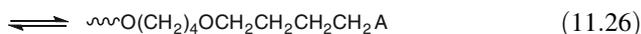
The alpha carbon of the oxonium ion is electron-deficient because of the adjacent positively charged oxygen. Propagation occurs at the alpha carbon of the oxonium by S_N2 reaction. However, S_N1 ring opening has been suggested for a monomer with two alkyl substituents at the alpha-position. Most cationic ring-opening polymerizations are highly regioselective with the formation of head-to-tail structures, only few cases contain head-to-head and tail-to-tail structures are found in some systems.

The cationic ring-opening polymerizations contain three species in equilibrium: Covalent ester **8**, ion pair **9**, and free ion **10** in equilibrium. The relative amounts of each species depend on the monomer, solvent, temperature, and other reaction conditions similar to the cationic polymerization of alkene.



There is usually little or no difference in reactivity between free ions and ion pairs as observed in the cationic chain polymerization. The presence of covalent species has been identified by NMR and other methods, but whether they are reactive or dormant is not very clear. The covalent propagation involves two steps as shown in Eqs. 11.25 and 11.26. The covalent propagation has been confirmed in the polymerization of THF by triflic esters. A mixture of oxonium ion and macroester is obtained when methyl triflate is mixed with THF. Covalent propagation is slower than ionic propagation by a factor of 10^2 – 10^3 or more. In most of cationic polymerization of cyclic ethers, the covalent species are present predominately. In the polymerization of THF by methyl triflate, covalent species account for about 95 % of species in CCl_4 solution. Ionic species increased to 95 % in the very polar solvent CH_3NO_2 . When covalent species are the major species, they are dormant species because of their lower reactivity as compared to ionic species. This slows

down the propagation and also allows sufficient time to complete the initiation. That results in a living polymerization by reversible deactivation of ionic propagation species as described in the living free radical polymerization, and shown below:

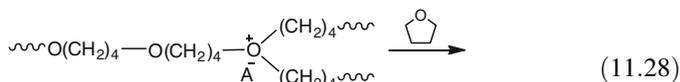
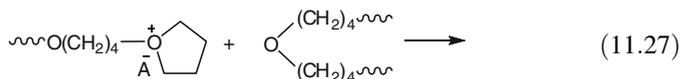


11.3.2.3 Termination and Transfer Processes

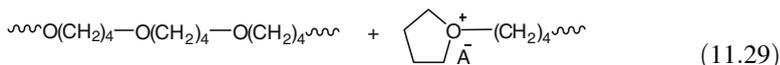
The cationic ring opening polymerization of cyclic ethers can proceed as living polymerization when irreversible chain-transfer reactions are absent [2]. These conditions can be achieved when an appropriate initiator is used to generate reversible covalent and ionic exchange propagating species. The suitable initiators are acylium and 1,3-dioxolan-2-ylum salts containing very stable counterions such as AsF_6^- , PF_6^- , and SbCl_6^- or with very strong acids (fluorosulfonic and trifluoromethane sulfonic acid) or their esters.

The chain transfer to polymer resulted in the propagation chain is terminated but the kinetic chain is unaffected. The reaction is similar to that of cationic polymerization of alkene as discussed in Chap. 8. The reaction involves the propagating chain being nucleophilic attacked by the ether oxygen of polymer chain, the same type of reaction involved in propagation to form the tertiary oxonium ion **11**. Subsequently, nucleophilic attack on **11** by monomer yields **12** and regenerates the propagating species as shown in Eqs. 11.27–11.29. The overall effect is a broadening of the molecular weight distribution. The molecular weight distribution in some reaction system is close to the distribution expected for a step polymerization (about 2). Chain transfer to polymer also occurs as an intramolecular reaction as well intermolecular reaction. The intramolecular reactions (back-biting reaction) results in the formation of cyclic oligomers instead of linear polymer. In other words, the chain ends in **11** are connected to each other. The competition between propagation and chain transfer to polymer depends on many factors. For instance, propagation is favored on steric grounds since attack by monomer is less hindered than attack by the ether oxygen of polymer chain. The relative nucleophilic activities of ether oxygens from monomer and polymer

are important that vary considerably depending on monomer ring size. Toward the end of polymerization, intramolecular (not intermolecular) chain transfer to polymer becomes progressively more important at lower monomer concentrations.

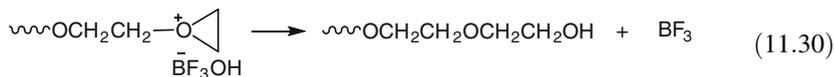


11



12

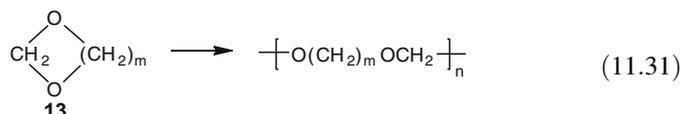
Termination reactions occur by combination of the propagating oxonium ion with either the counterion or an anion derived from the counterion as shown in Eq. 11.30. It is known that the use of protonic acids as initiators is limited by the nucleophilicity of the anion of the acid. Transfer of an anion from the counterion, for example, occurs to varying degrees depending on the stability of the counterion. Thus, counterions such as $(\text{PF}_6)^-$ and $(\text{SbCl}_6)^-$ have little tendency to bring about termination by transfer of a halide ion, while counterions of aluminum and tin have appreciable transfer tendencies; others such as $(\text{BF}_4)^-$ and $(\text{FeCl}_4)^-$ are intermediate in behavior.



