

IV. RING OPENING POLYMERIZATION

A. Scope of Ring Opening Polymerization

A wide variety of cyclic compounds has been successfully ring-opened to form polymers, for example:

- cyclic ethers
- cyclic esters (lactones)
- cyclic amides (lactams)
- cyclic acetals
- cyclic carbonates
- cyclic siloxanes

The ring opening polymerization process is similar to chain growth addition polymerization in that an initiating species is required to satisfy the valence at the head of the polymer chain, extent of reaction is measured in terms of monomer conversion, and (usually) no small molecule is condensed. The absence of a small molecule condensate means that polymerization cannot be driven; therefore, as in chain growth polymerization of olefins, thermodynamics of the polymerization process becomes an absolute criterion of the extent to which monomer can be converted to polymer. However, the thermodynamics of polymerization of most olefins is quite favorable due to the exothermic nature of converting π bonds into σ bonds. For cyclic compounds, the driving force for polymerization can vary over a much wider range, and one observes a variety of behaviors ranging from completely unreactive to spontaneously polymerizable under all conditions.

In considering the potential polymerizability of a given cyclic compound, both the thermodynamic and kinetics feasibility must be examined. The thermodynamic criterion, being absolute, is the more important. Here, one must compare the relative stabilities of the ring and linear structures. Table ROP-I shows heats of combustion of cycloalkanes per methylene group and the calculated strain per methylene group as a function of the ring size. It may be seen that the smallest rings (3- and 4-membered) have quite high heats of combustion indicative of high bond angle strain. Consequently, polymerization of these rings is highly exothermic and the thermodynamic criterion is very favorable. Angle strain decreases sharply for the 5-membered and vanishes for the 6-membered ring. Angle strain is virtually absent for 6-membered and larger rings because they can assume nonplanar (puckered) conformations. However, conformational strain exists for 5- and 7-11-membered rings, of two basic types. Torsional strain is found in 5- and 7-membered rings arising from eclipsed conformations on adjacent atoms of the ring. Transannular strain is found in 8-11-membered rings arising from repulsive interactions between substituents, which are forced to crowd positions in the interior of the ring.

Table ROP-I: Heats of Combustion and Strains of Cycloalkanes per Methylene Group

Ring Size	Heat of Combustion per Methylene Group (kJ/mole)	Strain per Methylene Group ^a (kJ/mole)
3	697.6	38.6
4	686.7	27.7
5	664.5	5.5
6	659.0	0.0
7	662.8	3.8
8	664.1	5.1
9	664.9	5.9
10	664.1	5.1
11	663.2	4.2
12	660.3	1.3
13	660.7	1.7
14	659.0	0.0
15	659.5	0.5
16	659.5	0.5
17	658.2	-0.8
<i>n</i> -alkane	659.0	0.0

^aCalculated as the heat of combustion per methylene group minus the value (659.0) for the *n*-alkane methylene group.

The data in Table ROP-I suggest that, in general, 6-membered rings are not polymerizable on thermodynamic grounds, and that 5- and 7-membered rings are only marginally so. Table ROP-II give enthalpy, entropy, and free energy changes for the conversion of cycloalkanes to the corresponding linear polymer. Note that polymerization is thermodynamically favored for all but the 6-membered ring.

Table ROP-II: Thermodynamics of Polymerization of Cycloalkanes at 25°C

Ring Size	ΔH_{lc} (kJ/mole)	ΔS_{lc} (J/mole-°C)	ΔG_{lc} (kJ/mole)
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

Table ROP-II also shows that the entropy change for polymerization of these smaller rings is uniformly unfavorable due to the loss of translational freedom of the monomer molecule. Thus, these polymerizations are enthalpy-driven, and they are characterized by a ceiling temperature. As ring size increases, the magnitude of the negative ΔS contribution gets smaller. For several notable systems, the ΔS of polymerization is positive, and one

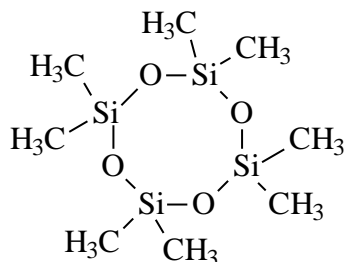
observes an entropy-driven ring-opening polymerization, which is characterized by a floor temperature. Depending on the sign of ΔH , then, four characteristic behaviors are possible, as shown in Table ROP-III.

Table ROP-III: Four Characteristic Thermodynamic Behaviors in Polymerization

ΔH	ΔS	Behavior
-	-	Ceiling temperature
-	+	Always spontaneous toward polymer
+	+	Floor temperature
+	-	Never spontaneous toward polymer

Ceiling temperature behavior is by far the most common and is characteristic of small rings. Floor temperature behavior is relatively rare; two of the best well-known examples are shown in Figure ROP-1.

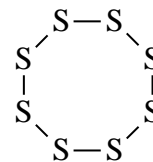
Figure ROP-1



octamethylcyclotetrasiloxane (OMCTS)

$$\Delta H_p \sim 0$$

$$\Delta S_p = 6.7 \text{ J/mole}^\circ\text{K}$$



elemental sulfur

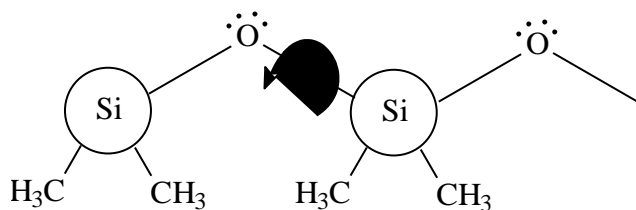
$$\Delta H_p = 13.5 \text{ kJ/mole}$$

$$\Delta S_p = 31 \text{ J/mole}^\circ\text{K}$$

Floor temperature behavior requires a positive ΔS for polymerization, which is very rare. It is usually only observed for large rings, containing large atoms from rows 3 or higher in the Periodic Table, which open to form flexible-chain polymers. Both monomers shown in Figure ROP-1 possess these characteristics. Because sulfur displays a moderately large positive ΔH , it will display a floor temperature. In fact, simple heating of elemental sulfur will produce polysulfide rubber; however, the process is reversible, and the rubber slowly decomposes back to elemental sulfur upon cooling. Depending on the true sign of ΔH , OMCTS may either be spontaneous toward polymer at all temperatures, or if ΔH is slightly positive, may possess a very low floor temperature.

Large rings minimize the loss of translational entropy upon polymerization (the monomer is large to begin with). A polymer with a flexible chain yields an offsetting gain in rotational entropy, due to crankshaft motions that are absent in the ring (Figure ROP -2).

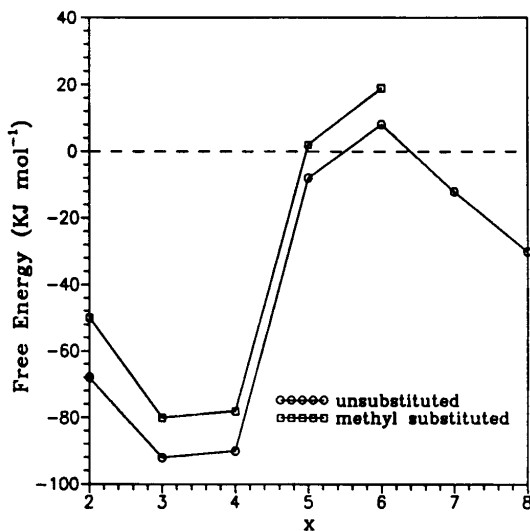
Figure ROP-2



oxygen swivel and large atomic radius of Si facilitate rotation

For all sized rings the presence of substituents decreases thermodynamic feasibility for polymerization, as shown in Figure ROP-3. Interactions between substituents are more severe in the linear polymer than in the cyclic monomer; ΔH is less negative and ΔS is more negative.

Figure ROP-3



The thermodynamics of polymerization may be treated quantitatively using eq IV-1. The ceiling temperature, T_c , is defined as the temperature at which the propagation and depropagation reaction rates are exactly equal at a given monomer concentration, $[M]_c$. Since the propagation/depropagation equilibrium can be established at an infinite number of different temperatures, there are an infinite number of T_c , $[M]_c$ data pairs. (Fig. 3-14 on p. 280 of Odian is helpful in visualizing this relationship).

$$\ln \frac{[M]_c}{[M]^0} = \frac{\Delta H^0}{RT_c} - \frac{\Delta S^0}{R} \quad \text{IV-1}$$

ΔH^0 and ΔS^0 are, respectively, the standard enthalpy and entropy of polymerization. The monomer concentration at the standard state, $[M]^0$, is generally specified to be either the undiluted liquid (bulk monomer) or a 1 M solution. It should be noted that when $[M]^0 = 1$ M, this term often disappears from eq IV-1, without explanation, when this equation is presented in the literature (for example, see eq. 3-178b on p. 280 of Odian). However, its

formal presence in the equations must be borne in mind, especially when the standard state is defined as pure monomer. In this case, $[M]^0$ is generally in the range of 5-12 M, depending on the density and molecular weight of the monomer.

One must also consider the kinetic criterion for polymerization. There must be a kinetic pathway for polymerization and/or depolymerization to occur. For example, the previous tables show that cycloalkanes (other than cyclohexane) should spontaneously polymerize at room temperature; however, such polymerizations have been rarely achieved due to lack of a suitable kinetic pathway. As a further example, OMCTS should spontaneously polymerize to form poly(dimethylsiloxane) at virtually any temperature. However, the reaction is observed to be nearly infinitely slow unless a nucleophile or electrophile is present. In contrast, the sulfur polymerization/depolymerization reaction is truly thermally spontaneous, occurring at reasonable rates in the absence of any catalyst.

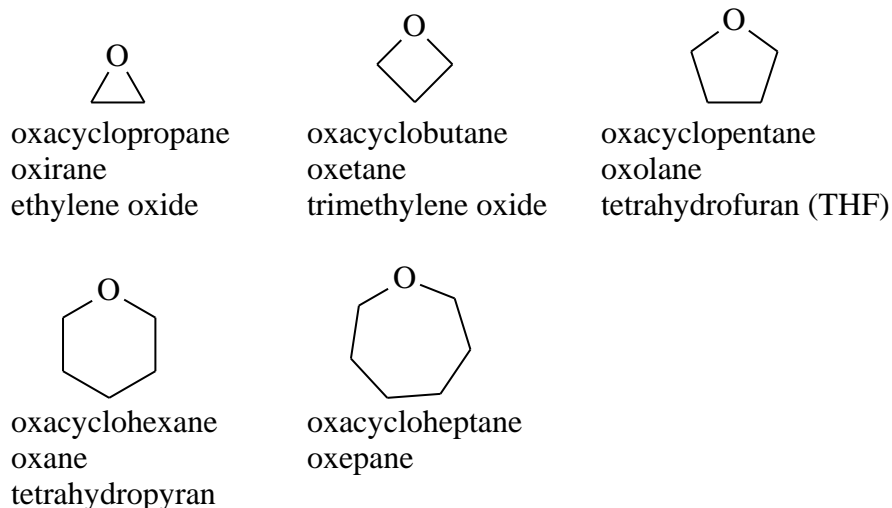
In a related sense, when one considers the availability of cyclic monomers, it turns out that monomers of ring size greater than eight members are unavailable due to kinetic considerations. In other words, the synthetic preparation of a particular monomer, say, a 10-membered ring, might be thermodynamically feasible at a particular temperature, but kinetically impractical due to the difficulty for ring closure.

B. Cyclic ethers

The ether linkage is quite stable, especially toward bases. As a result, cyclic ethers are polymerizable only by cationic initiators (kinetic criterion). The 3-membered ring epoxides are the sole exception; due to high strain, they are polymerizable by either cationic or anionic initiators.

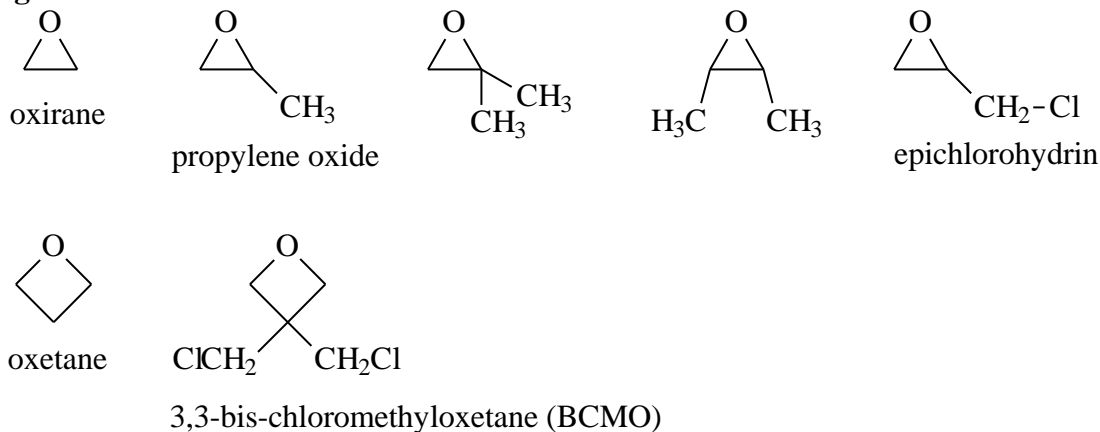
Cyclic ethers are known by a number of different names as shown in Figure ROP-4. In the IUPAC system, they are named simply as oxacycloalkanes. The common names are represented by the oxirane, oxetane, oxolane, etc., series. Other names imply derivatization from other heterocyclic compounds, e.g., tetrahydrofuran (THF).

Figure ROP-4



Three and 4-membered cyclic ethers, because of their high reactivity, will polymerize cationically, even when substituted; all of the monomers in Figure ROP-5 are known to readily polymerize.

Figure ROP-5

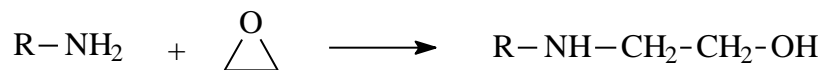


Oxolane (THF) is polymerizable cationically, but its thermodynamics of polymerization are marginal (low ceiling temperature). Substituted oxolanes are generally not polymerizable. Six-membered cyclic ethers such as oxane or 1,4-dioxane are not polymerizable. The 7-membered cyclic ether, oxepane, is polymerizable.

1. Anionic polymerization of epoxides

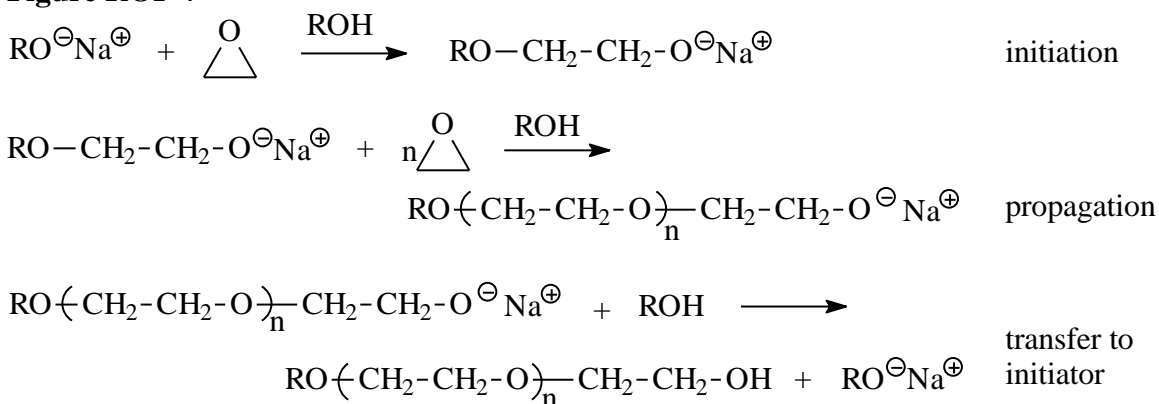
Anionic polymerization of epoxides can be initiated by hydroxides, alkoxides, metal oxides, organometallic compounds, and others. In these cases, the counterion is generally an alkali or other highly electropositive metal ion, and the growing species is highly ionic in nature. Coordination anionic polymerization can also be carried out using initiators derived from less electropositive metals such as aluminum or zinc. In these cases, the growing species is polar covalent. Neutral nucleophiles such as primary amines react readily with epoxides, but the primary addition product, an alcohol, is too weakly nucleophilic to sustain polymerization (Figure ROP-6).

Figure ROP-6



The most important commercial uses for the resulting oligomers and polymers are as polyether soft segments for polyurethanes and as nonionic surfactants. The anionic process is by far the more important commercially. As a typical example, one might initiate ethylene oxide with an alkoxide at 120°C, essentially in the bulk but with a minor amount of the corresponding alcohol used to homogenize the mixture (Figure ROP-7). This reaction would be carried out in an autoclave or similar pressure vessel.

