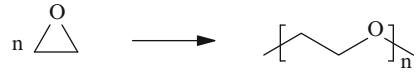
Chapter 5
Ring-Opening Polymerizations

5.1 Chemistry of Ring-Opening Polymerizations

Formation of polymers through ring-opening reactions of cyclic compounds is an important process in polymer chemistry. In such polymerizations, chain-growth takes place through successive additions of the opened structures to the polymer chain:

An example of the above is a ring-opening polymerization of ethylene oxide that results in formation of poly(ethylene oxide), a polyether:



The cyclic monomers that undergo ring-opening polymerizations are quite diverse. Among them are cyclic alkenes, lactones, lactams, and many heterocyclics with more than one heteroatom in the ring. Such polymerizations are ionic in character and may exhibit characteristics that are typical of ionic chain-growth polymerizations (e.g., effect of counterion and solvent). It would, however, be wrong to assume that these polymerizations necessarily take place by chain-propagating mechanisms. Actually, many such reactions are step-growth in nature, with the polymer size increasing slowly throughout the whole course of the process. There are, on the other hand, some cyclic monomers that do polymerize in a typical chain-growth manner.

5.2 Kinetics of Ring-Opening Polymerization

There is general similarity between the kinetics of many ring-opening polymerization and those of step-growth polymerizations that are discussed in Chap. 7. Some kinetic expressions in ring-opening polymerizations, on the other hand, resemble ionic chain-growth reactions.

There are several forms of the rate law that describe the cationic ring-opening polymerization. For living or polymerizations without termination, one can write

$$R_p = k_p[M^*][M]$$

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where [M*] is the concentration of the propagating oxonium ions. Such ions could be oxonium, sulfonium, and others. When, however, there is propagation–depropagation equilibrium, it can be expressed as follows:

$$\mathrm{M}_n^* + \mathrm{M} \underset{K_{\mathrm{Dp}}}{\overset{K_{\mathrm{P}}}{\rightleftharpoons}} \mathrm{M}_{n+1}^*$$

The rate expression can be written as propagation–depropagation

$$R_{\mathrm{p}} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = K_{\mathrm{p}}[\mathrm{M}^*][\mathrm{M}] - K_{\mathrm{DP}}[\mathrm{M}^*]$$

At condition of equilibrium, if we designate the monomer concentration $[\mathrm{M}]_{\mathrm{C}}$, and the polymerization rate is zero, we can write

$$K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}} = K_{\mathrm{DP}}$$

Hirota and Fukuda [1] described the quantitative dependence of the degree of polymerization on various reaction parameters for an equilibrium polymerization. The equilibrium can be described as

$$\mathrm{I} + \mathrm{M} \overset{K_{\mathrm{I}}}{\rightleftharpoons} \mathrm{M}^*$$

where, I is the initiating species. It is assumed that the equilibrium constants for the initiation and propagation are independent of the size of the propagating species. The concentration of the propagating chains [M*] of size n at equilibrium c then can be written as:

$$[\mathrm{M}^*] = K_{\mathrm{I}}[I]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}(K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})^{n-1}$$

The total concentration of molecules size N can be expressed as follows

$$[N] = \sum [\mathrm{M}_n^*]K_{\mathrm{I}}[\mathrm{I}]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}/(1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})$$

The total concentration of monomer segments that are incorporated into the polymer can also be expressed as follows:

$$[\mathrm{W}] = \sum_n [\mathrm{M}^*] = K_{\mathrm{I}}[\mathrm{I}]_{\mathrm{C}}[\mathrm{M}]_{\mathrm{C}}/(1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}})^2$$