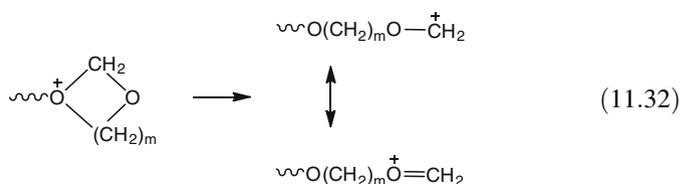
Termination may also occur by chain transfer with the initiator (e.g., alcohol or water) or with chain-transfer agent. The termination has been deliberated to carry out to produce polymers with specific molecular weights or telechelic polymers with specific end groups. For example, hydroxyl and amine end groups are obtained by using water and ammonia as chain-transfer agents; carboxyl-ended telechelics can be obtained by termination with ketene silyl acetal then followed by hydrolysis with base. The insolubility of polymer will also terminate the reaction because the active site is not accessible.

11.3.3 Polymerization of Cyclic Acetals

The cyclic structure of cyclic acetals contains at least one 1,1-dialkoxy grouping [(RO)₂CH₂ or (RO)₂CHR] [2]. They can be easily polymerize by cationic initiation. Various 1,3-dioxocycloalkanes **13** are commonly used such as 1,3-dioxolane ($m = 2$), 1,3-dioxepane ($m = 4$), and 1,3-dioxocane ($m = 5$) are commonly used. The polymers of cyclic acetal can be considered as copolymers of the O(CH₂)_m and OCH₂ units. The 6-membered ring cyclic acetal, 1,3-dioxane ($m = 3$), is too stable to be polymerized. The polymerization reaction of cyclic acetal is shown below:



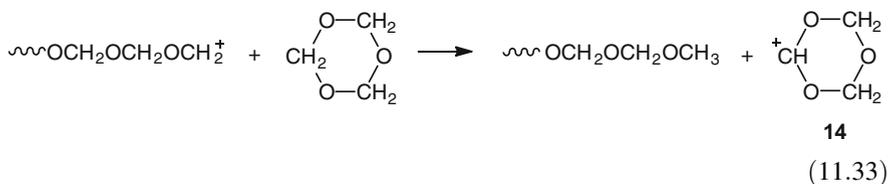
Two kinds of propagating chains were proposed for the reaction mechanisms of cyclic acetal polymerization as shown in Eq. 11.32. Both experimental and computational data indicate that more than 99.9 % of the propagating species are oxonium ions for unsubstituted 1,3-dioxocycloalkanes. Since oxonium ions are 100-fold lower in reactivity toward propagation than oxycarbocations, propagation is predominately carried by oxonium ions [5]. However, the propagation by oxycarbocations is significant for 2-alkyl-1,3-dioxocycloalkanes. The 2-alkyl substituent provides the additional stabilization of positive charge center and the steric hindrance that lead the propagation through oxonium ions.



1,3,5-trioxane, the cyclic trimer of formaldehyde, by cationic ring opening polymerization yields the same polymer, polyoxymethylene, as the cationic polymerization of formaldehyde (Sect. 8.5.2). This polymerization has been carried out in industry using boron trifluoride etherate in the presence of water. The 1,3,5-trioxane polymerizes in spite of containing 6-membered ring, because the polymerization occurs with simultaneous precipitation of crystalline polymer. The heat of crystallization makes the process an exothermic polymerization. The

polymerization of 1,3,5-trioxane proceeds with the formation of polymer-formaldehyde equilibrium. Thus, the reaction involves an induction period for the build-up of the equilibrium concentration of formaldehyde. This induction period also corresponds to a built-up in 1,3,5,7-tetroxocane by the insertion of formaldehyde into 1,3,5-trioxane. Polymer is not formed until both formaldehyde and 1,3,5,7-tetroxocane appear. Formaldehyde (a lesser extent) and 1,3,5,7-tetroxocane decrease the induction period by increasing the rate of propagation to have the crystalline polymer precipitated out. Then, the polymerization is accelerated by converting 1,3,5-trioxane monomer to crystalline polymer directly. The polymerization is usually carried out in bulk or at high monomer concentration to depress cyclic oligomer formation via chain-transfer reaction.

The reaction of transfer and termination of cyclic acetals are similar to the cyclic ether. Chain transfer to polymer (both inter- and intramolecular) is faster in cyclic acetal polymerizations as compared to cyclic ethers because acetal oxygens in the polymer chain are more basic than the corresponding ether oxygens. The trioxane polymerization exhibits an additional termination reaction by chain transfer. The propagating chain with monomer via hydride ionic transfer to form methoxy terminated polymer and carbocation **14**. The **14** can reinitiate the polymerization.



11.3.4 Kinetic Characteristics

The reaction kinetics of cationic ring-opening polymerization depend on its reaction mechanism [2]. Some polymerizations can be described the same as the cationic polymerization of carbon-carbon double bonds. If the polymerizations are with little or no termination, the kinetic expressions of living polymerization can be followed. The cationic ring-opening polymerizations of larger sized ring (≥ 4) take place without terminations and are reversible. The propagation-depropagation equilibrium can be expressed by



The polymerization rate can be expressed by

$$R_p = \frac{-d[M]}{dt} = k_p[M^*][M] - k_{dp}[M^*] \quad (11.35)$$

At the equilibrium, the polymerization rate is zero, then

$$k_p[M]_c = k_{dp} \quad (11.36)$$

where $[M]_c$ is the equilibrium monomer concentration.

Combining Eqs. 11.35 and 11.36, give the polymerization rate as

$$\frac{-d[M]}{dt} = k_p[M^*]([M] - [M]_c) \quad (11.37)$$

Integrate Eq. 11.37 and yield

$$\ln\left(\frac{[M]_0 - [M]_c}{[M] - [M]_c}\right) = k_p[M^*]t \quad (11.38)$$

where $[M]_0$ is the initial monomer concentration.