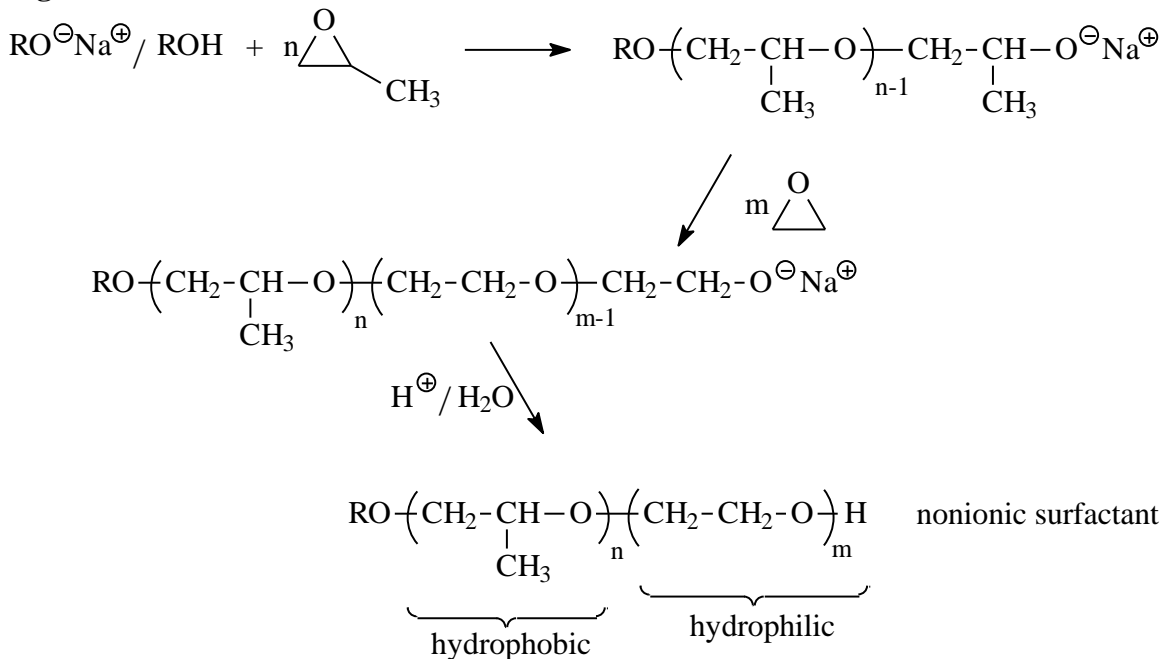
Figure ROP-7



As shown in Figure ROP-7, a typical initiating cocktail consists of alkoxide dissolved in its parent alcohol, i.e., only a portion of the alcohol initiator is ionized. Within such a mixture, the exchange of protons and sodium ions is rapid. Thus, all alcohol moieties participate in the initiation reaction (via the “transfer to initiator” reaction) and create a polymer chain

Anionic polymerizations of 3-membered cyclic ethers display the characteristics of living polymerizations in that there is no termination step in the absence of deliberately added terminating agents. Thus, commercially available block copolymers are synthesized as shown in Figure ROP-8.

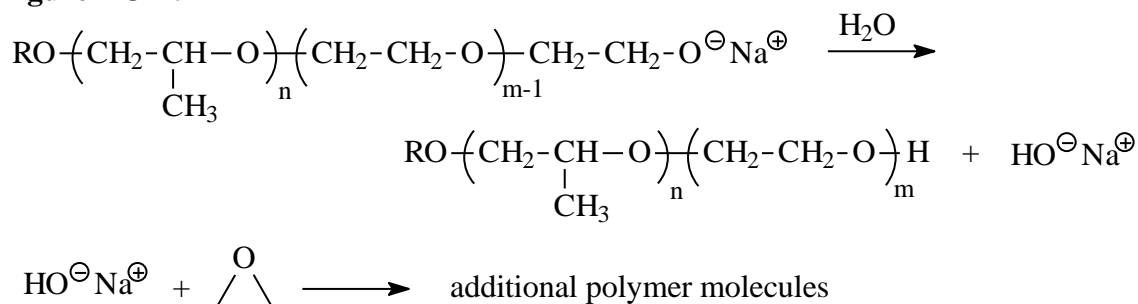
Figure ROP-8



It is important to note that regarding termination of the polymerization (Figure ROP-8, last step), if monomer is still present, water is not sufficiently acidic to quench the

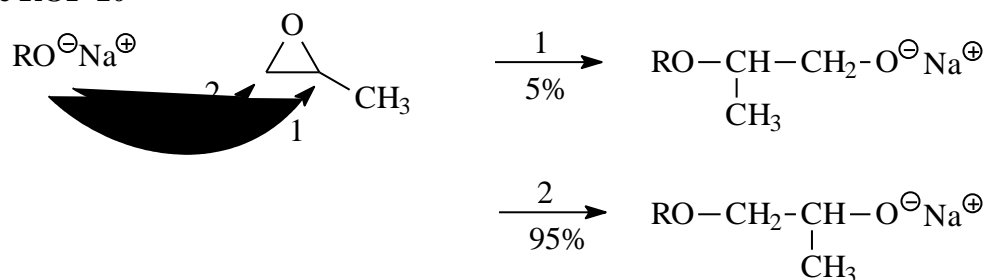
polymerization. The hydroxide ion so-formed can reinitiate polymerization, as shown in Figure ROP-9.

Figure ROP-9



For propylene oxide propagation, nucleophilic attack is overwhelmingly ($\geq 95\%$) at the less hindered methylene carbon (Figure ROP-10). This is undesirable with regard to further utilization of the product. Typically the terminal hydroxyl groups on the polyether are reacted with isocyanate groups during polyurethane synthesis. The secondary hydroxyl groups are less reactive with isocyanates than primary hydroxyl groups, by a factor of about three.

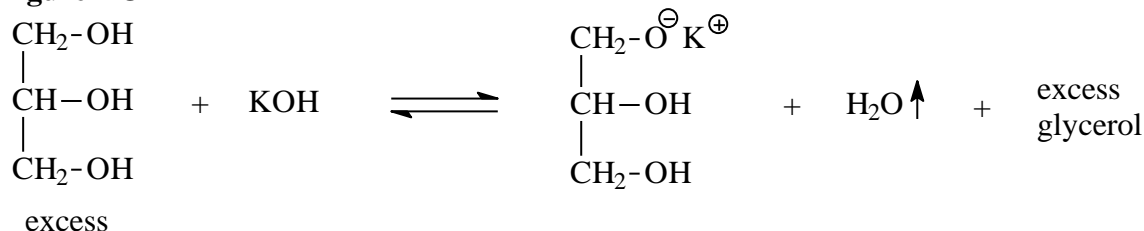
Figure ROP-10



In practice, this problem can be overcome by end-capping the poly(propylene oxide) PPO with one or more ethylene oxide repeat units. This would involve addition of a small amount of ethylene oxide (enough to provide at least one or two repeat units per PPO molecule) after complete consumption of the propylene oxide.

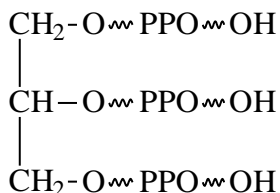
In practice, the reactive alkoxide sites are often formed *in situ*. This method is particularly important when a multifunctional alcohol initiator is used. The method is illustrated in Figure ROP-11 using glycerol as a typical multifunctional initiator.

Figure ROP-11



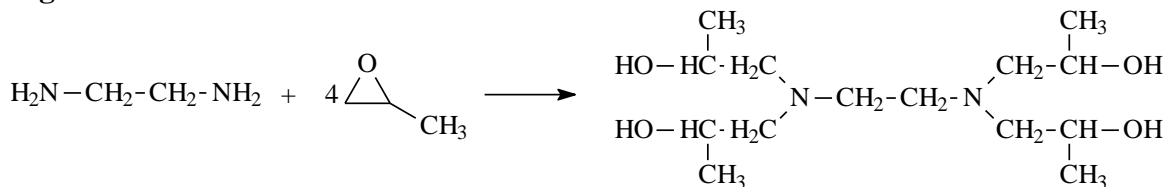
It is critical that the water be removed quantitatively to drive the equilibrium completely to the right (this is necessary to prevent initiation of monofunctional chains by hydroxide ion). After all water is removed, then the monomer can be added. As discussed earlier, all hydroxyl groups participate in polymerization, even though all are not instantaneously ionized. The final polymer product is a three-arm star PPO triol (Figure ROP-12).

Figure ROP-12



Higher functional polyols can be built up from propylene oxide and a polyamine such as ethylene diamine (Figure ROP-13). This synthesis takes advantage of the fact, discussed previously, that amines only add one molecule of epoxide per replaceable hydrogen.

Figure ROP-13



Since the anionic polymerization of epoxides is of a living nature, the number average degree of polymerization will be determined by the stoichiometric ratio of consumed monomer to initiator and should be independent of the amount of basic catalyst. Thus,

$$\bar{X}_n = \frac{[M]_o - [M]}{[I]_o} \quad \text{IV-2}$$

where, $[M]_o$ = initial monomer concentration
 $[M]$ = instantaneous monomer concentration
 $[I]_o$ = initiator concentration

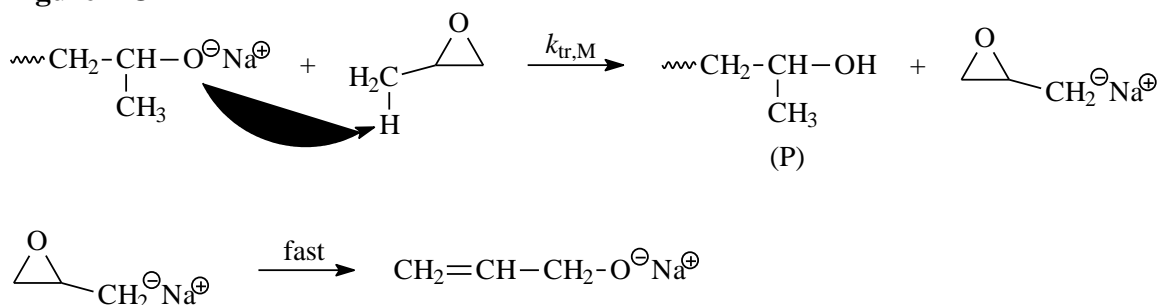
Note that $[I]_o$ indicates the total molar concentration of ethanol, glycerol, ethylene diamine, or whatever active hydrogen-containing compound is being used to initiate the growing chains, regardless of the amount of basic catalyst. For example, if the initiator consisted of 8×10^{-2} M ethanol plus 2×10^{-2} M sodium ethoxide, then $[I]_o = 10^{-1}$ M. If the structural unit from the initiator (i.e., the chemical unit within the polymer that represents the initiator residue) comprises an appreciable fraction of the polymer, then it is customary to include it within the calculation of the degree of polymerization:

$$\bar{X}_n = \frac{[M]_o - [M] + [I]_o}{[I]_o}$$

IV-3

The anionic polymerization of propylene oxide is not perfectly living due to the presence of chain transfer to monomer (there still is no inherent termination step), as shown in Figure-ROP-14.

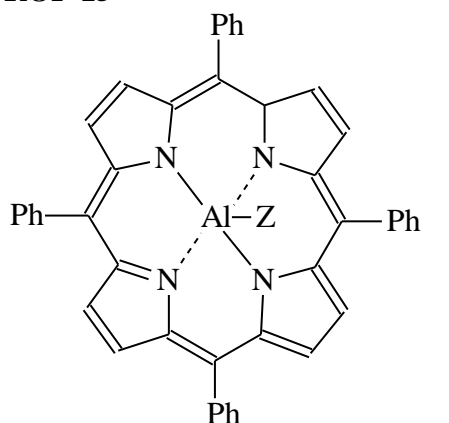
Figure ROP-14



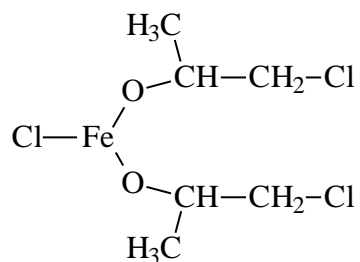
2. Anionic coordination polymerization of epoxides

Polymerization of epoxides can also be carried out using initiators based on metals, such as aluminum and zinc that are considerably less electropositive than the alkali metals. The resulting polymerizations are termed anionic coordination polymerizations. The principle advantage of these initiators is that homogeneous reactions can be obtained without the need of protic solvents such as alcohols; higher molecular weights are therefore theoretically possible. Examples of such initiators are shown in Figure ROP-15.

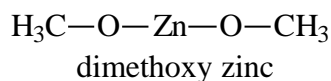
Figure ROP-15



aluminum tetraphenylporphyrin
Z = Cl, OR, R, or OOCR



ferric chloride-propylene oxide
adduct (Pruitt-Baggett initiator)



Propagation in these systems is believed to be a concerted process involving insertion of monomer into the polar covalent metal-oxygen bond, as shown in Figure ROP-16.

PSC 301
Problem Set 9

1. Name and describe the nature of the three types of strain found within cyclic compounds.
2. What structural features are typically found within cyclic compounds that display floor temperature behavior?
3. What mole ratio of ethylene oxide (MW = 44.1 g/mol) to sodium ethoxide/ethanol (MW of ethanol = 46.1 g/mol) would be needed to produce poly(ethylene oxide) with $M_n = 2,000$ g/mole? **ANSWER = 44.3**
4. For the polymerization-depolymerization equilibrium of any monomer that displays a ceiling temperature, the following relationship holds:

$$\ln \frac{[M]_c}{[M]^0} = \frac{\Delta H^\circ}{RT_c} - \frac{\Delta S^\circ}{R}$$

For THF, $\Delta H^\circ = -23.4$ kJ/mole and $\Delta S^\circ = -82.4$ J/mole-K, with standard state monomer concentration specified as 1 M. What is the maximum conversion possible for THF polymerization conducted in the bulk at 50°C (323 K)? **ANSWER: 68.2%**

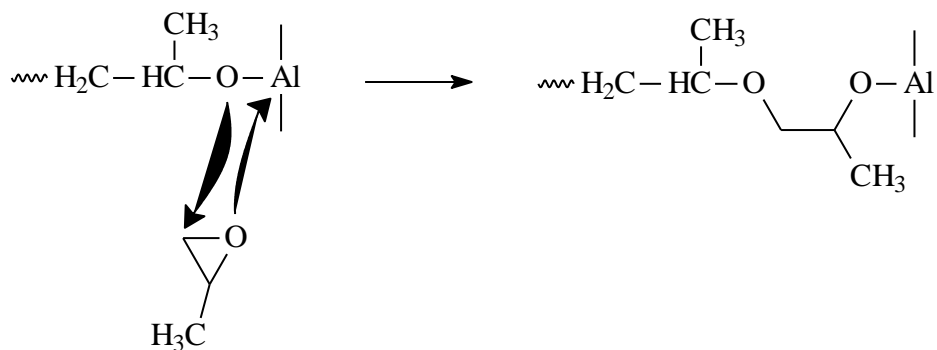
$R = 8.31$ J/mole-K

density of THF @ 50°C = 0.75 g/mL

molecular weight (MW) of THF = 72.1 g/mol

5. Show the sequence of chemical reactions one would use to produce a propylene oxide (MW = 58 g/mol) -based triol of $M_n = 1,700$ g/mole using 1,1,1-trimethylolpropane (MW = 134 g/mol) as initiator and KOH as catalyst. Please calculate the required molar ratio of monomer to initiator, and describe the preferred order of introduction of the reagents and any other considerations necessary for successful bulk polymerization. (Assume essentially complete monomer conversion and that chain transfer is negligible.) **ANSWER: Molar ratio = 27/1 (moles propylene oxide/moles trimethylolpropane).**

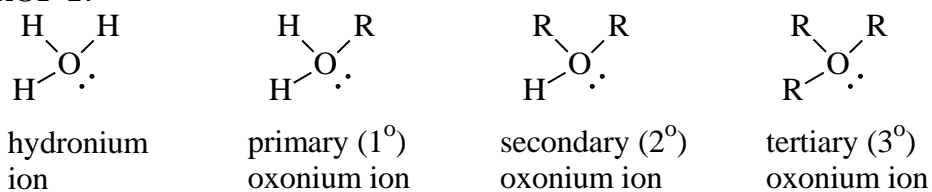
Figure ROP-16



3. Cationic polymerization of cyclic ethers

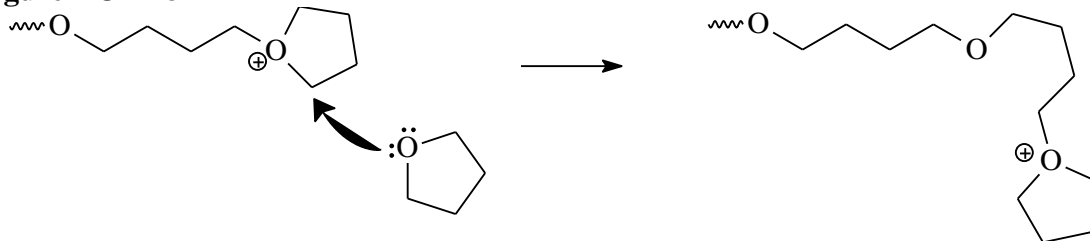
Propagation in the cationic polymerization of cyclic ethers proceeds through a reactive tertiary oxonium ion chain end. The various types of oxonium ions are classified in Figure ROP-17.

Figure ROP-17



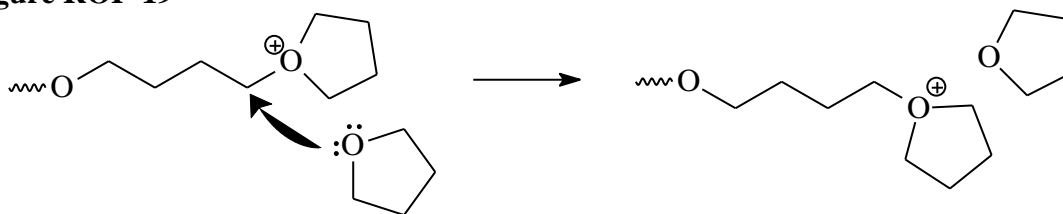
The propagation reaction mechanism is demonstrated in Figure ROP-18 for the case of THF propagation.

Figure ROP-18



For almost all cyclic ethers, the propagation reaction is S_N2 , as shown. Carbons that are α to a positively charged oxygen atom are electrophilic and susceptible to nucleophilic attack by monomer. Attack at the acyclic α -carbon results in no net consumption of monomer and simply represents an equilibrium exchange reaction (Figure ROP-19).