This allows us to express the average degree of polymerization that is $[W]/[N]$ as follows:

$$\mathrm{DP} = \frac{1}{1 - K_{\mathrm{p}}[\mathrm{M}]_{\mathrm{C}}}$$

We can describe the rate of polymerization in terms of $-\mathrm{d}[M]/\mathrm{d}t$ as

$$R_p = -d[M]/dt = K_p([M^*]M) - [M])$$

The expression can be integrated to yield:

$$\text{In}\left(\frac{[M]_0 - [M]_C}{[M] - [M]_C}\right) = k_p[M^*]t$$

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

5.3 Polymerization of Oxiranes

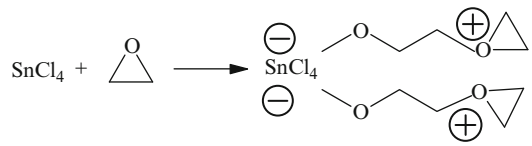
Polymerizations of oxiranes or epoxides occur by one of three different mechanisms: (1) cationic, (2) anionic, and (3) coordination. In this respect the oxiranes differ from the rest of the cyclic ethers that can only be polymerized with the help of strong cationic initiators. It appears, though, that sometimes coordination catalysis might also be effective in polymerizations of some oxetanes. The susceptibility of oxirane compounds to anionic initiation can be explained by the fact that these are strained ring compounds. Because the rings consist of only three atoms, the electrons on the oxygen are crowded and are vulnerable to attack [2].

5.3.1 Cationic Polymerization

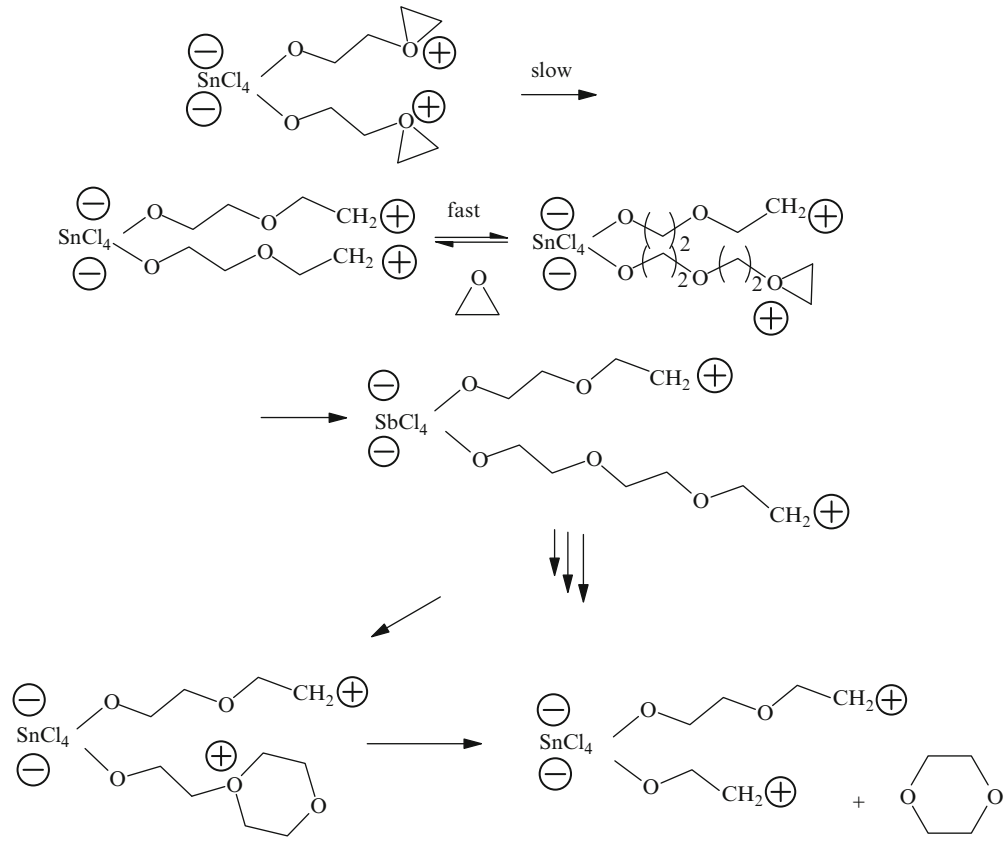
Various Lewis and protonic acids are capable of initiating cationic polymerization of epoxies. Among them, the following metal salts are effective in polymerizations of ethylene and propylene oxides [3, 4]: $ZnCl_2$, $AlCl_3$, $SbCl_5$, BF_3, BCl_3, $BeCl_2$, $FeCl_3$, $SnCl_4$, and $TiCl_4$. Often these polymerizations can be carried out in bulk without any solvent, particularly in the laboratory. The mechanism of these reactions can be complex, however, depending upon the particular Lewis acid used. In fact, not all of these polymerizations can even be treated in general terms as cationic. For instance, ferric chloride initiated polymerizations of epoxides initially proceed by a mechanism that has all the superficial features of cationic polymerization. After the initial stages, however, the polymerizations proceed by a coordination mechanism. This is discussed further in this section.