The equilibrium monomer concentration $[M]_c$ is obtained by direct analysis or by determining the intercept of a plot of polymerization rate versus initial monomer concentration as shown in Fig. 11.1. The polymerization data are then plotted according to Eq. 11.38 as shown in Fig. 11.2. A straight line is obtained and its slope is $k_p[M^*]$. Since $[M^*]$ can be obtained from measurements of the number-average molecular weight of living polymer, one can determine the propagation rate constant. The concentration of the propagating chain is reciprocal to the concentrations of initiator and coinitiator (living polymerization equation). For the case, the concentration of propagating centers changes with time, integration of Eq. 11.38 yields

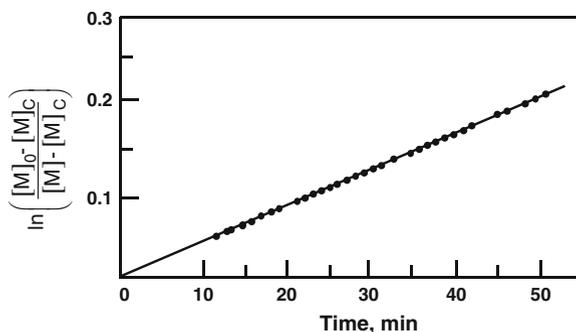
$$\ln\left(\frac{[M]_1 - [M]_c}{[M]_2 - [M]_c}\right) = k_p \int_{t_1}^{t_2} [M^*]t \quad (11.39)$$

where $[M]_1$ and $[M]_2$ are the monomer concentrations at times t_1 and t_2 , respectively.

The quantitative dependence of the degree of polymerization on various reaction parameters has been described by an equilibrium polymerization involving initiation



Fig. 11.2 Disappearance of monomer in the polymerization of tetrahydrofuran by $(C_6H_5)_2CH^+(SbCl_6)^-$ at $25^\circ C$; a plot of Eq. 11.38 [2]



followed by propagation (Eq. 11.34). The degree of polymerization is then given by

$$\bar{X}_n = \frac{[M]_0 - [M]_c}{[I]_0 - [I]_c} \quad (11.41)$$

where $[M]_c$ and $[I]_c$ are the unreacted monomer and initiator concentrations at equilibrium. The polymer molecular weight increases with decreasing $[I]_0$ and increasing $[M]_0$. Larger values of k_p , (the equilibrium constant for Eq. 11.34) and smaller values of K_i yield higher polymer molecular weights by decreasing $[M]_c$ and increasing $[M]_0$, respectively.

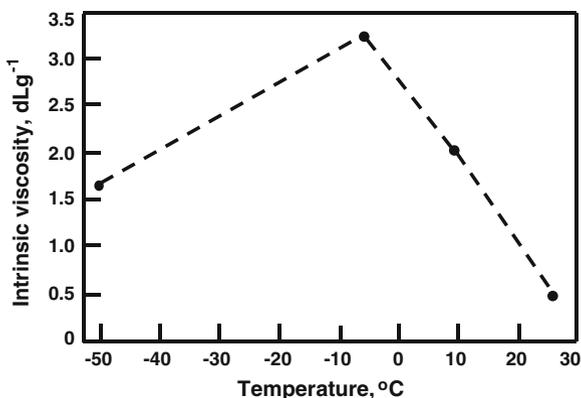
11.3.5 Thermodynamic Characteristics

The temperature effect on the rate of polymerization of cyclic ethers and acetals is dependent on types of monomers, solvents, initiators, and coinitiators [2]. The effect is generally similar to those observed in ionic polymerizations of alkenes. The rate of polymerization is almost always increased with increasing temperature, so the E_{Rp} is positive. Typical values of E_{Rp} are in the range 20–80 kJ mol⁻¹ with most of values in the upper range.

The effect of temperature on the degree of polymerization is more complex [2]. For most polymerization, increasing the temperature decreases the polymer molecular weight because of increased rates of transfer and termination relative to propagation. Table 11.3 shows this effect for the polymerization of oxetane by boron trifluoride through the intramolecular chain transfer to polymer, the formation of cyclic tetramer is increased with increasing temperature. In other polymerizations, the propagating rate is increased with increasing temperature, but the termination and transfer reactions may not be appreciably affected. That results in an increase in polymer molecular weight. Figure 11.3 shows this example observed in the polymerization of tetrahydrofuran. The molecular weight of

Table 11.3 Effect of temperature on polymerization of oxetane [2]

Temperature (°C)	Intrinsic viscosity of polymer (dLg ⁻¹)	Ultimate conversion of monomer (%)	Proportion of tetramer (%)
-80	2.9	95	4
0	2.1	94	10
50	1.3	64	66
100	1.1	62	62

Fig. 11.3 Effect of temperature on polymer molecular weight in the BF₃ polymerization of tetrahydrofuran. [2]

polymer increases initially with increasing temperature up to about -5°C and then subsequently decreases at higher temperatures. The rate of termination is relatively unaffected at the lower temperatures but increases with temperature at the higher temperatures.