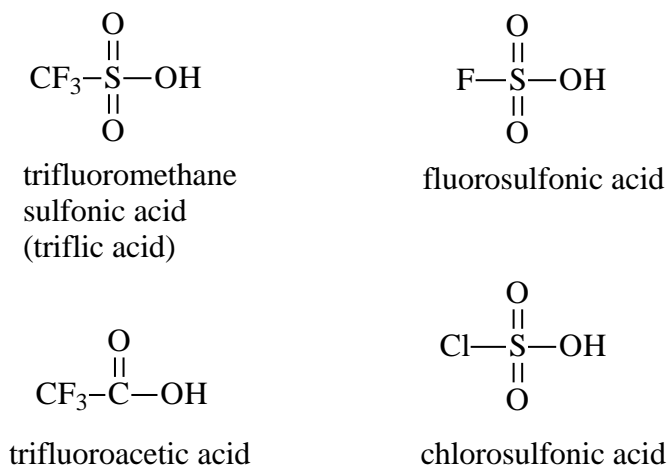
Figure ROP-19



a. Initiation

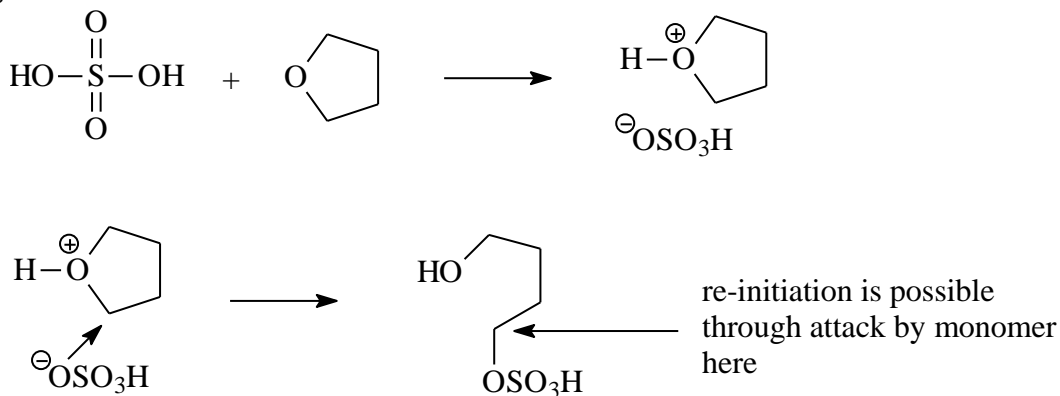
Protonic Acids. Only very strong acids, which result in non-nucleophilic counterions are capable of producing high molecular weight polymers. Examples of such strong acids are shown in Figure ROP-20.

Figure ROP-20



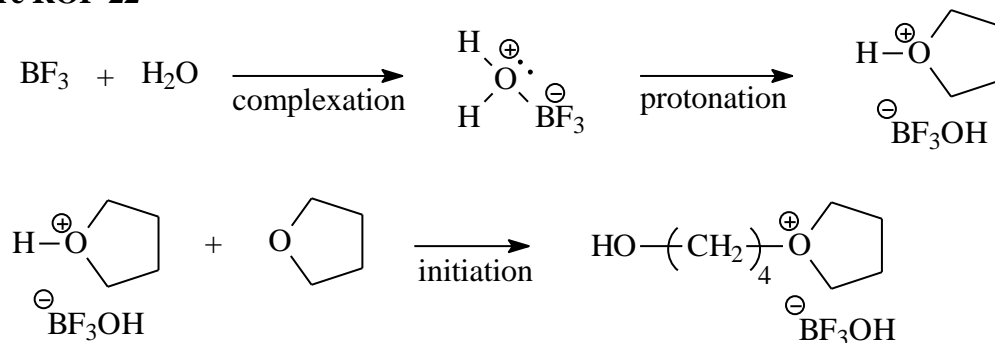
Weaker acids, such as sulfuric acid, are not very effective for initiating and sustaining the ring-opening process because the counterion is too nucleophilic. For cyclic ether polymerization, the counterion competes with the monomer for attack at the α -carbon of the growing chain. In Figure ROP-21, the first step shown is common to all protonic acids initiators: protonation of the cyclic ether to produce a 2° oxonium ion. However, in the second step, bisulfate ion attacks the α -carbon before monomer has a chance, and collapse with the gegenion (i.e., termination) results. Re-initiation is possible through the route indicated, so sulfuric acid is able to slowly produce oligomers. As acid strength rises, the rate of collapse relative to propagation goes down, and the ease of re-initiation goes up (termination becomes rapidly reversible (quasiliving polymerization conditions)).

Figure ROP-21



Lewis Acids. Anions of low nucleophilicity are most readily formed by complexing Lewis acids with a suitable protogen or cationogen (Figure ROP-22).

Figure ROP-22

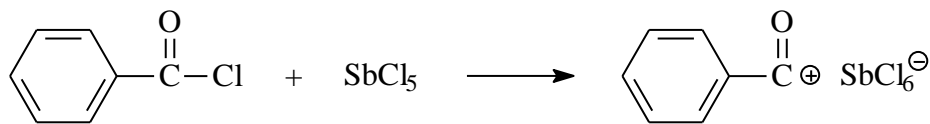


The reaction sequence in Figure ROP-22 illustrates a general principle. Initiation is often a sequence of several reactions and is complete only after the general propagating species has been produced.

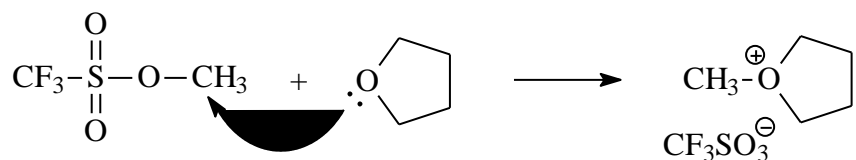
Carbenium Ions. Lewis acids in conjunction with cationogens (as mentioned above) can be used to produce free carbenium ions *in situ* (Figure ROP-23, Reaction 1), or alkyl esters or anhydrides of strong acids can be used to directly transfer a positive alkyl species to monomer (Figure ROP-23, Reaction 2) to form a tertiary oxonium ion.

Figure ROP-23

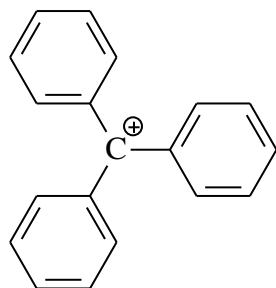
Reaction 1



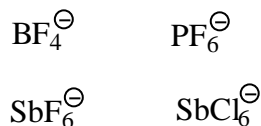
Reaction 2



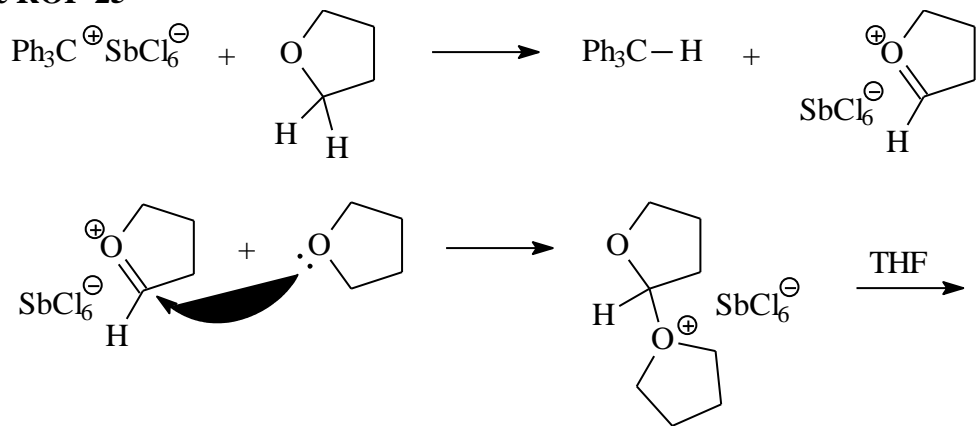
In addition, certain inherently stable carbenium ions such as triphenylmethyl (trityl) carbocation (Figure ROP-24) can be isolated as crystalline salts (with suitably stable gegenion) and can be used as shelf-stable initiators.

Figure ROP-24

with a stable anion taken from the following group:

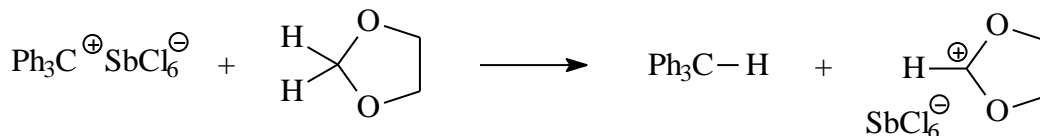


Initiation by some carbocations, especially trityl, involves hydride abstraction from monomer to form an oxy-carbenium ion, which is the true initiator. This sequence is shown in Figure ROP-25 using THF as a model monomer.

Figure ROP-25

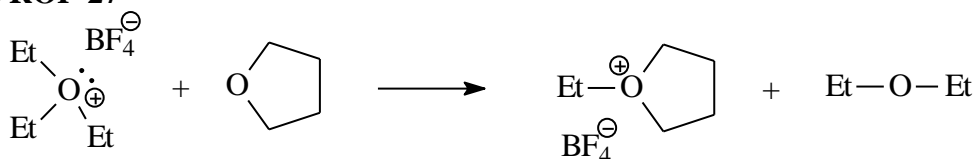
This hydride abstraction reaction is so facile with 1,3-dioxolane that it can be used to create a pre-formed oxy-carbenium ion initiator (Figure ROP-26).

Figure ROP-26



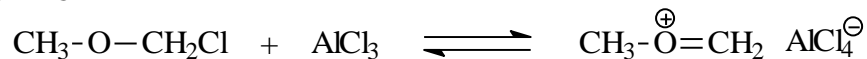
Oxonium Ions. Preformed trialkyl oxonium salts such as triethyloxonium tetrafluoroborate are efficient initiators or cyclic ether polymerizations; however, the initiation process involves generation of diethyl ether, which may act as a chain transfer agent (Figure ROP-27).

Figure ROP-27



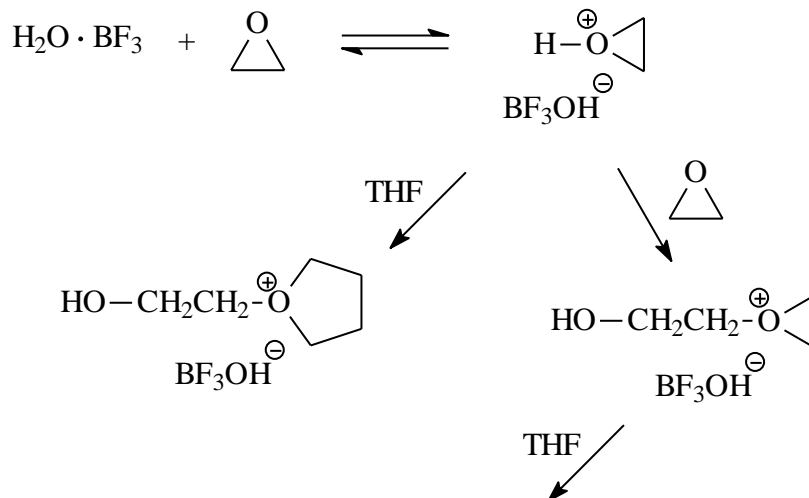
Oxonium ions can also be generated *in situ*. Particularly useful are the reactions of α -chloro ethers with Lewis acids (Figure ROP-28).

Figure ROP-28



Promoted Initiation. Since THF and other cyclic ethers of ring sizes greater than 4 are relatively unreactive compared to the epoxides, it has been found convenient in some cases to accelerate initiation by addition to the higher cyclic ether of a small amount of epoxide. In this usage the epoxide is termed a “promoter.” For most epoxides, in the presence of a Lewis acid and a protogen, the reaction is believed to proceed as shown in Figure ROP-29.

Figure ROP-29

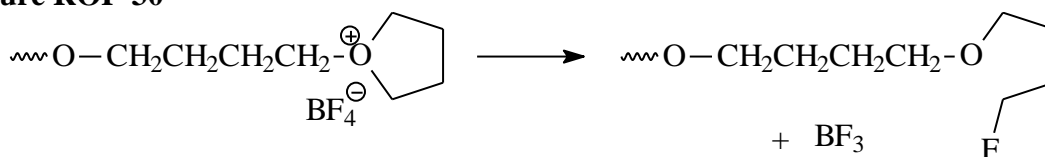


Whether the first-formed 2° oxonium ion reacts immediately with THF or first adds one or more additional epoxide units will depend on the relative amount of epoxide used. Epichlorohydrin is a very efficient and convenient promoter (liquid at room temperature) and was frequently used in the early literature to promote THF polymerization.

b. Termination and Transfer Reactions

Termination. Under certain conditions, especially when THF is the monomer, cationic polymerizations of cyclic ethers are living and characterized by narrow molecular weight distributions of the product polymer. Proper selection of the negative counterion is critical so that termination can be avoided altogether or at least made to be reversible. For example, when the counterion is a metal halide derived from a Lewis acid, termination is characteristically by transfer of a halide ion to the chain end. As shown in Figure ROP-30, this reaction becomes important with BF_4^- counterion at 25°C; the resulting primary fluoride chain end is not easily re-ionized (termination is absolute).

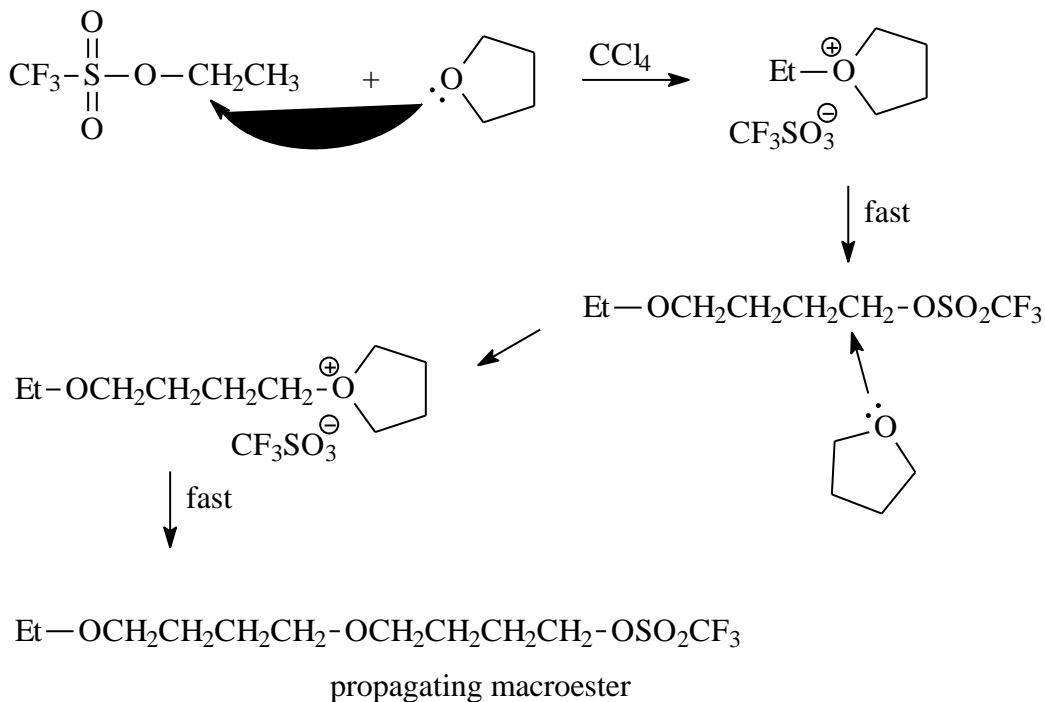
Figure ROP-30



The termination reaction above can be greatly reduced if a more non-nucleophilic counterion is chosen, for example, from the following group: AsF_6^- , PF_6^- , SbF_6^- , or SbCl_6^- .

For polymerizations initiated by strong protic acids or their esters, termination may often be reversible (quasiliving conditions) and one obtains a propagating macroester polymerization (Figure ROP-31). This process is particularly likely to occur in a non-polar medium, which promotes collapse with the gegenion.

Figure ROP-31



Chain Transfer. A number of different chain transfer reactions can occur in cyclic ether cationic polymerization. Some depress the number average molecular weight; others such as chain transfer to polymer, do not. Intermolecular and intramolecular chain transfer to polymer are shown in Figures ROP-32 and ROP-33, respectively. The latter is often referred to as backbiting.