Stannic chloride yields only low molecular weight poly(ethylene oxide) from ethylene oxide (molecular weight below 5,000) when the reaction is carried out in ethylene chloride at room temperature. Some dioxane and dioxolane also form in the process. Following reaction scheme was proposed [2–6]:

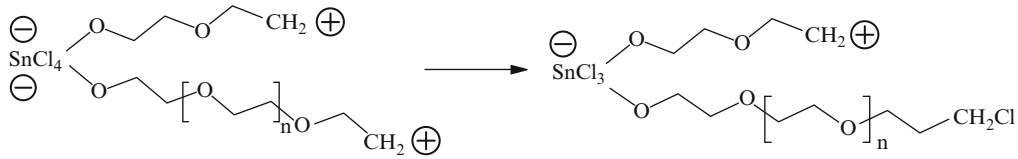
Initiation



Propagation



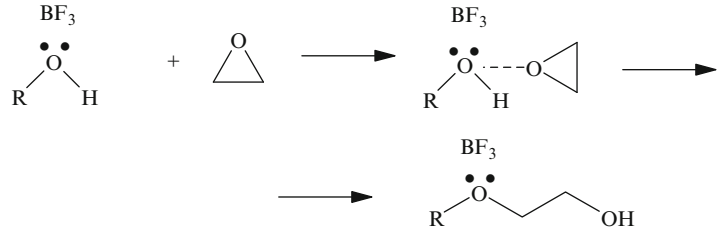
Termination



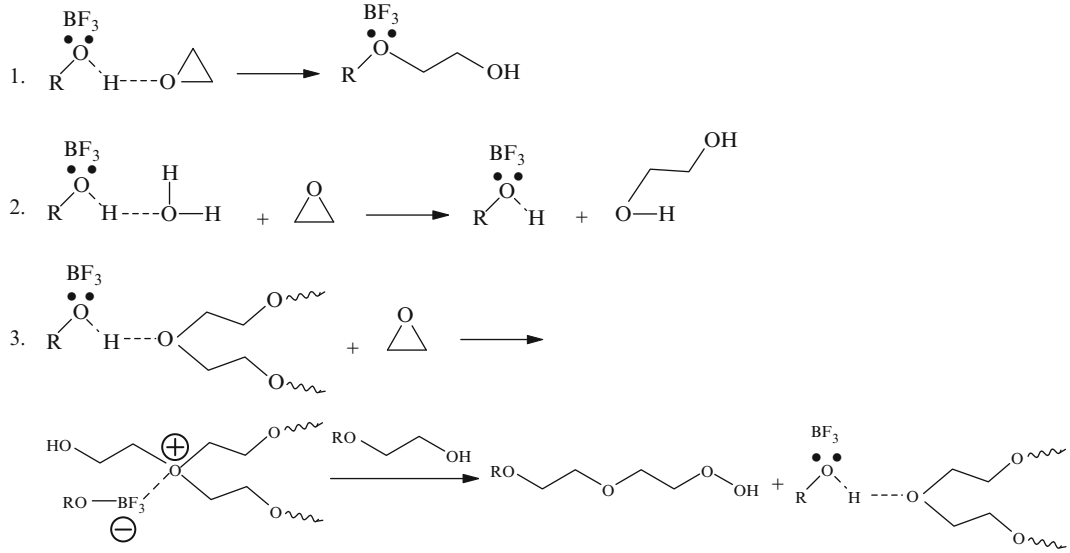
The initiation step depends upon formation of oxonium ions. Because a carbon cation intermediate is indicated, it was suggested [4] that the propagation probably occurs by ether exchange that results from a nucleophilic attack by the monomer on the oxonium ion.