The enthalpies and entropies of polymerization of different cyclic ethers and acetals are summarized in Table 11.4. The data of carbonyl monomer, formaldehyde, are included for the purpose of comparison. As compared with the enthalpies and entropies of alkene polymerization (Table 7.16), the ΔH values of 3- and 4-membered ring are comparable to those of alkenes. Both values are appreciably larger than the value of formaldehyde. The conversion of a carbonyl π bond to a σ bond is not as exothermic as the corresponding conversion of an alkene π bond. The ΔH values of the larger sized cyclic monomers are much lower than those of alkenes. The ΔS values of most cyclic monomers are considerably smaller as compared to those of the alkenes and carbonyls. The results indicate that the cyclic monomers, having less degree of freedom to begin with, the loss in disorder on polymerization (ΔS) are less than for noncyclic monomers. Ethylene oxide is an exception because of its highly strained 3-membered ring. The ΔS values for few of the cyclic monomers, tetrahydrofuran, and 3,3-bis(chloromethyl)oxetane, are similar to the lowest values observed for alkene monomers. The ΔH values of different cyclic ethers and acetals follow closely to the order expected from the relative stability of the ring size. The 3- and 4-membered cyclic monomers undergo the most exothermic polymerizations that are decreasing fast with large

Table 11.4 ΔH and ΔS of polymerization of cyclic ethers [2]

Monomer	Ring size	$-\Delta H$ (KJ/mol)	$-\Delta S$ (J/mol K)
Ethylene oxide	3	94.5	174
Oxetane	4	81	–
3,3-Bis(chloromethyl) oxetane	4	84.5	83
Tetrahydrofuran	5	23.4	82.4
1,3-Dioxolane	5	17.6	47.7
4-Methyl-1,3-dioxolane	5	13.4	53.1
Trioxane	6	4.5	18
1,3-Dioxepane	7	15.1	48.1
2-Methyl-1,3-dioxepane	7	8.8	37.2
4-Methyl-1,3-dioxepane	7	9.2	38.9
1,3-Dioxocane	8	18.3	–
1,3,6-Trioxane	8	13.0	21.3
2- <i>n</i> -Butyl-1,3,6-trioxane	8	7.9	16.3
1,3,6,9-Tetraoxacycloundecane	11	8.0	6.2
Formaldehyde	–	31.1	79.2

sized ring. For example, trioxane, the 6-membered ring monomer has a ΔH very close to zero. Due to the steric hindrance, substituents on a ring structure decrease the tendency to polymerize and the ΔH value is lowered. For instance, the ΔH values of the substituted 1,3-dioxolane, 1,3-dioxepane, and 1,3,6-trioxane monomers are lower than that of the corresponding unsubstituted monomers. Substituted oxetanes are an exception to this generalization, the strain effect is overweight the substitution effect.

11.3.6 Commercial Applications of Polymers of Cyclic Ether

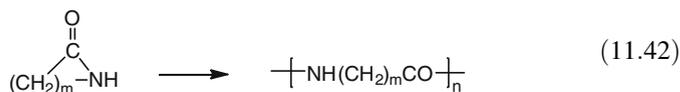
One of the most important industrial applications of polymers of cyclic ether is to make polyether macrodiols for polyurethane industry. They are telechelic polyethers having hydroxy terminal groups. They are synthesized from the polymerizations and copolymerizations of ethylene and propylene oxides as well as polymerization of tetrahydrofuran. The commercial macrodiols in the molecular weight range of 500–6,000 and are used to produce polyurethane and polyester block copolymers including the thermoplastic polyurethane and polyester elastomers. The polyether macrodiols are also referred to as polyether glycols or polyols (trade names: Carbowax, Jeffox, Polyglycol, Polymeg, and Terathane). The medium molecular weight ($\sim 20,000$) of ethylene oxide and propylene oxide polymers and copolymers are used as hydraulic fluids and lubricants, additives in cosmetics, and binders in ceramic and powder metallurgy by taking the advantage of their hydrophilic properties. The high molecular weight (10^5 – 10^6) of ethylene oxide polymers are used in flocculation, denture adhesives, packaging films, thickening agent in paints, and so on.

The copolymers made from epichlorohydrin with ethylene oxide and allyl glycidyl ether are useful elastomers. These materials (trade names: Epichlomer, Herclor, and Hydrin) have good resistance to fuel, oil, ozone, and heat. They also exhibit low temperature flexibility and high permeation resistance toward air and vapors of hydrocarbons and fluorocarbons.

Epoxy resin [6, 7] contains 3-membered oxirane terminal groups that can be ring opening polymerized with either multifunctional base or acid to form cross-linked polymers. They exhibit excellent adhesive strength and chemical resistance, high thermal resistance, and mechanical strength. They have been used extensively in electronic industry as bonding adhesive, electrical insulations for large power equipment, composites for aerospace industry, baking enamels for appliances and cars, and so on. The photo initiated cationic ring opening polymerization of epoxy resin has been utilized in electronics, printing, and coating.

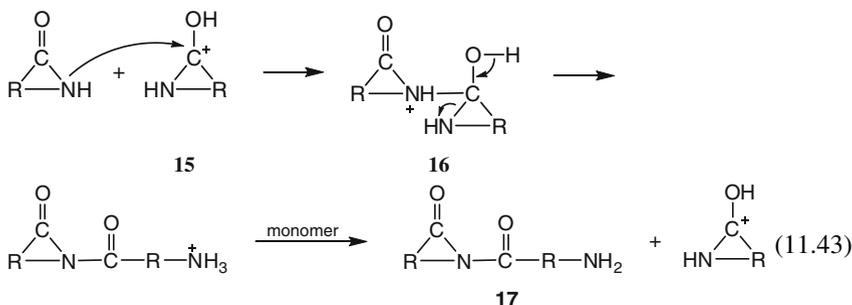
11.4 Lactams

The polymerization of lactams (Eq. 11.42) can be initiated by bases, acids, and water. Initiation by water is the most often used method for polymerization of lactams in industry [2]. Anionic initiation is also used in industry to produce objects directly in molds through bulk polymerization. Cationic initiation is not useful, because the conversions and polymer molecular weights are low. Nylon 6 is produced commercially which accounts for almost one-third of all polyamides. Nylons 11 and 12 are specialty polyamides which are used in the applications requiring high moisture resistance and hydrolytic stability.