Figure ROP-32

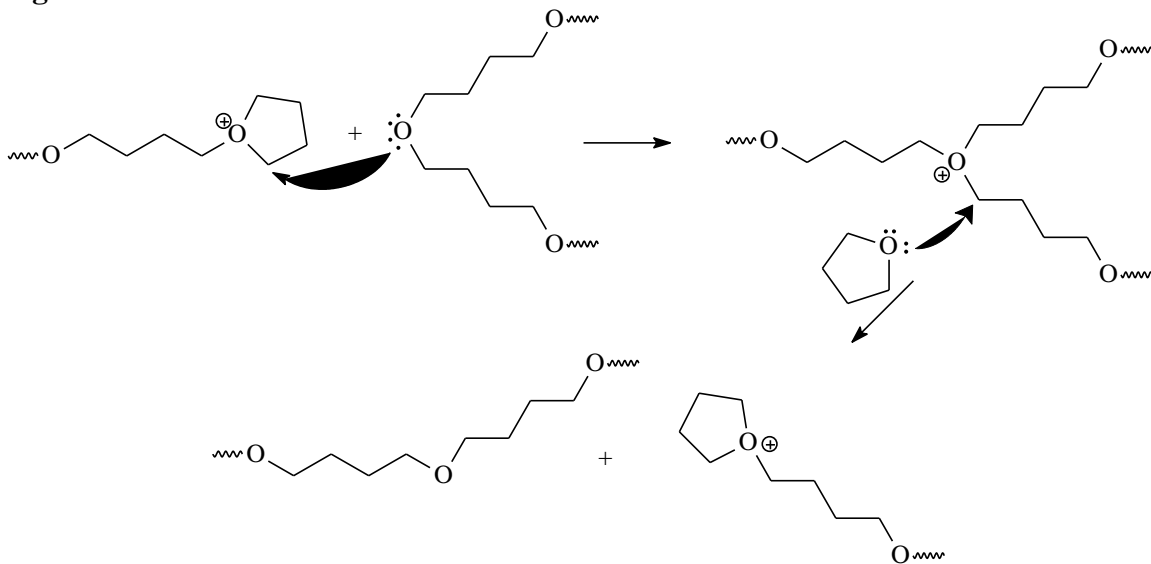
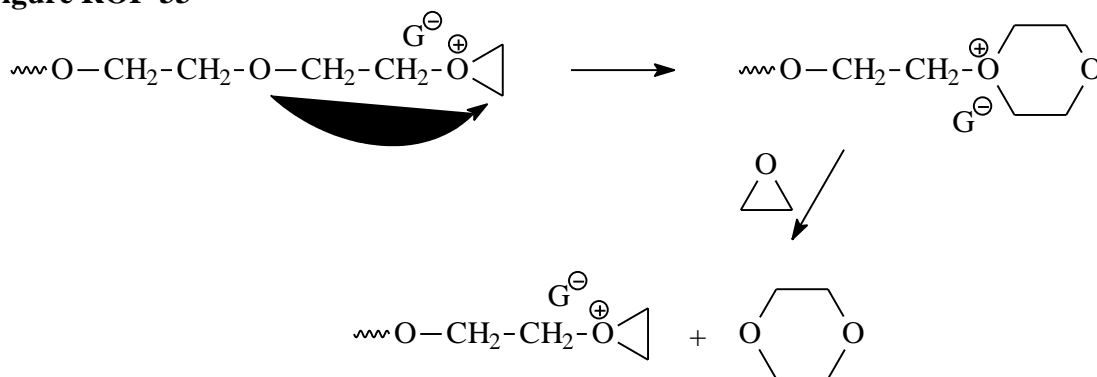
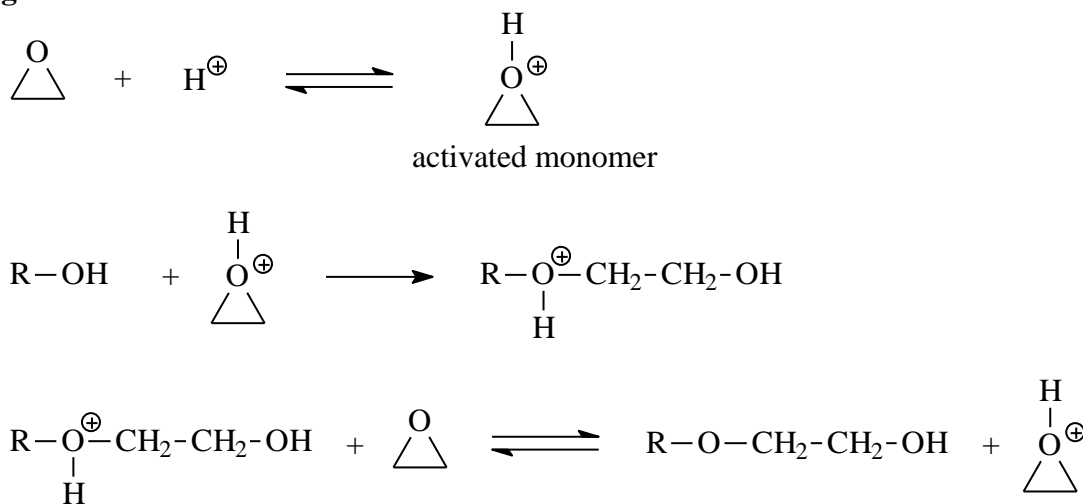


Figure ROP-33



Nucleophilicity of monomer relative to the polymer chain ether is lowest for the three-membered cyclic ether. In many cases, 1,4-dioxane (cyclic dimer) is the major product of cationic polymerization of oxirane. Recently, however, conditions have been defined whereby polymerization can be carried out using an activated monomer (AM) mechanism. This has the advantage of suppressing cyclic oligomer formation. The AM mechanism is caused to occur by slow monomer addition (starvation conditions) to a mixture of acid catalyst (either Bronsted or Lewis type) and alcohol initiator (Figure ROP-34). The key to maintaining AM conditions is the use of a relatively large concentration of alcohol and a low concentration of monomer. This has the technological drawback of severely limiting the molecular weight of the target polymer. The AM technique has been successfully demonstrated for propylene oxide and epichlorohydrin.

Figure ROP-34



Chain transfer is also known to occur with acyclic ethers (Figure ROP-35) and active hydrogen-containing compounds (Figure ROP-36).

Figure ROP-35

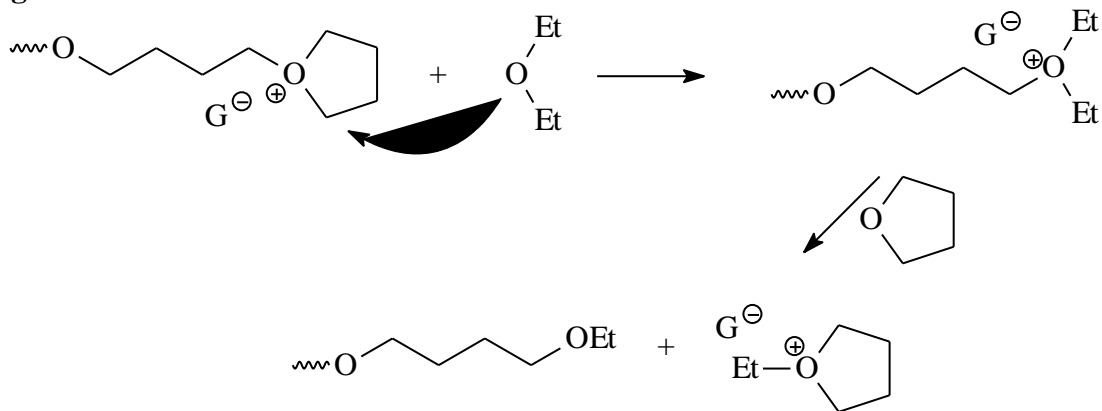
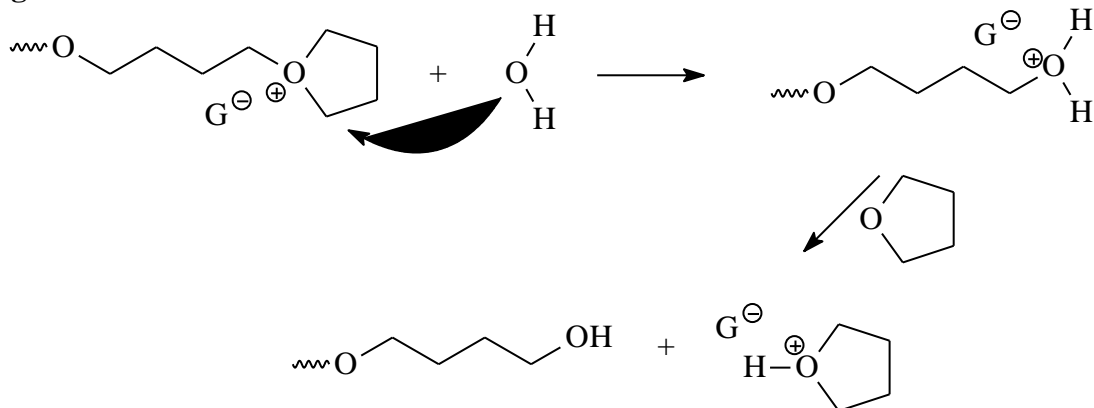


Figure ROP-36

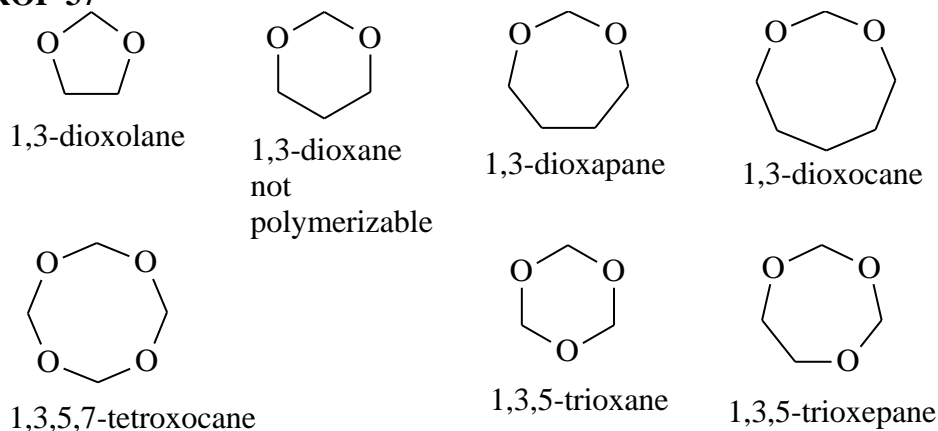


Depropagation. THF forms low polydispersity polymers only when initiation is fast, and when conversion and polymerization time are kept low.

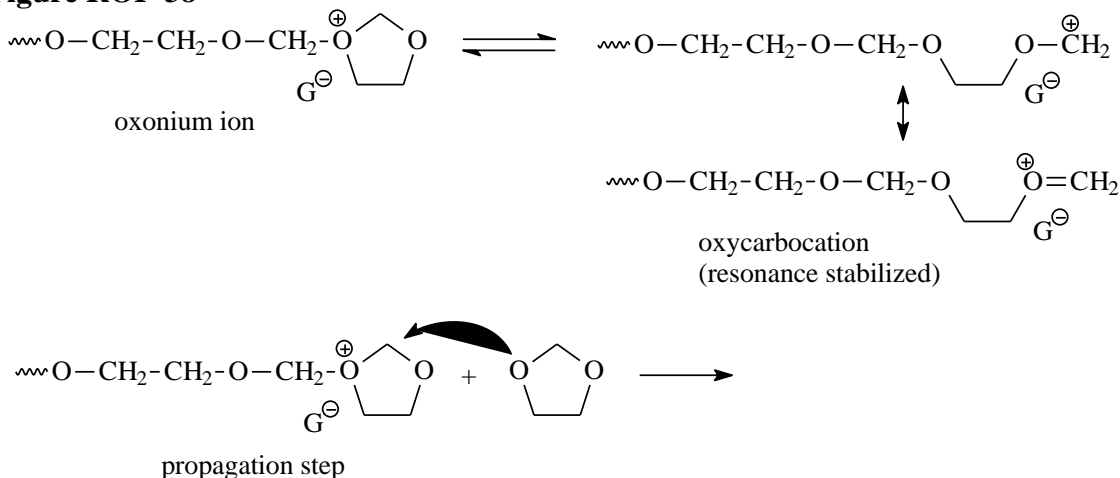
The importance of depropagation at moderate temperatures is related to the marginally favorable thermodynamic parameters for THF: $\Delta H^{\circ} = -23.4$ kJ/mole and $\Delta S^{\circ} = -82.4$ J/mole-K. For this reason, THF polymerizations are generally carried out at ambient temperatures or below (0 - 35°C) and in the bulk or concentrated solution.

4. Cationic Polymerization of Cyclic Acetals

Cyclic acetals are closely related to cyclic ethers and are polymerizable only by cationic initiators. The commonly encountered cyclic acetals are shown in Figure ROP-37; they are characterized by the presence of at least one $-\text{OCH}_2\text{O}-$ or $-\text{OCHRO}-$ linkage within the ring. Of the various 1,3-dioxacycloalkanes, only the six-membered ring is not polymerizable.

Figure ROP-37

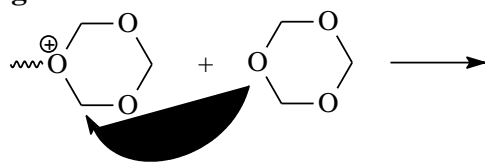
The active species in cyclic acetal polymerizations are believed to be oxonium ions, similar to those found in cyclic ether polymerizations. However, there is strong evidence suggesting that the oxonium ions are in equilibrium with a smaller concentration of open-chain oxycarbocations (Figure ROP-38).

Figure ROP-38

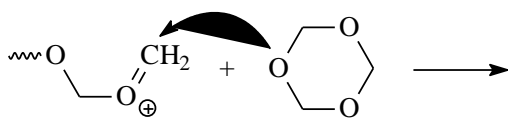
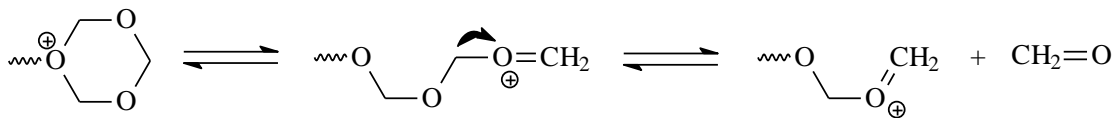
Experimental data and theoretical calculations are in agreement that more than 99.9% of the propagating species are oxonium ions for unsubstituted 1,3-dioxacycloalkanes. Since the oxycarbocation is at most only 100 times higher in reactivity, propagation is predominantly (10 to 1) carried by the oxonium ion. For 2-alkyl-1,3-dioxacycloalkanes, however, propagation is believed to occur mostly through the oxycarbocation.

Evidence for the existence of oxycarbocations is provided by the observation of complex equilibria among monomer, polymer, formaldehyde, and smaller and larger cyclics. For example, in polymerization of 1,3,5-trioxane, an induction period persists until an equilibrium concentration of formaldehyde has been formed; then polymerization proceeds (Figure ROP-39).

Figure ROP-39



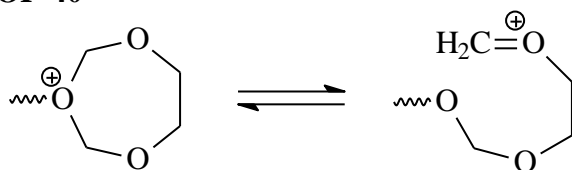
normal oxonium ion propagation



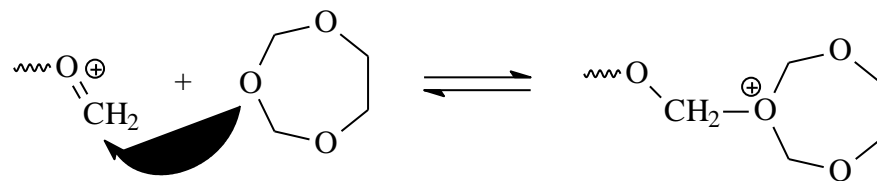
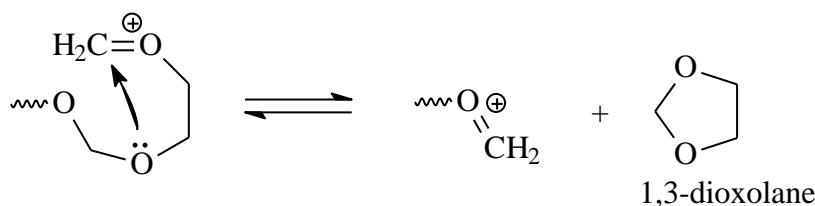
resume propagation

Figure ROP-40 shows the formation of an equilibrium concentration of 1,3-dioxolane (smaller cyclic) during polymerization of 1,3,5-trioxepane.