Boron trifluoride forms complexes with oxygen-containing compounds, like water, alcohols, and ethers. When it initiates the polymerization of epoxides, it can associate simultaneously with several different moieties. These are the monomeric cyclic ethers, as well as the open-chain polymeric ether groups, and the hydroxy groups on the chain ends. In addition it can also associate with the hydroxy groups of water. The following illustration shows the type of equilibrium that can take place [2]:

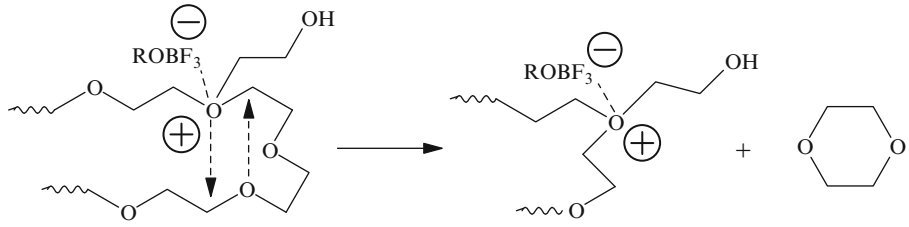
The alcohols and open-chain ethers have comparable basicities toward the coordinated acid ROH: BF_3. Ethylene oxide, on the other hand, is much less basic than the open-chain ethers [6]. In the initiation step, therefore, the monomer reacts with the coordinated acid [1]:



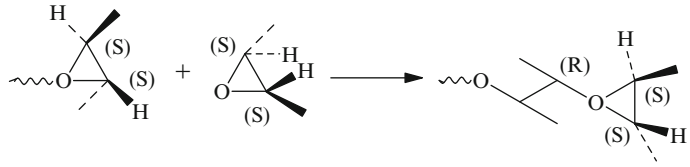
During propagation three different reactions can occur [2]:



This reaction is also accompanied by formation of dioxane. It is actually a step of depolymerization:

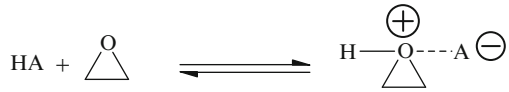


The ring-opening reaction, a nucleophilic substitution, usually takes place with an inversion of configuration at the carbon atom that undergoes the nucleophilic attack [8, 9, 11]. This can be illustrated as follows:

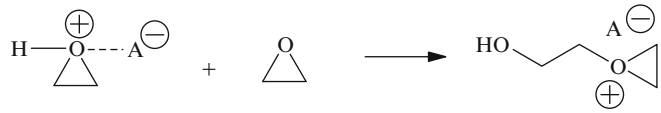


Alkyl substituents on the ethylene oxide ring enhance the process of cationic polymerization. For instance, ethylene oxide yields only low molecular weight oils with strong Lewis acids. Tetramethylethylene oxide, on the other hand, is converted readily by BF_3 into high molecular weight polymers that are insoluble in common solvents [10].