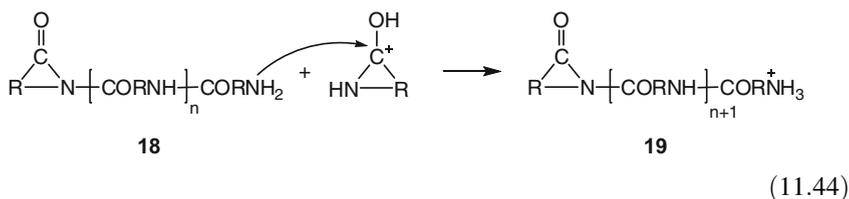


11.4.1 Cationic Polymerization

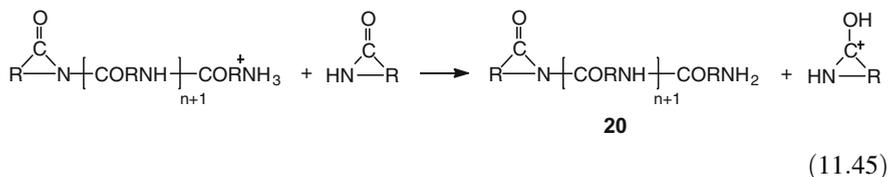
A various of protonic and Lewis acids can initiate the cationic polymerization of lactame. The reaction follows the mechanism of acid-catalyzed nucleophilic substitution reactions of amides as shown in Eq. 11.43. Initiation occurs by nucleophilic attack of monomer on protonated monomer **15** to form an ammonium salt **16** that subsequently undergoes proton exchange with monomer to yield **17** and protonated monomer.



Propagation proceeds in a similar manner as a nucleophilic attack by the primary amine end group of a growing polymer chain **18** on protonated monomer to yield **19** as shown in Eq. 11.44.



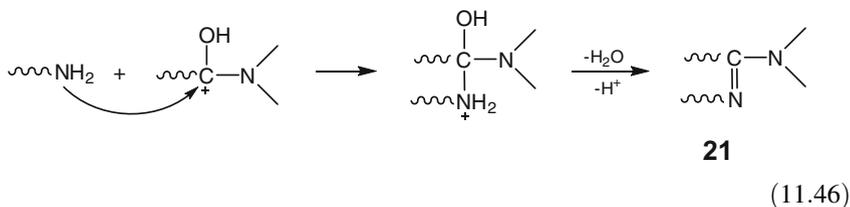
Then **19** undergoes proton exchange with monomer as below:



20 is an AB type of monomer which can be self propagated through the reaction between amine and lactam end groups. Actually, the lactam end groups are protonated prior to reaction. The reaction is similar to Eq. 11.44. Although this reaction is only a minor contribution to the overall conversion of lactam to polymer, it determines the final degree of polymerization. There are intermolecular nucleophilic attack of amine on amide linkages within a polymer chain which result in cyclic oligomer formation. Overall, the molecular weight distribution of the polymer is close to the Flory most probable distribution.

Various side reactions greatly limit the conversions and polymer molecular weights of cationic polymerization of lactams. The highest achievable molecular weights are 10,000–20,000. The most significant side reaction is amidine **21** formation as shown in Eq. 11.46. Propagation of the polymer chain and amidine

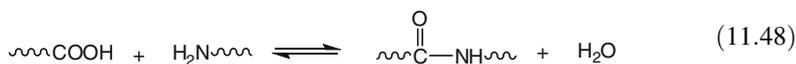
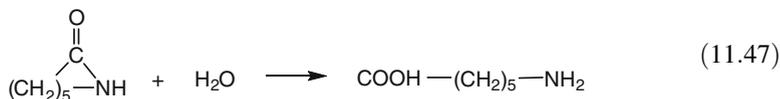
formation proceed through the common intermediate **20** formed by attaching an amine group to the protonated carbonyl of any amide group. The formation of amidine formation decreases the concentration of amine groups in the reaction system which leads to a slower rate of reaction. The water released during the formation of amidine can initiate polymerization but at a slower rate. Furthermore, amidine groups react rapidly with acidic initiators to generate relatively unreactive salts that decreases the rate and degree of polymerization.



Both the hydrolytic and anionic routes described below require that a lactam have a hydrogen on the nitrogen. Therefore, the N-alkylated lactams can only be polymerized by cationic route. The commercial applications for N-alkylated polyamides are limited, because they are low in melting points from the lack of hydrogen bonding.

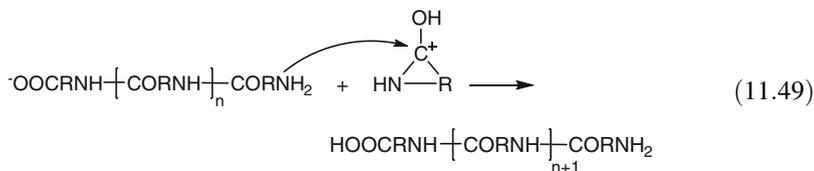
11.4.2 Hydrolytic Polymerization

When water initiator is used to polymerize the lactam, the polymerization is called hydrolytic polymerization [2]. It is a special case of cationic polymerization. This reaction has been used extensively in the production of Nylon 6 from ϵ -caprolactam commercially. Several equilibria are involved in the polymerization. These are hydrolysis of the lactam to ϵ -amino-caproic acid (Eq. 11.47), step polymerization of the amino acid with itself (Eq. 11.48), and the initiation of ring-opening polymerization by the amino acid obtained from Eq. 11.47.