Figure ROP-40

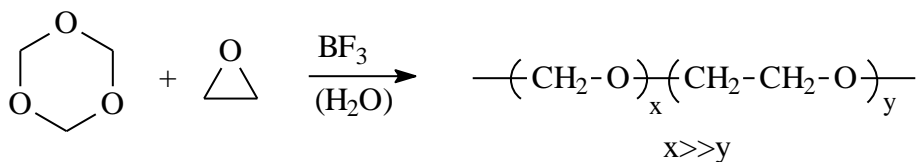


equilibrium propagating species

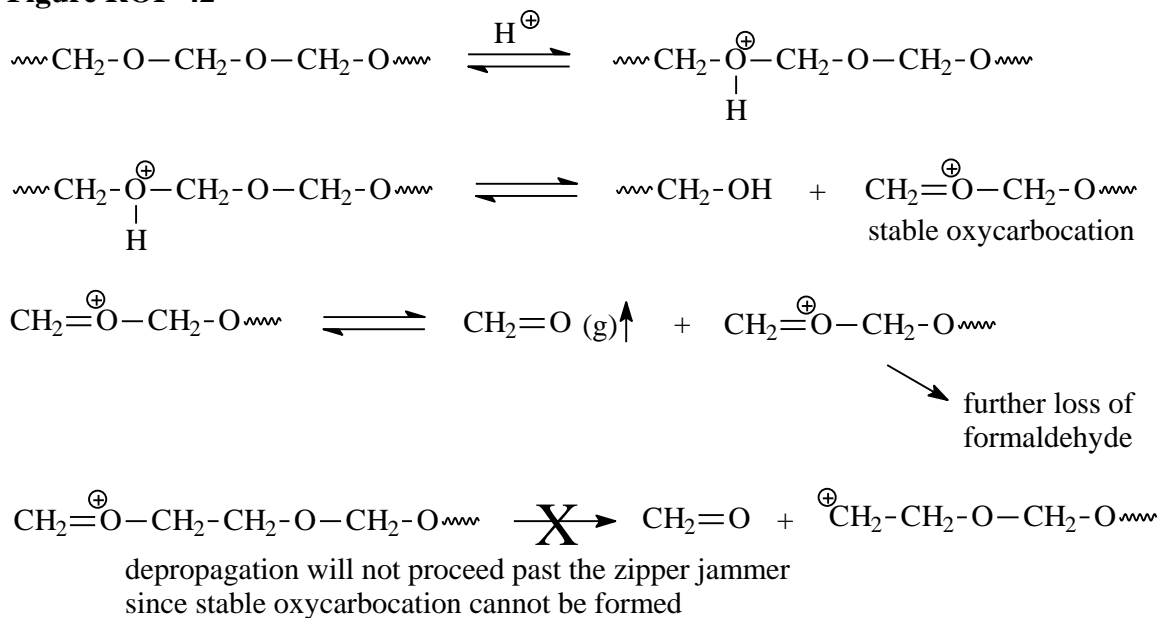


resume propagation

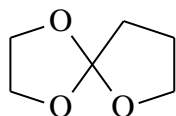
Commercial Polyoxymethylene. The polymerization of 1,3,5-trioxane (commonly called simply trioxane) is carried out on an industrial scale to produce polyoxymethylene, a highly crystalline, insoluble engineering thermoplastic (Celcon®). The commercial product is actually a copolymer of trioxane and a small amount of either ethylene oxide or other cyclic ether (Figure ROP-41).

Figure ROP-41

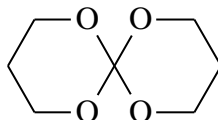
The incorporation of a very small quantity of random ethylene oxide units is necessary to prevent depropagation of the polymer under low pH conditions. Depropagation is facile due to the combination of a low ceiling temperature and a volatile monomer (formaldehyde). Figure ROP-42 shows the depropagation (unzipping) reaction induced by acid. Ethylene oxide is termed a “zipper jammer.”

Figure ROP-42

Bicyclic Ortho Esters and Spiro Acetals. Several bicyclic compounds containing acetal linkages (see Figure ROP-43) are known to display the unusual property of zero or positive change in volume (expansion) upon polymerization. The resulting polymers are poly(ester-ethers) with unremarkable densities; thus, the expansion properties are due to unusually high densities for these monomers. This has been attributed to the high density of atoms near the point of fusion of the two rings.

Figure ROP-43

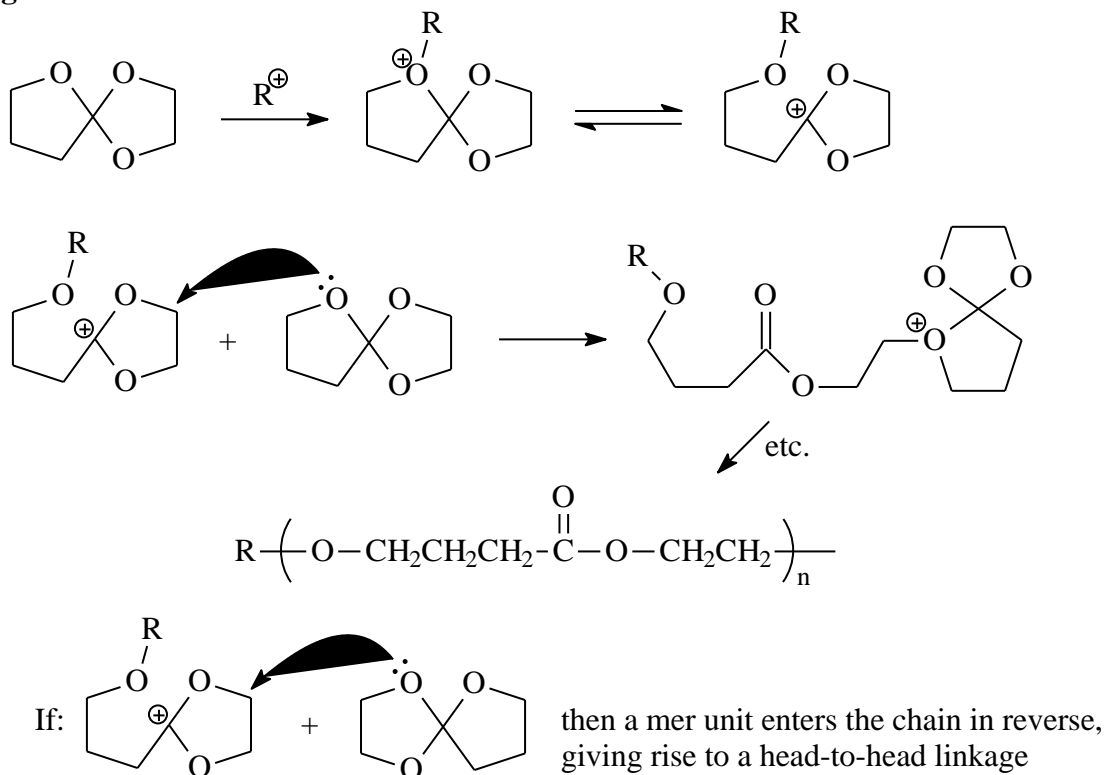
1,4,6-trioxaspiro[4.4]nonane
a spiro ortho ester



1,5,7,11-tetraoxaspiro[5.5]undecane
a spiro orthocarbonate

These monomers are polymerizable only by cationic initiators, and propagation involves oxonium ion/oxycarbocation active species (Figure ROP-44).

Figure ROP-44

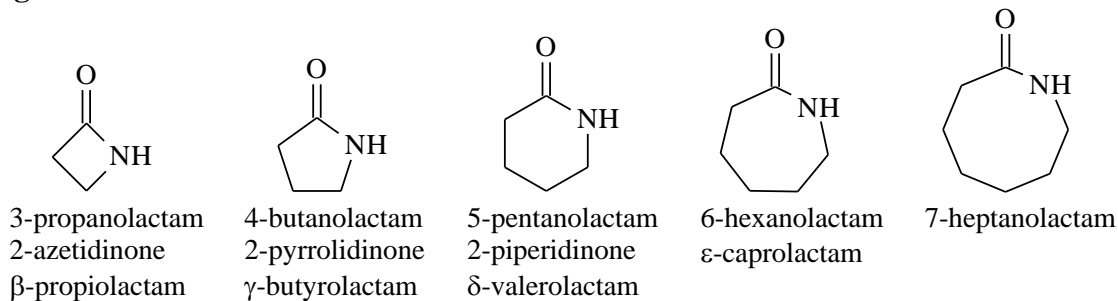


C. Cyclic Amides (Lactams)

Acids, bases, and water can initiate the polymerization of lactams. The water-initiated process, termed hydrolytic polymerization, is the basis for the commercial production of Nylon-6 by ring-opening polymerization of ϵ -caprolactam. The base-initiated process is useful for the laboratory preparation of polyamides; the cationic process is, in general, not useful.

As shown in Figure-ROP-45, lactams may be named as alkanolactams (IUPAC system), by using the specialized nomenclature of heterocyclic chemistry, or by using common names based upon the parent carboxylic acid.

Figure ROP-45



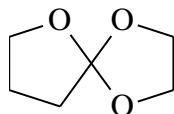
PSC 301
Problem Set 10

1. Please explain the following facts as they relate to the kinetic and thermodynamic criteria for ring opening polymerization.
 - a) Three and four-membered cyclic sulfides readily polymerize in the presence of acid or base, but five-membered and larger cyclic sulfides do not polymerize under any conditions.
 - b) Three, four, five, and seven-membered (and probably higher) cyclic ethers are readily polymerizable by acids, but only the three-membered cyclic ether, oxirane, is polymerizable by acid and base.

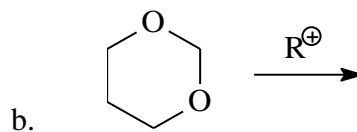
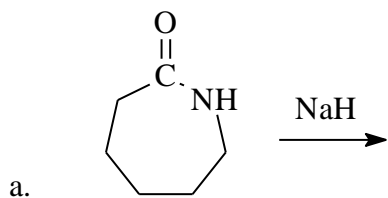
Which monomer below would be expected to have the lowest ceiling temperature?



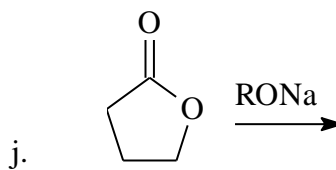
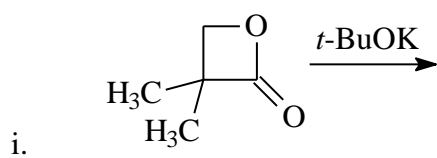
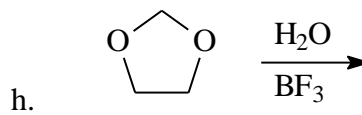
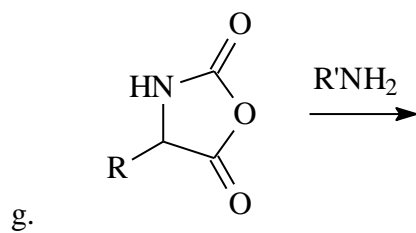
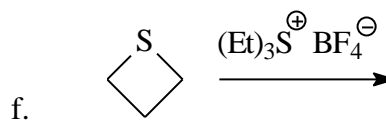
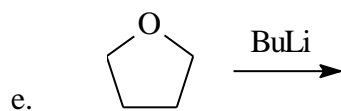
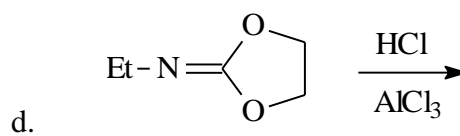
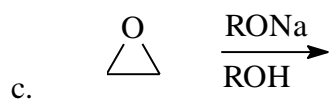
2. Show the two modes of enchainment (head-to-tail and head-to-head) of the following monomer under cationic polymerization conditions.



3. Cationic polymerization of 1,3,5-trioxepane (7 membered cyclic acetal) is characterized by an induction period. Addition of 1,3-dioxolane (5 membered cyclic acetal) is found to shorten the induction period. Explain, preferably with the aid of chemical equations.
4. For each polymerizable system below, show the mechanism of initiation and propagation.



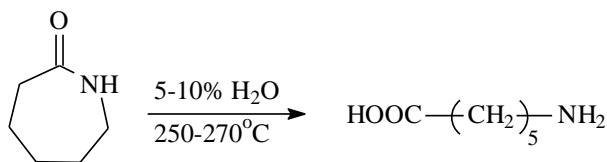
Problem Set 10



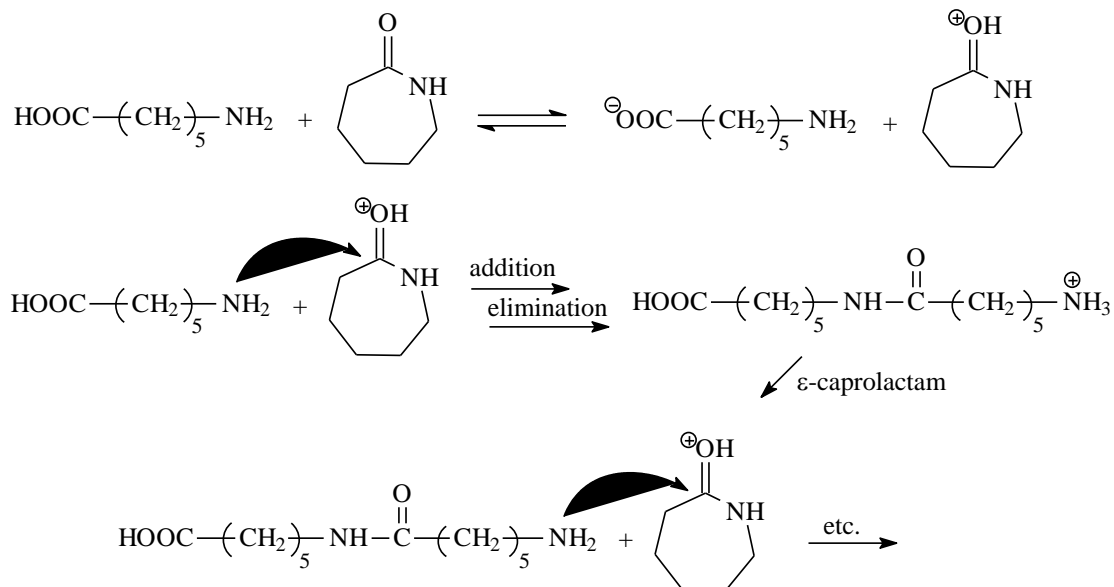
1. Hydrolytic Polymerization

Hydrolytic polymerization of ϵ -caprolactam involves heating monomer in the presence of water for 12-24 h, as shown in Figure ROP-46. The exact amount of water is unimportant with regard to the final molecular weight of the product, although it does affect the kinetics of the process. Ring-opened monomer serves as a source of both acid (catalyst) and primary amine (initiator of ring-opening polymerization). Condensation polymerization is a minor competing reaction throughout the process; however, when all of the monomer has been exhausted through the ring opening it becomes important in determining the final molecular weight.

Figure ROP-46
HYDROLYSIS OF MONOMER



ACID-CATALYZED RING OPENING



CONDENSATION POLYMERIZATION



In the commercial process, control of the final molecular weight is usually achieved by reducing the residual water content to a certain specified level and by introduction of a monofunctional acid chain stopper. The latter causes the free amine groups to be consumed, and thus the polymer is stabilized against molecular weight

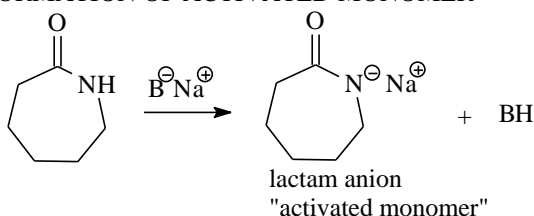
changes. Monomer and cyclic oligomers are removed by hot water extraction or vacuum distillation.

2. Anionic Polymerization (Activated Monomer Mechanism)

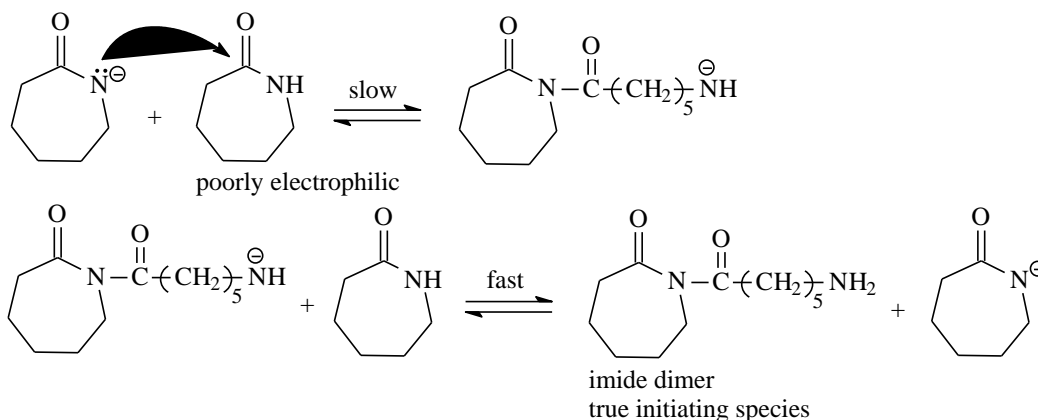
Anionic polymerization of lactams can be initiated with a variety of strong bases including alkali metals, metal hydrides, metal amides, and organometallic compounds. Propagation proceeds by an activated monomer mechanism as shown in Figure ROP-47. An induction period persists until a significant concentration of the imide dimer has been formed.

Figure ROP-47

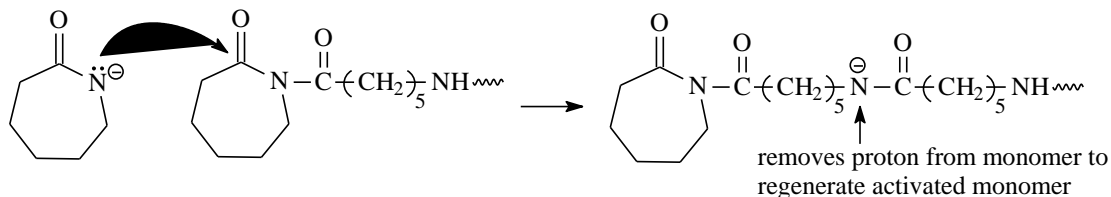
FORMATION OF ACTIVATED MONOMER



FORMATION OF AMIDE DIMER



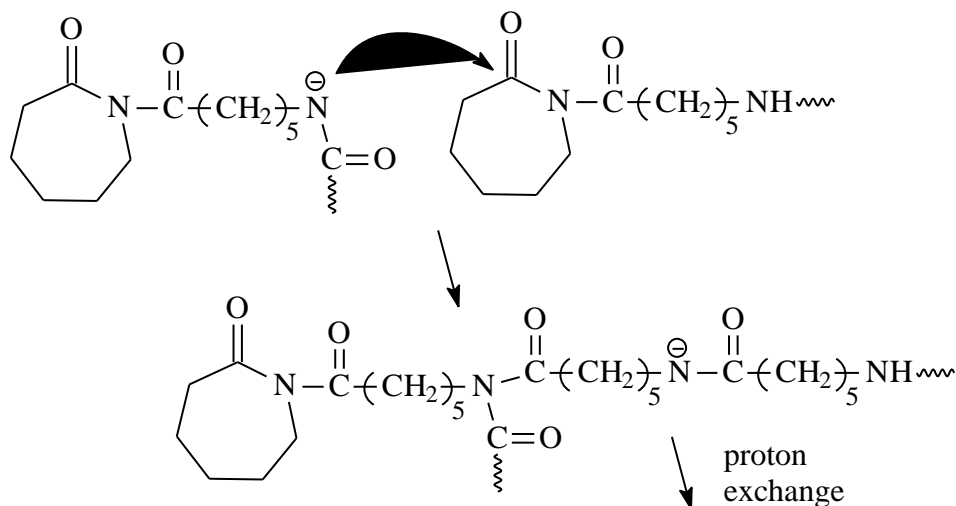
GENERAL PROPAGATION STEP



A unique feature of the activated monomer mechanism is that the rate of polymerization is usually independent of monomer concentration.