The COOH group of the amino acid protonates the lactam to form cationic active species that can be nucleophilic attacked by amine to initiate the reaction.

The propagation process follows the same manner in the cationic polymerization as shown in Eq. 11.49. The product subsequently protonates lactam and propagation continues.

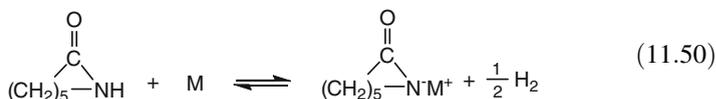


The overall rate of conversion of ring-opening polymerization of ϵ -caprolactam (Eq. 11.47) is higher than the step polymerization of ϵ -amino-caproic acid (Eq. 11.48) by more than an order of magnitude. The self polymerization of ϵ -amino-caproic acid accounts only a few percent of the total polymerization of ϵ -caprolactam. The polymerization is acid catalyzed as shown in Eq. 11.49, amines and water are poor initiators. The polymerization rate in the presence of water is first-order in lactam and second-order in COOH terminated molecule.

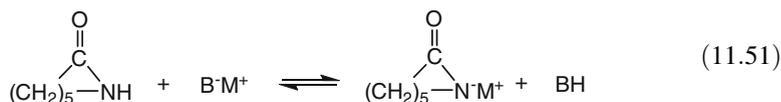
Although the self polymerization of ϵ -amino-caproic acid is only a minor contribution to the overall conversion to polymer, it determines the final degree of the polymerization at equilibrium since the polymer undergoes self-condensation. Usually, most of the water used to initiate polymerization is removed after about 80–90 % conversion in order to drive the reaction to high molecular weight. Thus, the molecular weight polymer can be controlled by the initial amount of water, monomer concentrations, and the addition of small but specific amount of mono-functional acid. The molecular weight distribution is followed the statistic probability distribution proposed by Flory. The amidines formed in hydrolytic polymerization of lactam do not limit the molecular weight, because the carboxyl end groups of growing chain are quite reactive toward amidine groups.

11.4.3 Anionic Polymerization

Strong bases such as alkali metals, metal hydrides, metal amides, metal alkoxides, and organometallic compounds are used to initiate the polymerization of a lactam [2]. The lactam anion is forming using metal as shown in Eq. 11.50.

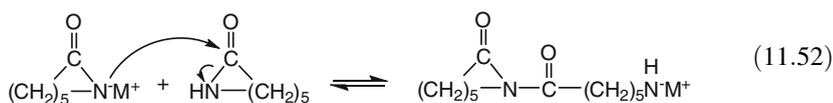


or with a metal derivative as shown in Eq. 11.51.

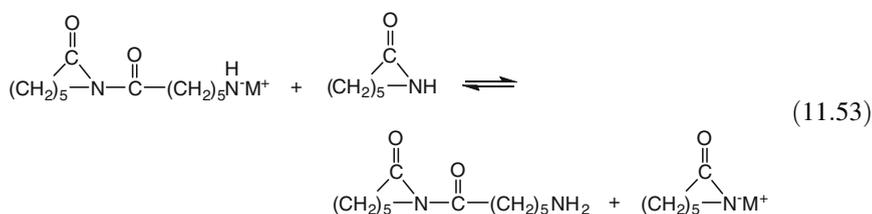


The use of an alkali metal or metal hydride gives a high concentration of lactam anion, but side reactions contaminate the product with amines and water that destroy reactive initiating and propagating species. The use of weaker bases produces a lower concentration of lactam anion unless the equilibrium is pushed to the right of the chemical reaction equation. The use of most bases contaminates the system with the conjugate acid (BH) of the base that also destroys reactive species. The preferred method of initiation consists of generating and purifying the lactam anion first, then the purified anion is used to initiate the polymerization.

The lactam anion reacts with monomer in the second step of the initiation process by a ring-opening transamidation to form primary amine anion as below:



The lactam anion is not stabilized by conjugation with a carbonyl group. It is highly reactive and rapidly abstracts a proton from monomer to form the imide dimer and regenerate the lactam anion.



The lactam polymerization is limited by using strong base alone. There are the induction periods as discussed before and the reaction is only limited to more reactive lactams such as ϵ -caprolactam and 7-heptanolactam. The less reactive lactams such as 2-pyrrolidinone and 2-piperidinone, are much sluggish toward polymerization by strong base alone. The formation of the imide dimer is difficult from these relatively unreactive lactams. The limitations can be overcome by

The polymerization rate is dependent on the concentrations of base and N-acyl lactam, which determine the concentrations of activated monomer and propagating chains, respectively. The degree of polymerization increases with conversion and monomer concentration but decreases with N-acyl lactam concentration. These characteristics are qualitatively similar to those of living polymerization, but lactam polymerization is not living polymerization. Due to the side reactions, the decay of activated monomer and propagating chain concentration is very rapid. The side reactions include hydrogen abstraction from C–H bonds α - to amide carbonyls to form β -ketoimides and β -ketoamides and then subsequently to generate side products through Claisen-type condensation reactions. The latter reaction yields water as a product which decreases the concentrations of activated monomer and N-acyl lactam.

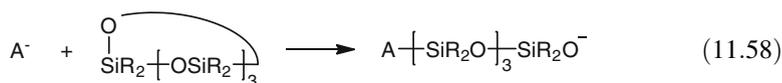
The molecular weight distribution (MWD) is usually broader than the most probable distribution as a result of branching at the later stages of reaction. The polymeric amide anion attacks the lactam end group of another polymer chain to form branching. Further branching will occur through Claisen condensation. The MWD is considerably broader when an N-acyl lactam is not used because the initiation is slow. The high PDI is also due to the polymer chains initiated early, grow for longer times than those initiated later.

11.4.4 Reactivity of Lactam

The polymerization reactivity of lactam depends on ring size and type of initiation. The reactivity of cationic and hydrolytic polymerizations is wider spread than does anionic polymerization due to their lower reactivity. The 6-membered lactam can undergo polymerization in anionic polymerization, whereas most of 6-membered cyclic monomers are unreactive toward ring-opening polymerization. The substituted lactams exhibit lower reactivity than that of unsubstituted lactams due to the steric hindrance effect at the reaction site.

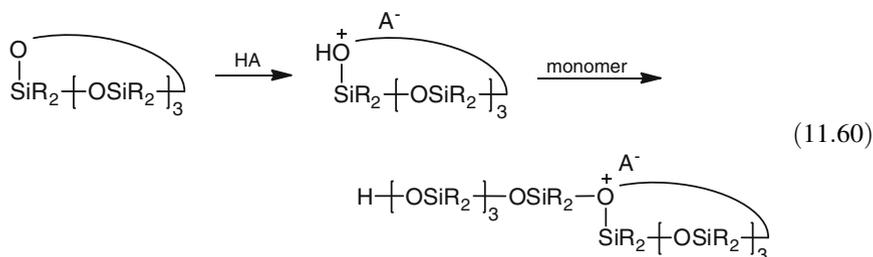
11.5 Cyclosiloxanes

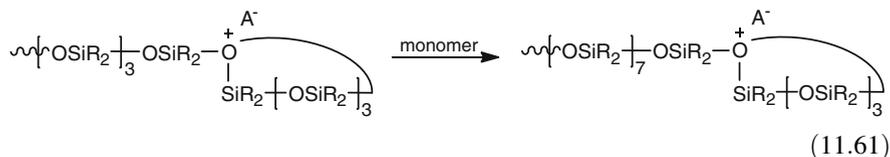
The high molecular weight polysiloxane is synthesized by either cationic or anionic ring opening polymerization of trimer or tetramer of cyclic siloxanes [2]. The anionic polymerization of cyclic siloxanes can be initiated by alkali metal hydroxides, alkyls, and alkoxides, silanolates such as potassium trimethylsilanoate, $(\text{CH}_3)_3\text{SiOK}$, and bases. Both initiation and propagation involve a nucleophilic attack on monomer similar to the anionic polymerization of epoxides as shown below:



It is interesting to note that the enthalpy of polymerization of cyclic siloxanes, ΔH , is nearly zero and entropy ΔS is positive by $6.7 \text{ J mol}^{-1} \text{ K}^{-1}$ [8, 9]. The driving force of this polymerization is the increase in entropy on polymerization. The positive ΔS values for the cyclic siloxane probably result from the high degree of flexibility of the linear polymer chains and the large sized atoms of Si. This flexibility leads to greater degrees of freedom in the linear polymer compared to the cyclic monomer.

The cationic process is more complicated and less understood than the anionic process. Various protonic and Lewis acids are used to initiate cationic polymerization of cyclic siloxanes. Most of the cationic polymerization proceeds by simultaneously step polymerization and ring-opening polymerization. The initiation starts with the protonation of monomer then followed by subsequent reaction with monomer to form the tertiary oxonium. The propagation step follows the similar nucleophilic attack of monomer on the tertiary oxonium ion as shown below:





Polysiloxane (silicone) is a very important commercial polymer. It possess an unusual combination of properties which can sustain a wide temperature range (-100 to 250°C). It exhibits very good low temperature flexibility because its low T_g of -127°C . Silicone is very stable to high temperature, oxidation, and chemical and biological environments because its strong and long Si–O bond and wide Si–O–Si bond as compared with carbon–carbon bond. It has been used widely in our daily life such as sealants, coatings, medical implants, and so on.

11.6 Copolymerization

Considerable ring-opening copolymerizations have been performed either using similar type cyclic monomers (e.g., two kind cyclic ethers or two kind lactams) or using different type cyclic monomers (e.g., cyclic ether with lactam) [2]. The copolymerizations between cyclic monomers with alkene and other compounds are also extensively studied. Ring-opening copolymerization is very complicated. For copolymerization proceeds by the *activated monomer* mechanism such as cyclic ether and lactams, the actual monomers are the activated monomers. The concentration of two activated monomers may be different from the comonomer feed. Calculations of monomer reactivity ratios using the feed composition will introduce errors. Most of ring-opening copolymerizations involve propagation–depropagation equilibria which need to handle the experimental data very carefully to determine the reactivity ratio of each monomer.

The situation is more complicated when there are additional equilibria between polymer and cyclic oligomer or by intermolecular chain transfer to polymer which result in reshuffling of monomer units. It is possible to avoid or minimize the reshuffling equilibria by using mild initiators, low conversions, and highly reactive monomers. However, reactions of near-complete reshuffling of monomer units have been observed in industrial practice. For instance, the anionic copolymerization of octamethyl cyclotetrasiloxane (M_1) and 1,3,5,7-tetramethyl-1,3,3,7-tetravinyl cyclotetrasiloxane (M_2) (feed ratio 9:1) by potassium silanolate at 130°C . The initial copolymer is very rich in M_2 , and this monomer is exhausted early. Further reaction results not only in conversion of M_1 but also redistribution of the M_2 units. Silicon 29 NMR shows the M_2 units to be in blocks at short reaction times but statistically distributed at long reaction times. Similar results have been observed in the cationic copolymerization of methyl glyoxylate and 1,3-dioxolane [2].