The anionic polymerization of lactams is characterized by a number of side reactions that lead to greater product complexity; for example, at high conversions branching can occur as shown in Figure ROP-48.

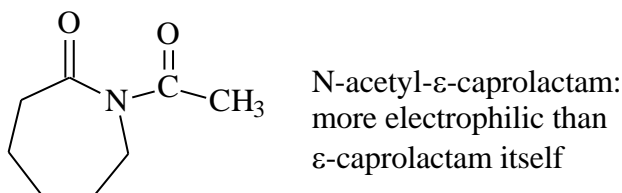
Figure ROP-48



Moreover, many polymerizations are further complicated by heterogeneity of the reaction mixture caused by crystallization and precipitation of the formed nylon polymer.

To avoid the induction period associated with formation of the imide dimer, or to facilitate polymerization of the less reactive lactams, e.g., 2-piperidinone, an N-acyllactam such as N-acetyl-ε-caprolactone (Figure ROP-49) may be added to the polymerization mixture to serve as an initiator. In the presence of N-acetyl-ε-caprolactam, the degree of polymerization is governed largely by the monomer/N-acyllactam ratio, and the rate is determined by the concentration of base and N-acyllactam.

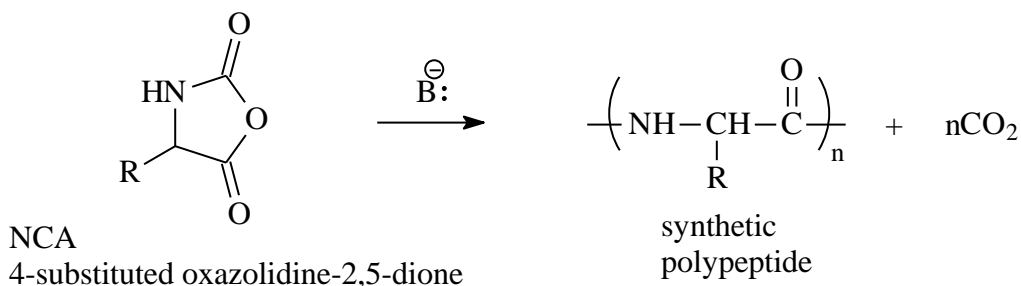
Figure ROP-49



D. N-Carboxy-α-Amino Acid Anhydrides

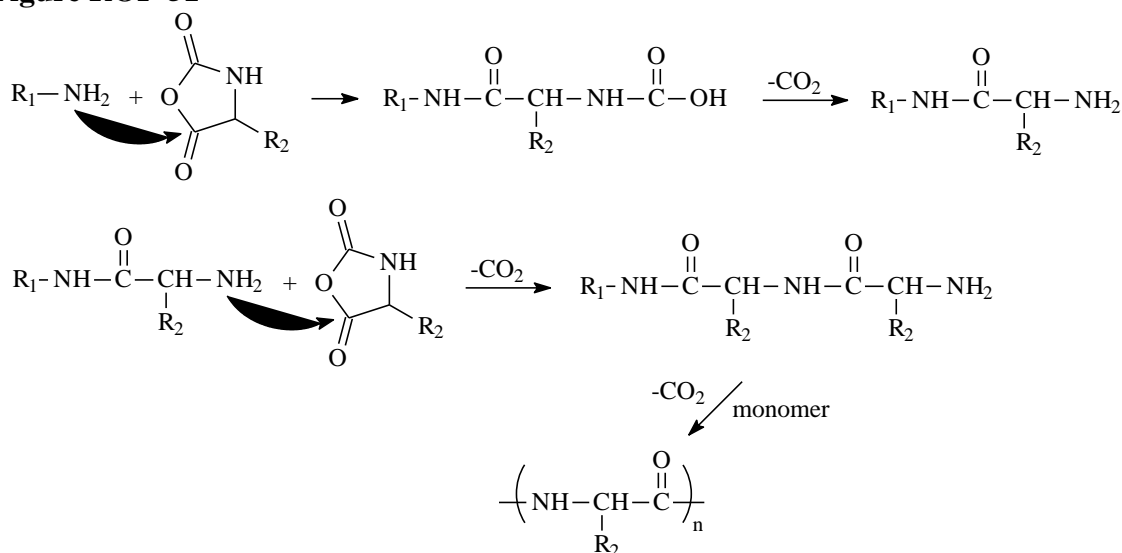
N-Carboxy-α-amino acid anhydrides (NCA)s are polymerized by a number of nucleophilies and bases to yield substituted nylon-2 polymers or synthetic polypeptides, as shown in Figure ROP-50. During polymerization, each monomer unit loses a molecule of CO₂.

Figure ROP-50



The mechanism of ring opening polymerization depends on the base strength of the initiator. Primary aliphatic amines, which are highly nucleophilic but weakly basic, induce a relatively slow, so-called “normal” polymerization mechanism. Stronger bases (or poorer nucleophiles) such as organometalics, metal hydrides, alkoxides, hydroxides, and tertiary amines induce a more rapid, activated monomer mechanism. The normal mechanism is illustrated in Figure ROP-51.

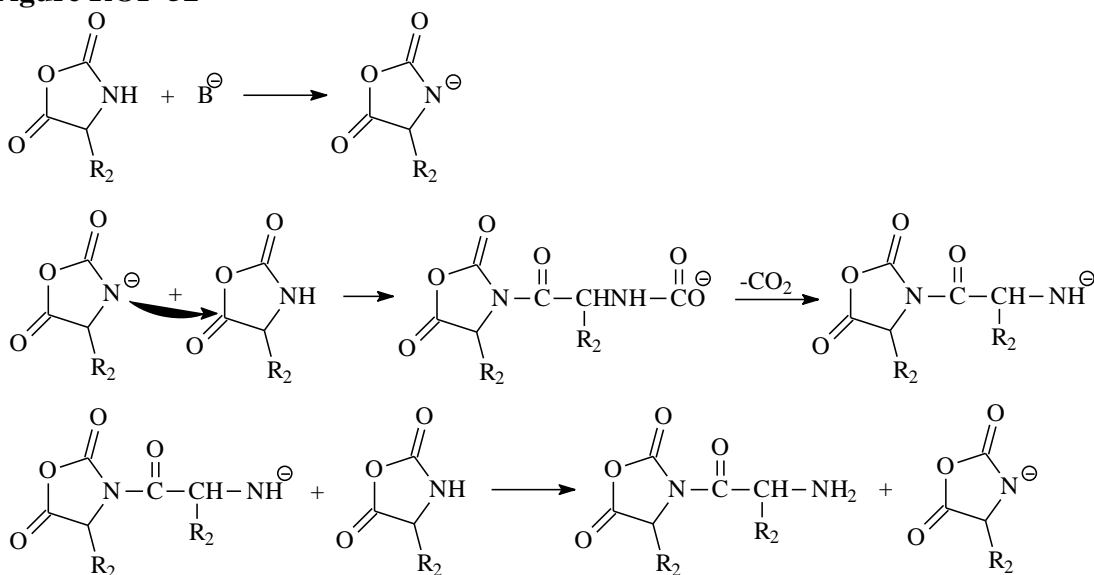
Figure ROP-51



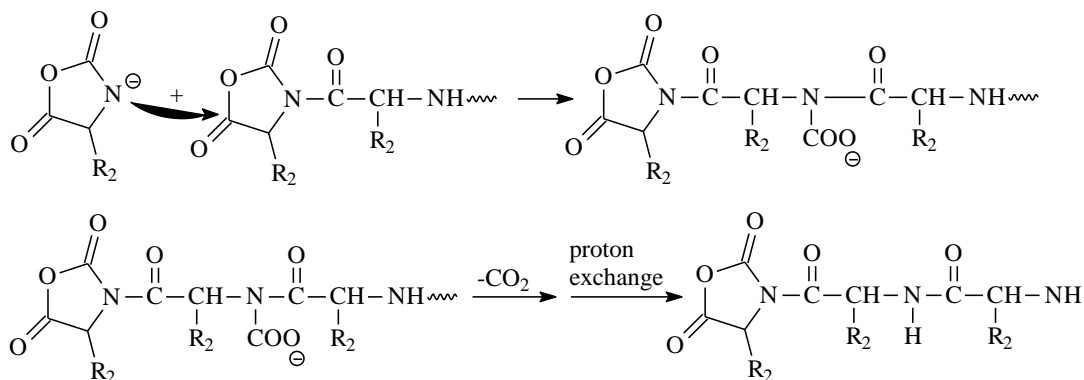
The normal mechanism displays characteristics of a living polymerization insofar that the degree of polymerization is proportional or equal to the monomer/initiator ratio. The molecular weight distribution is sometimes narrow, but is often broadened by heterogeneity (polymer precipitation or formation of polypeptide secondary structure).

Polymerizations initiated by strong bases proceed by an activated monomer mechanism that is analogous to that observed in lactam polymerization. The base serves to remove a proton from monomer to create the NCA anion (activated monomer), as shown in Figure ROP-52. Initiation involves nucleophilic attack by NCA anion on NCA followed by proton transfer with another monomer molecule to regenerate the anion. The rate of polymerization is typically much faster than that for the normal mechanism.

Figure ROP-52



GENERAL PROPAGATION STEP

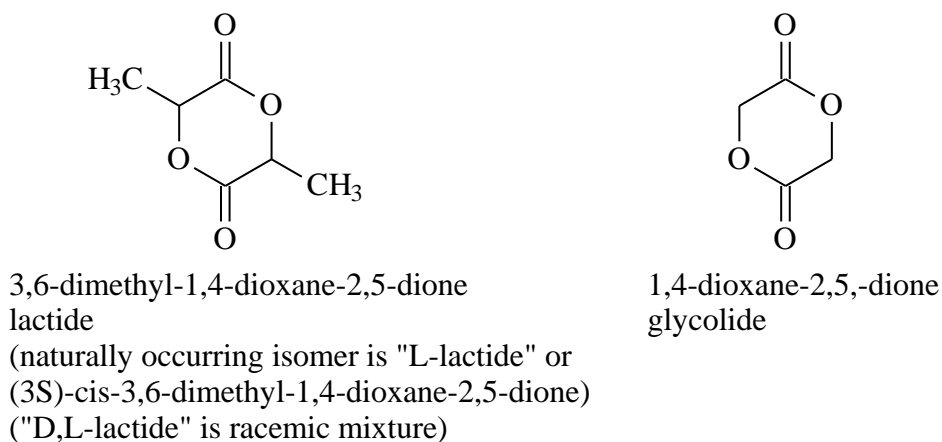
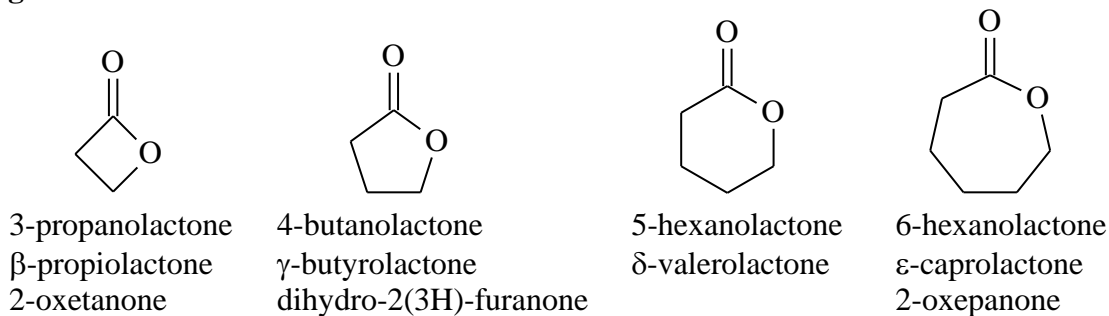


Tertiary aliphatic amines are especially useful as catalysts of the activated monomer mechanism, especially for the production of high molecular weight polypeptides; more powerful bases such as organometallic compounds yield lower molecular weights due to side reactions. Secondary amines often produce a situation in which both normal and activated monomer mechanisms operate simultaneously. The preponderance of one over the other depends on nucleophilic strength of the amine, more hindered secondary amines favor the activated monomer mechanism.

E. Cyclic Esters (Lactones)

A number of polymerization pathways are available for lactones including cationic, anionic, and anionic coordination. The monomers are generally named as a derivative of the parent acid, as shown in Figure ROP-53.

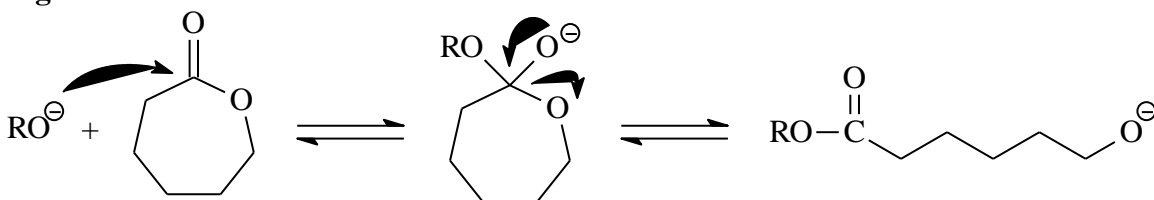
Figure ROP-53



1. Anionic Polymerization of Lactones

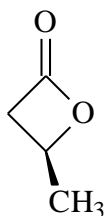
Anionic polymerization of lactones may be initiated by a variety of bases including hydroxides, alkoxides, metal oxides, and organometallic compounds. For almost all lactones, ring opening proceeds via acyl-oxygen cleavage, as demonstrated in Figure ROP-54.

Figure ROP-54



Evidence for acyl-oxygen cleavage comes from end-group analysis. For example, in Figure ROP-54, alkyl-oxygen cleavage would result in an ether instead of ester head group. Also, when a chiral carbon is attached to the alkyl oxygen, as in β -butyrolactone (Figure ROP-55), retention of configuration is observed. Cleavage of the alkyl-oxygen bond would lead to racemization.

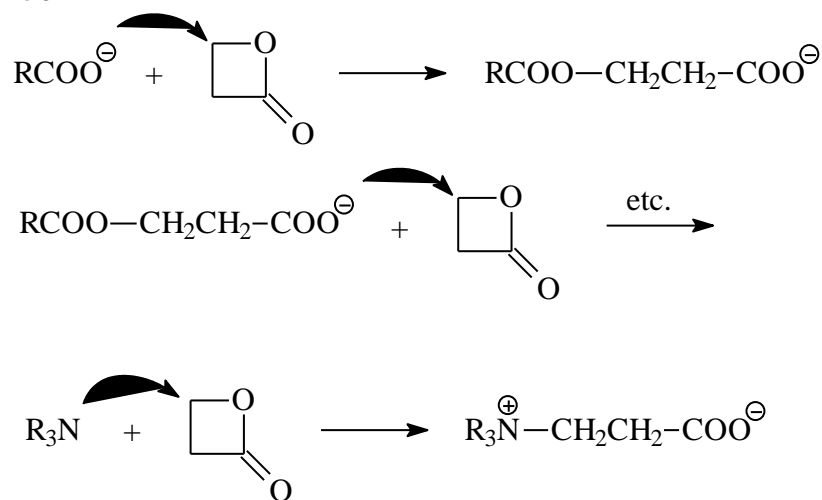
Figure ROP-55



In general for anionic polymerization initiated by alkoxides, chain transfer to monomer and termination are insignificant or absent (living conditions); however, significant chain transfer to polymer (transesterification) occurs and leads to molecular weight distribution broadening and production of cyclic oligomers.

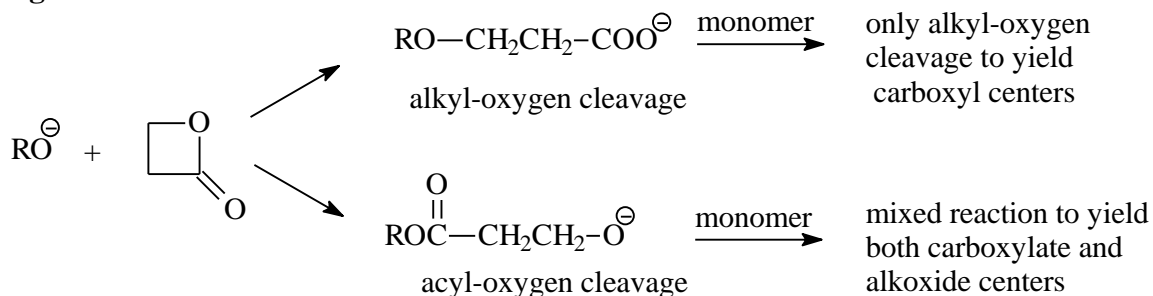
β -Propiolactone shows interesting polymerization behavior due to high strain in the four-membered ring. Unlike larger lactones, it can be initiated by weakly nucleophilic initiators such as metal carboxylates, tertiary amines, and phosphines. In these cases, ring opening occurs through alkyl-oxygen cleavage as shown in Figure ROP 56. For the neutral amine or phosphine initiators, polymerization is thought to proceed through a zwitterionic propagating species.

Figure ROP-56



If a stronger nucleophile such as an alkoxide is reacted with β -propiolactone, both alkyl-oxygen and acyl-oxygen cleavage occur leading to mixed carboxyl and alkoxy propagating centers. However, the former can react with monomer only by cleavage of alkyl-oxygen bonds; whereas, the alkoxy propagating centers can react with either. Thus, all of the centers are converted to the carboxyl type after only a few propagations (Figure ROP-57).

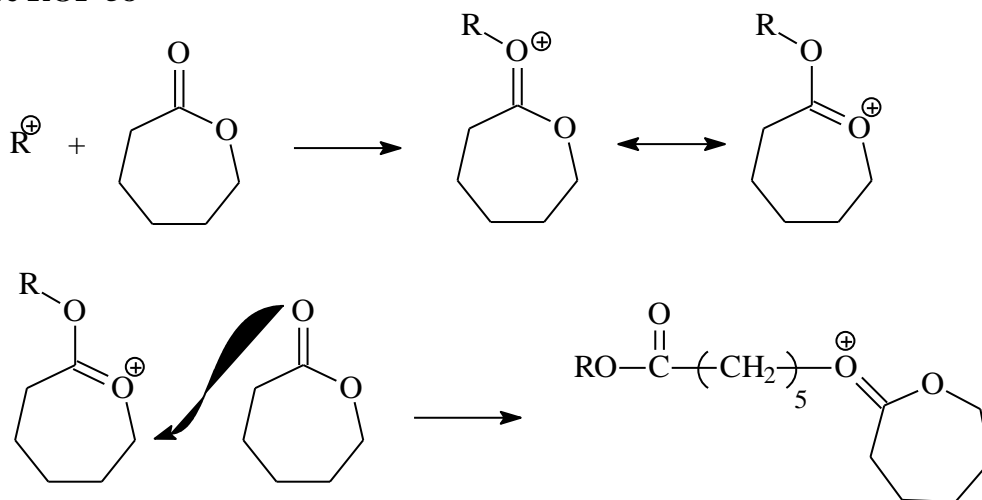
Figure ROP-57



2. Cationic Polymerization of Lactones

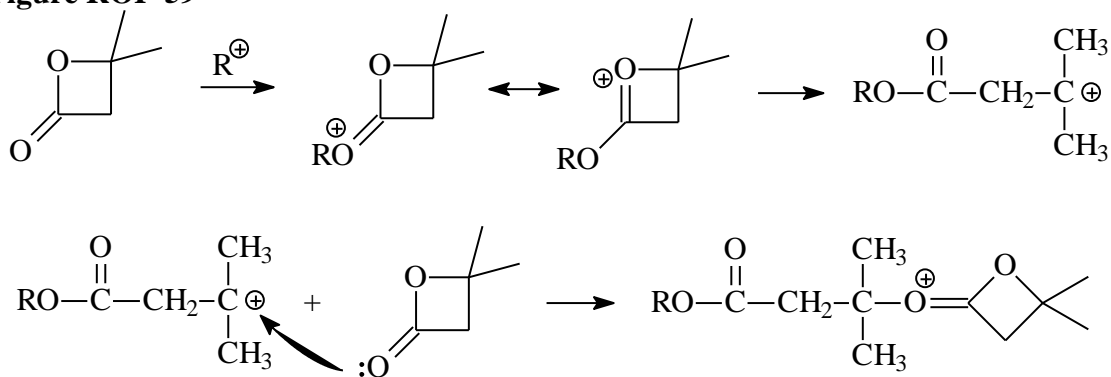
Cationic polymerization of lactones may be initiated by the same range of initiators used for cyclic ethers. The mechanism was poorly understood for some time, due to the fact that no single mechanism is universal for all lactones. However, end-group analysis and trapping experiments have shown that the principle mode of ring opening for most lactones is attack by the electrophilic initiating moiety onto the exocyclic oxygen, followed by alkyl-oxygen cleavage (Figure ROP-58).

Figure ROP-58



The general mechanism above is similar to the polymerization of cyclic ethers in that the ring-opening step is bimolecular ($\text{S}_{\text{N}}2$). However, for β,β -dimethyl- β -propiolactone the ring-opening step is $\text{S}_{\text{N}}1$ due to the formation of a stable *tertiary* carbocation (Figure ROP-59).

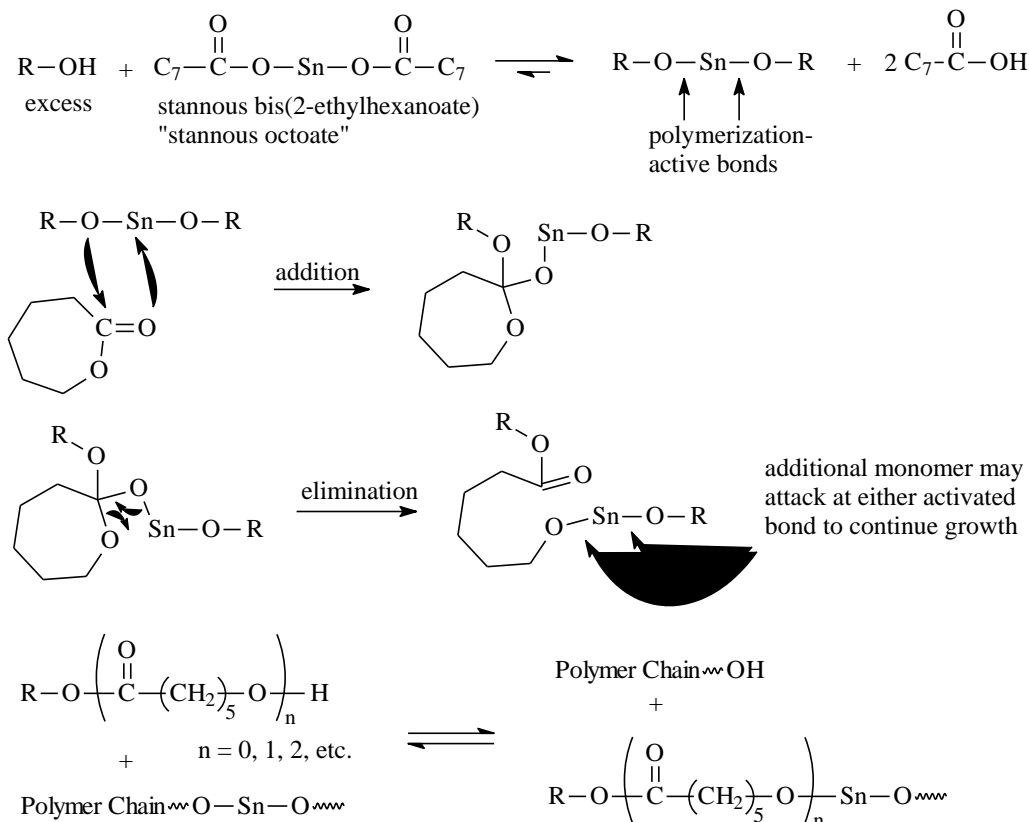
Figure ROP-59



3. Anionic Coordination Polymerization of Lactones

Many polymerizations of lactones are classified as anionic coordination polymerizations, characterized by a propagating chain end that is not ionic, but rather consists of a polar covalent bond between oxygen and a metal such as Al or Sn. The active chain ends are often in equilibrium with a dormant species, typically an alcohol. Examples of compounds that catalyze/initiate coordination polymerization of lactones are aluminum porphyrins, aluminum alkoxides, tin alkoxides, and tin esters. Figure ROP 60 illustrates the polymerization of ϵ -caprolactone catalyzed by stannous octoate and initiated by an alcohol.

Figure ROP-60



An important feature of the stannous octoate-catalyzed polymerization of lactones is the equilibrium pictured at the bottom of Figure ROP-60. This equilibrium lies far to the right, but because the Sn catalyst is typically at very low concentration, most of the growing chains will exist in the dormant hydroxyl form.

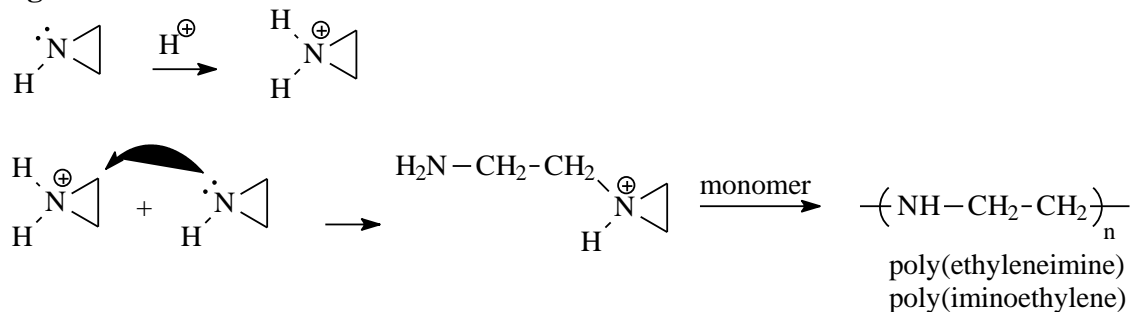
Stannous octoate is used commercially to produce hydroxy-terminated poly(ϵ -caprolactone). It is also the principle catalyst used for polymerization of the two 1,4-dioxane-2,5-diones, glycolide and lactide. The resulting polymers are of interest for bio-medical applications such as surgical sutures and controlled drug delivery because they are biocompatible and biodegradable. Biodegradation involves biological hydrolysis to the corresponding α -hydroxy acids (e.g. L-lactic acid), which are then eliminated through existing metabolic pathways (e.g. Krebs cycle).

F. Nitrogen Heterocyclics

1. Cyclic amines

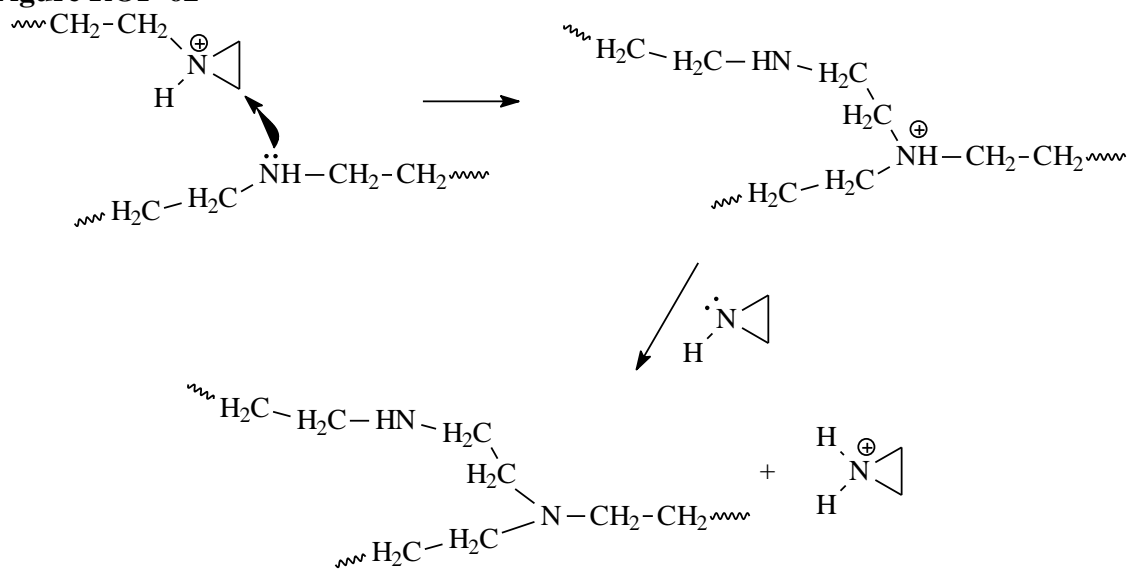
Cyclic amines, referred to as imines, are polymerized by acids. Most investigations have involved the 3-membered ring, which is called ethylene imine or aziridine. The polymerization mechanism, shown in Figure ROP-61, is very similar to the mechanism observed in the cationic polymerization of cyclic ethers. The propagating center is a tertiary ammonium ion, and the propagation step involves nucleophilic attack by monomer on the carbon that is α to the positive nitrogen.

Figure ROP-61



The polymerization of ethylene imine is actually more complex than indicated in Figure ROP-61. Extensive branching occurs through attack on the growing centers by secondary amine groups along the polymer chain. The resulting acyclic tertiary ammonium ions yield a proton to monomer, thereby starting a new chain (Figure ROP-62). Attack by polymer amine groups can also occur intramolecularly, producing cyclic oligomers and linear chains connected to cyclics.

Figure ROP-62

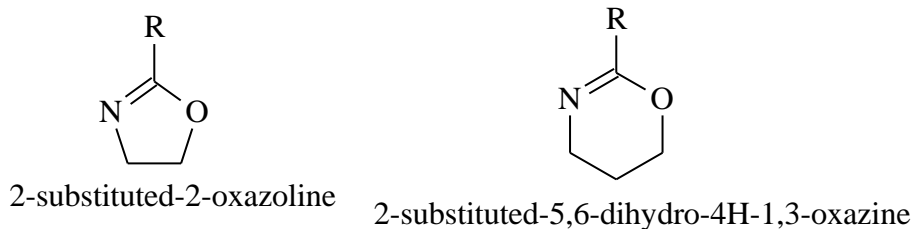


The aziridine ring can tolerate one substituent and remain polymerizable; however, two substituents render the monomer non-polymerizable. The 4-membered imine (azetidine) is also polymerizable by a similar cationic mechanism.

2. *endo*-Imino Cyclic Ethers

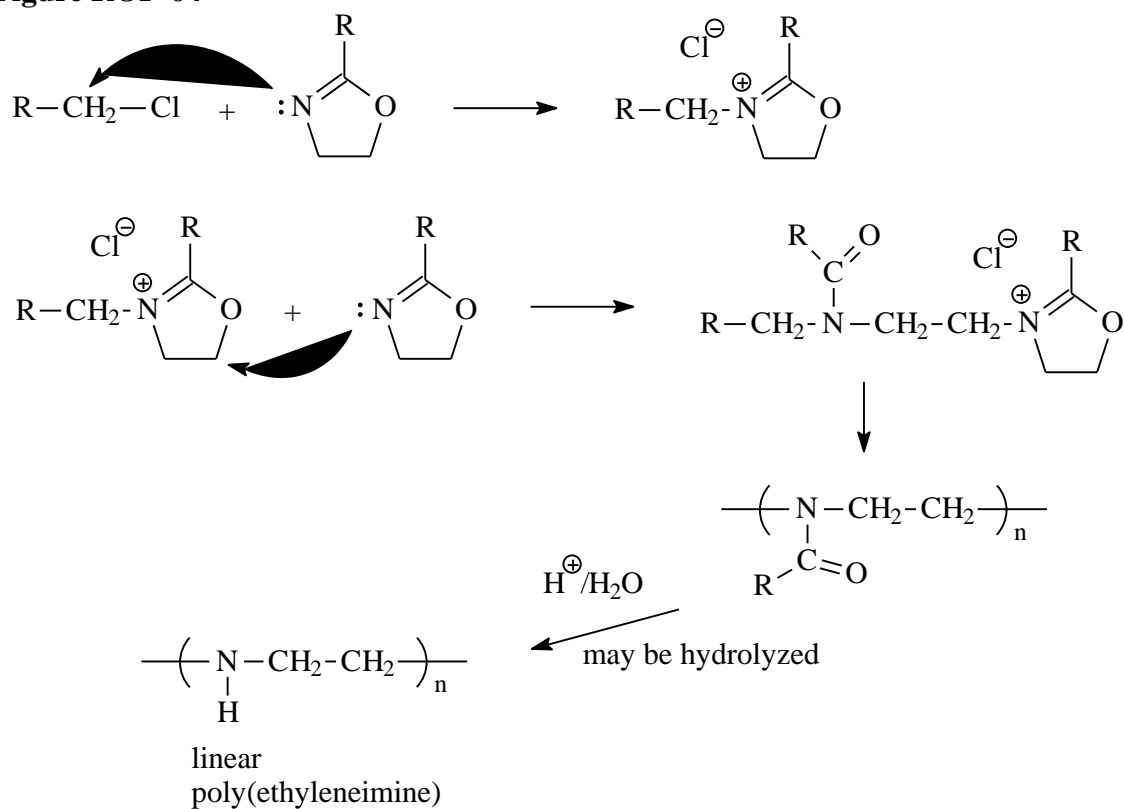
endo-Imino cyclic ethers are characterized by the $-O-C=N-$ linkage within the ring. The most studied monomers are the 5-membered, 2-substituted 2-oxazolines (Figure ROP-63), and to a lesser extent the 6-membered, 2-substituted-5,6-dihydro-4H-1,3-oxazines (Figure ROP-63).

Figure ROP-63



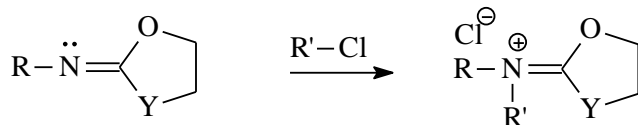
The mechanism by which these monomers polymerize is technically cationic, but the kinetic reactivity derives more from the strongly nucleophilic nitrogen in the monomer rather than through the use of strong-acid initiators. As shown in Figure ROP-64, initiation typically involves nucleophilic attack by monomer on a primary alkyl halide, yielding an oxazolinium ion and a halide counterion. Propagation then consists of nucleophilic attack by monomer on the CH_2 group next to oxygen, i.e., alkyl-oxygen cleavage (Figure ROP-64).