Counterion effects similar to those in ionic chain copolymerizations of alkenes are present. Monomer reactivity ratios are also sensitive to solvent and temperature. Some ring-opening polymerizations proceed two different mechanisms, simultaneously. The monomer reactivity ratios for any co-monomer pair are unlikely to be the same for the two different propagations. Any experimentally determined r values are the combination of two different r values.

The selection of adequate initiator is extremely important for copolymerizations between monomers containing different polymerizing functional groups. Basic differences in the propagating centers (oxonium ion, amide anion, carbocation, etc.,) for different types of monomer may exclude some kind of copolymerizations. Even when two different types of monomers have similar propagating centers, they may not have completely compatible two crossover reactions. For example, oxonium ions initiate cyclic amine polymerization, but ammonium ions do not initiate cyclic ether polymerization.

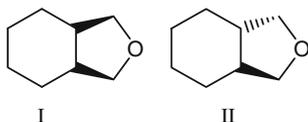
The copolymerization of cyclic ether with acetal discussed previously produces commercial important product (Sect. 11.3.3). Copolymerization is used extensively for silicone polymers. Varying amounts of substituents such as phenyl or vinyl are introduced into the basic poly(dimethyl siloxane) structure to modify properties of the final product. Phenyl groups improve the low-temperature flexibility of silicone polymers by decreasing their low-temperature crystallinity. Their high-temperature performance and miscibility with organic solvents are also improved. Vinyl groups allow more efficient crosslinking by either hydrosilation or peroxides.

A wide range of different block copolymers has been synthesized by using the sequential ring-opening polymerization. These include various copolymers made from two different cyclic monomers containing the same functional group such as two cycloalkenes, cyclic ethers, lactams, lactones, etc. There are very few reports of block copolymers of lactams or cyclic siloxanes produced by sequential addition which may be due to the exchange reactions occurred in the polymerization.

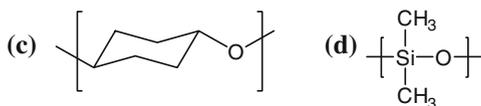
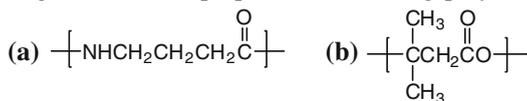
Furthermore, many block copolymers can be obtained by sequential polymerization of a cyclic monomer and an alkene monomer such as the combination of methyl methacrylate with epoxide, polystyrene with ethylene oxide or hexamethyl cyclotrisiloxane, etc. Actually, it is easier to obtain block copolymers from these combinations than to obtain the corresponding statistical copolymers. Synthesis of a statistical copolymer requires that various homo- and cross-propagation rates are similar. Synthesis of a block copolymer by sequential addition requires that the system be living with one or the other and the cross-propagation proceeding at a reasonable rate. Thus, anionic copolymerization of styrene with ethylene oxide does not occur because the addition of alkoxide ion to the carbon-carbon double bond and homopropagation of polystyryl anion are less favored as compared to the addition of polystyryl anion to ethylene oxide and homopropagation of alkoxide anion. However, block copolymerization is easily achieved by adding ethylene oxide to living polystyrene. Triblock polymers can be obtained in some system using appropriate difunctional initiators.

11.7 Problems

1. Discuss why cyclic alkane monomer does not undergo ring-opening polymerization as readily as cyclic ether or cyclic amide from the aspects of thermodynamic and kinetic point of view. Write out the reaction mechanism to explain your answers.
2. Please compare and discuss the polymerizability of following two monomers to undergo ring-opening polymerization.



3. Compare and discuss the differences in rate of polymerization and degree of polymerization among free radical polymerization, step polymerization and ring-opening polymerization.
4. Give structures of cyclic monomers, initiators, and reaction conditions that might be used to prepare the following polymers:



5. Please explain why anionic polymerization of propylene oxide is usually limited to produce a relatively low molecular weight polymer.
6. The molecular weight of ring-opening polymerization of ethylene oxide initiated by sodium methoxide in alcohol is limited to 10,000. Please explain why. How would you change the polymerization condition to obtain the polymer to have molecular weight higher than 50,000?
7. Please explain the following observations:
 - (a) A small amount of epichlorohydrin greatly increases the rate of the polymerization of tetrahydrofuran by BF_3 even though epichlorohydrin is much less basic than tetrahydrofuran.
 - (b) The addition of small amounts of water to the polymerization of oxetane by BF_3 increases the polymerization rate but decreases the degree of polymerization.
8. What are the roles of an acylating agent and activated monomer in the anionic polymerization of lactams?

9. The monomer reactivity ratios of anionic copolymerization (using an acetylated initiator) of ϵ -caprolactam (M_1) and α -pyrrolidinone (M_2) can be calculated using standard copolymerization equation to be $r_1 = 0.75$ and $r_2 = 5.0$ with the conclusion that ϵ -caprolactam is eight times more reactive than α -pyrrolidinone. However, the experimental data show reversed reactivity behavior. Please propose the reaction mechanism to explain the observation [10].
10. Please explain why the epoxy resin usually exhibits better adhesive strength than acrylate resin. The epoxy resin usually made from bisphenol A with epichlorohydrin in presence of base. Please write the chemical reaction involved in this synthesis. Explain why the oxirane ring of epoxy resin can be opened either by acid or base and write out their reaction mechanisms.

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