Figure ROP-64

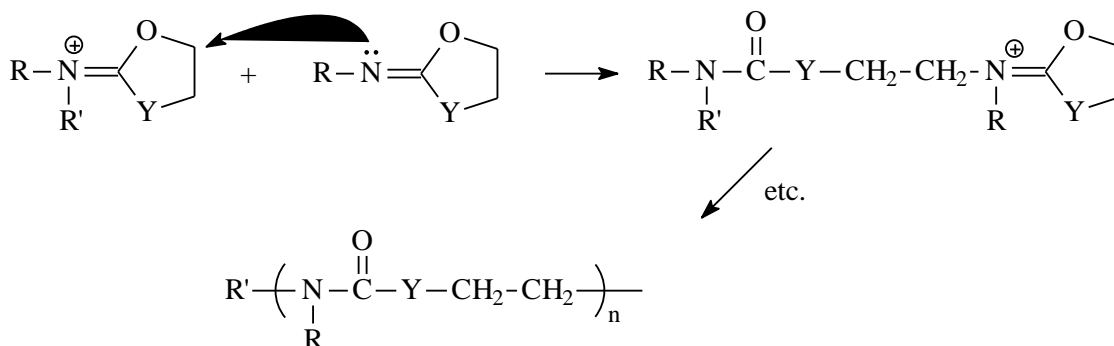


3. *exo*-Imino Cyclic Ethers

A variety of 5-membered *exo*-imino cyclic ethers (Figure ROP-65), in which the imino nitrogen is external to the ring, are known to polymerize by a cationic mechanism.

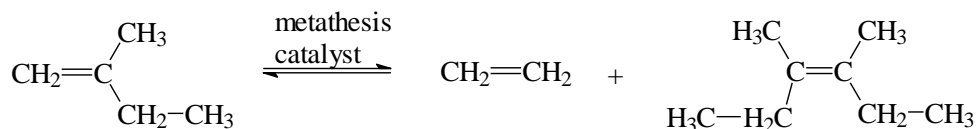
Figure ROP-65

Y = O iminocarbonate
 Y = NR 2-imini-1,3-oxazoline
 Y = CH₂ 2-iminotetrahydrofuran



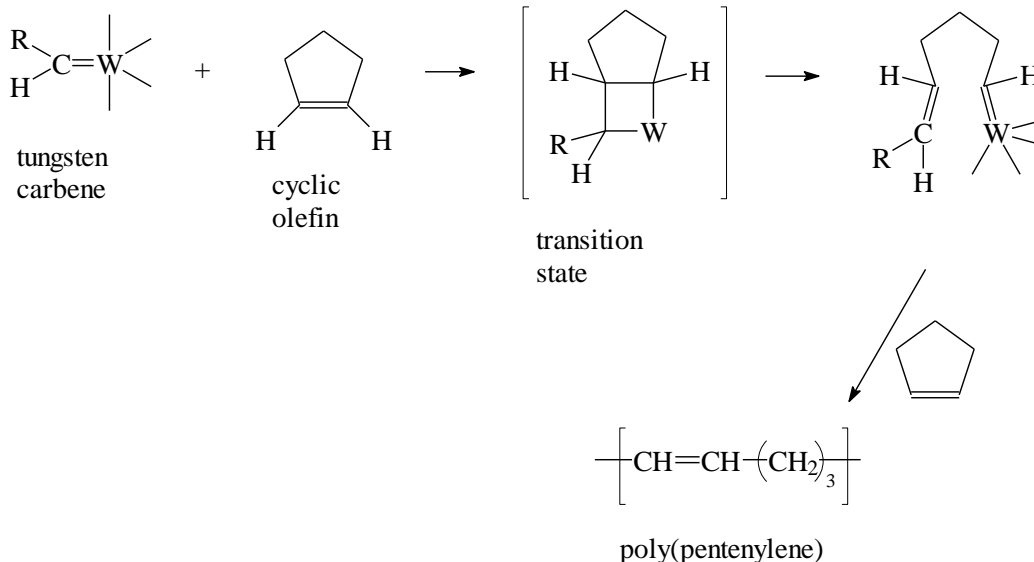
G. Ring Opening Metathesis Polymerization (ROMP)

Metathesis is the interchange of alkylidene groups about olefins catalyzed by certain coordination catalysts. The reaction shown in Figure ROP-66 illustrates a common synthetic technique used in metathesis reactions of 1-olefins: the ethylene gas can be driven off to produce a high yield of the larger olefin. Often the equilibrium constant is on the order of one, and the *cis* and *trans* isomers are produced in nearly equal proportions with a slight bias toward *trans*. Tungsten (W) compounds are particularly effective; the catalysts are formed by the reaction of WCl₆ with alcohol and ethylaluminum dichloride (EADC). Other transition metals such as ruthenium, molybdenum, rhenium, and titanium are also effective. The active intermediate is a metal carbene and the transition state involves a four-membered ring containing the metal.

Figure ROP-66

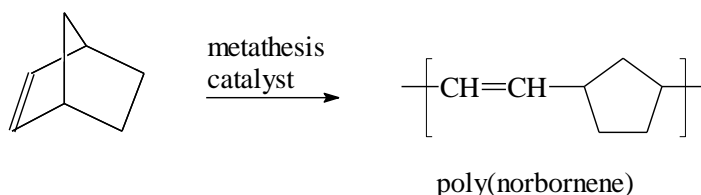
If the olefin is cyclic, polymerization occurs as shown in Figure ROP-67.

Figure ROP-67



The first recognized metathesis polymerization was probably that of norbornene (Figure ROP-68), which is practiced commercially today:

Figure ROP-68

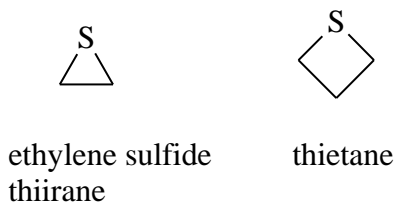


H. Cyclic Sulfides

Cyclic sulfides are analogous to cyclic ethers, and the two families of compounds share many common characteristics. There are two main differences. The kinetic reactivity of the cyclic sulfides is higher than that of the cyclic ethers due to the more polarizable carbon-sulfur bond; however, the thermodynamic tendency toward polymerization of the cyclic sulfides is lower because of lower ring strain due to the larger atomic radius of sulfur compared to oxygen. Thus only the three and four-membered cyclic sulfides have been polymerized; five and higher membered rings are believed to be non-polymerizable due to little or no strain in the ring.

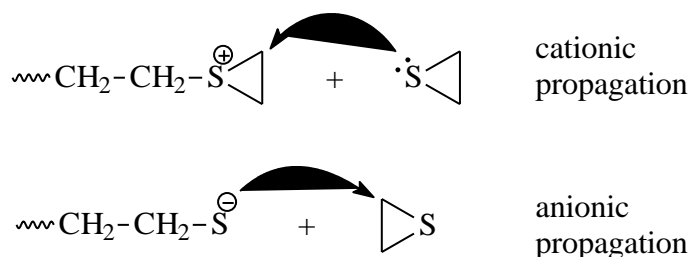
The three and four-membered cyclic sulfides are named as shown in Figure ROP-69.

Figure ROP-69



Both the 3 and 4-membered cyclic sulfides are readily polymerizable by either acid or base. This illustrates their higher kinetic reactivity relative to cyclic ethers, because it will be recalled that the 4-membered cyclic ether is only polymerized by acids. The mechanisms for acid and base initiated polymerization are shown in Figure ROP 70.

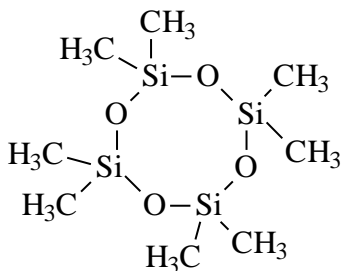
Figure ROP-70



I. Cyclosiloxanes

Polysiloxanes have commercial importance as thermally stable, weatherable sealants, paint binders, gasketing materials, and elastomers. They may be made either through step-growth or ring-opening polymerization, but only the ring-opening process affords high molecular weight. Both cationic and anionic processes can be carried out, and both often display characteristics of living polymerizations. The most common monomer is the cyclic tetramer, octamethylcyclotetrasiloxane (OMCTS), shown in Figure ROP-71.

Figure ROP-71



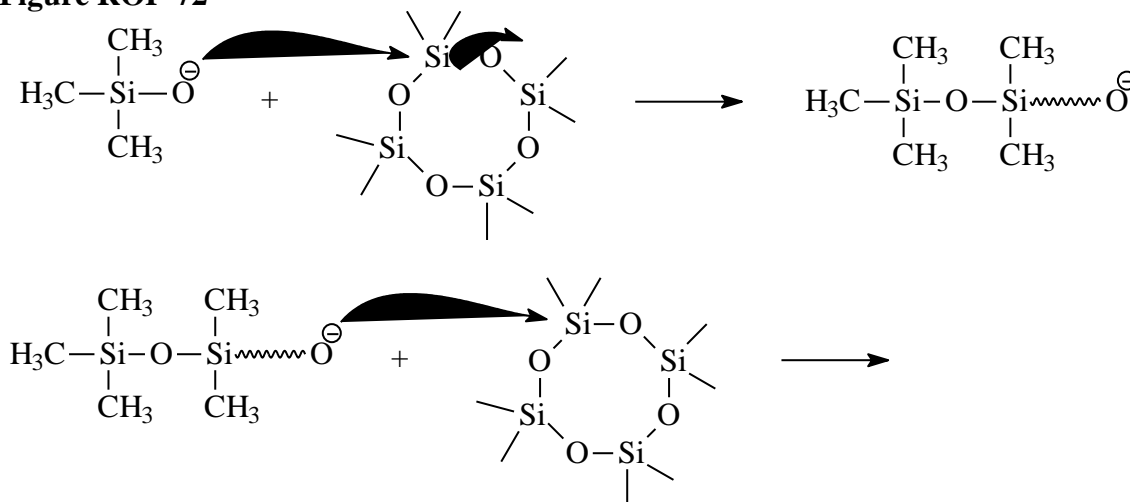
1. Anionic polymerization

Anionic polymerization of OMCTS can be affected by a variety of bases including:

- MO (metal oxides)
- MOH (metal hydroxides)
- MOR (metal alkoxides)
- MOSi(CH₃)₃ (metal silanolate)

Polymerization proceeds according to the mechanism shown in Figure ROP-72.

Figure ROP-72

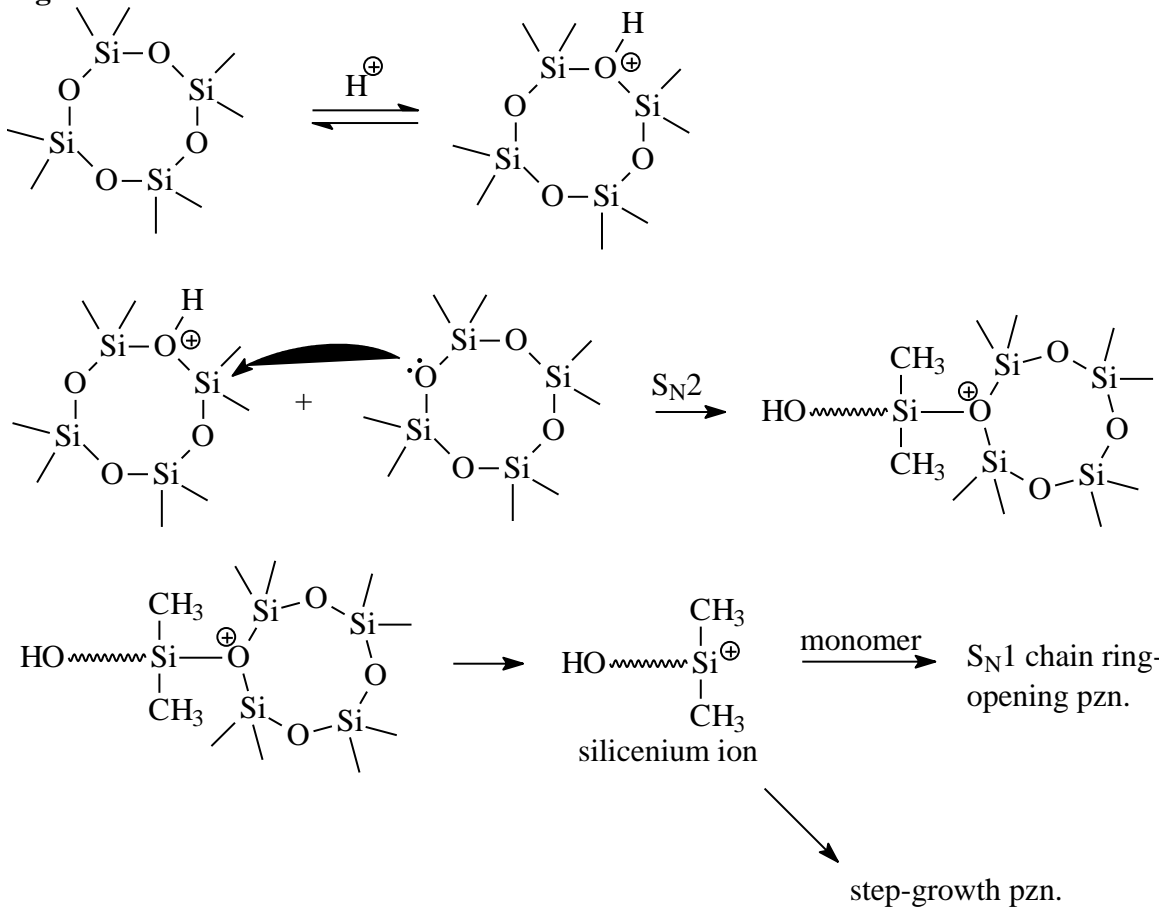


As discussed earlier, the polymerization of OMCTS is isoenthalpic ($\Delta H \cong 0$) and remarkably has a positive ΔS ($= 6.7 \text{ J/mol-K}$). It therefore displays floor temperature behavior. The positive entropy change is attributed to the high degree of flexibility of the linear polymer chain due to the large atomic radius of silicon. Also the loss in translational entropy upon polymerization is minimal because the rings are large.

2. Cationic polymerization

Cationic polymerization is more complicated than the anionic process and probably involves a combination of ring-opening chain and step-growth polymerizations. Initiation consists of protonation (or cationation) of monomer followed by subsequent reaction with monomer to form the tertiary oxonium ion (Figure ROP-73).

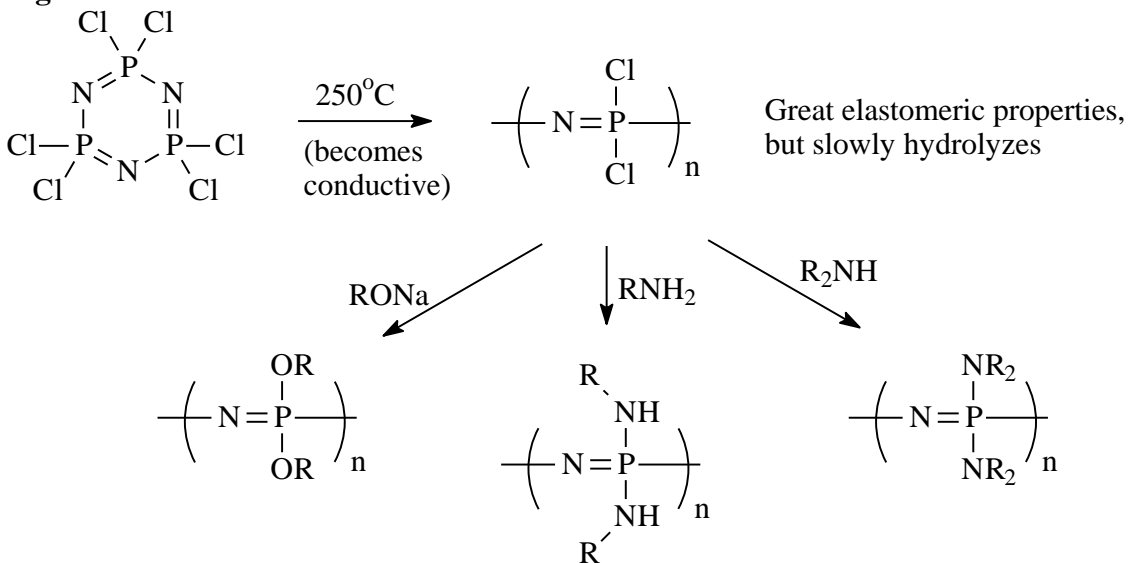
Figure ROP-73



J. Cyclic phosphazenes

Polyphosphazenes are polymers characterized by a totally inorganic backbone consisting of alternating phosphorous-nitrogen single and double bonds. The parent polymer is obtained by the thermal polymerization of hexachlorocyclotriphosphazene (Figure ROP-74). The resulting polymer has excellent elastomeric properties including outstanding thermal stability; however, it is hydrolytically unstable. Substitution of the chloro side groups for alkoxide or amine creates stable derivatives.

Figure ROP-74



K. Zwitterionic Ring-Opening Polymerization

Certain combinations of cyclic nucleophiles and electrophiles undergo spontaneous polymerization without the need for an initiator. As shown in Figure ROP-75, nucleophilic attack of 2-oxazoline on β -propiolactone forms a zwitterionic species, which may then polymerize by a step-growth mechanism.

Figure ROP-75