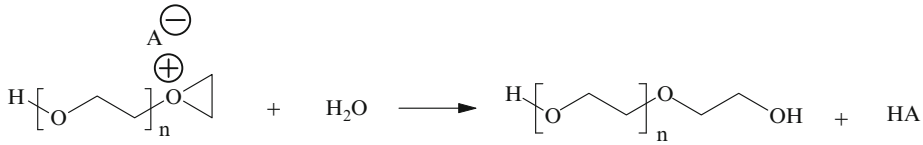
When proton donors initiate the polymerizations of epoxides, only low molecular weight products result. The reaction is quite straightforward. Oxonium ions form during the initiation step as follow:



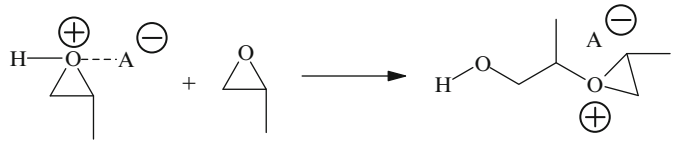
Propagation is the result of a ring-opening attack by a monomer:



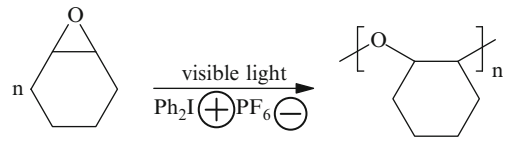
Chain-growth can terminate by a reaction with water:

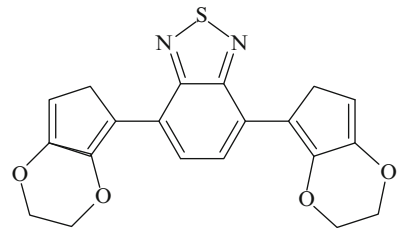


In cationic polymerizations of propylene oxide the ring-opening step involves a direct attack on the oxonium ion at the carbon that bears a more labile bond to the oxygen:



Cationic ring-opening polymerization of oxiranes can also be carried out photochemically (photochemical reactions are discussed in Chap. 10). Yagci and coworkers reported polymerizations of cyclohexene oxide with the aid of highly conjugated thiophene derivatives [12]. The reaction is illustrated as follows:



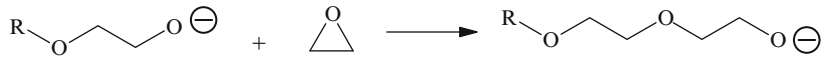


The cationic polymerization was initiated at room temperature upon irradiation with light in the visible region in CH_2Cl_2 solutions in the presence of diphenyliodonium hexafluorophosphate and the thiophene derivative. According to the suggested mechanism, Ayodgan et al. [12] discuss the formation of *exciplex* (see Chap. 10) by the absorption of light. Subsequent electron transfer from excited Photosensitizer to iodonium ion yields radical cations of the thiophene derivatives. The resulting strong Bronsted acid derived from this process catalyzes the cationic polymerization.

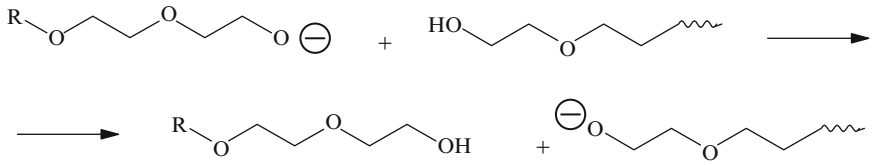
5.3.2 Anionic Polymerization

Anionic polymerizations of ethylene oxide were originally observed as early as 1894 [13]. A step-growth mechanism for these polymerizations was proposed later [14]. This mechanism is now well established [14]. The conversion increases linearly with time and the molecular weight also increases with conversion. Reactions with bases like sodium or potassium hydroxides or alkoxides yield only low molecular weight polymers. The initiation, an S_N2 displacement, results in formation of an alkoxide ion:

Subsequent propagation may occur by nucleophilic displacement involving a new alkoxide ion formation in each addition:

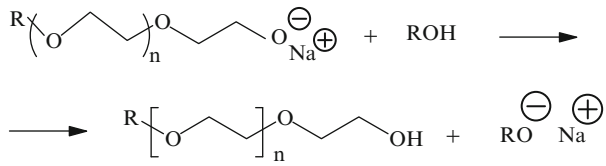


Termination takes place by a transfer to a hydroxy group of another molecule. It can also take place to a terminal hydroxyl group of a formed polymer, which starts new chain-growth from the second unit:



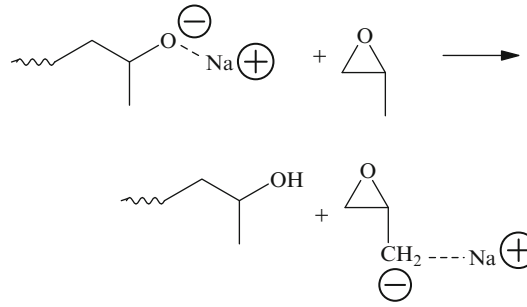
The chain ends remain active and higher molecular weights can be obtained by further additions of the monomer.

The reaction is often more complex than is shown above, because many such polymerizations, catalyzed by alkali hydroxides or alkoxides, are carried out in the presence of alcohols. This is done to achieve a homogeneous system. Such conditions, however, lead to exchange reactions:

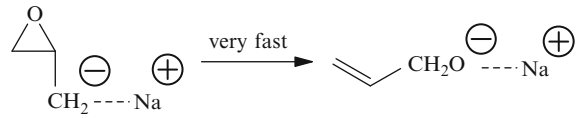


Of course, the exchanges, as shown above, affect the kinetics of the process. The extent of these reactions is subject to the acid strength of the alcohols present, including the terminal hydroxyl groups of formed polymers. If their acidities are approximately equal, the exchange reactions take place throughout the whole course of the polymerization [2].

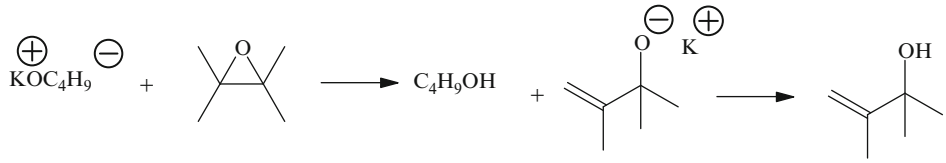
One of the reasons for the relatively low molecular weights of the products is the low reactivity of the epoxide ring toward anionic propagation. Another reason is the tendency to chain transfer to monomers, particularly in polymerizations of substituted ring structures, like, for instance, in propylene oxide:



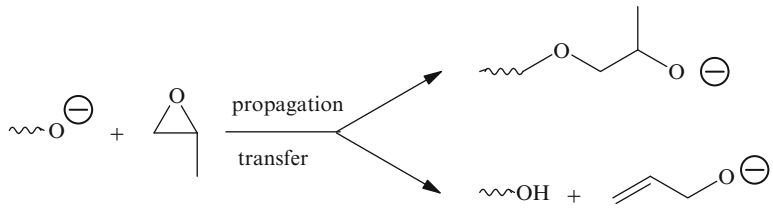
The newly formed species rearranges rapidly:



Such transfer reactions are E-2 type eliminations. This was shown on tetramethylethylene oxide that undergoes the reaction when treated with catalytic amounts of potassium *t*-butoxide [5]:

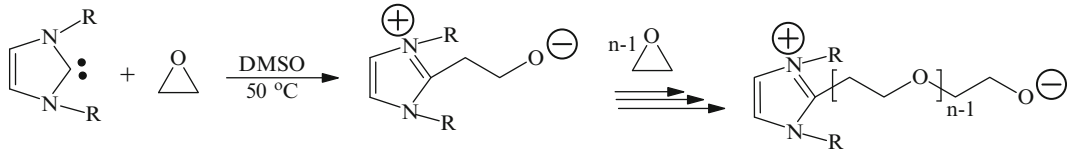


In propylene oxide polymerization, therefore, the E-2 type elimination reaction is in competition with propagation:



There are both allyl and propenyl ether end groups in the products, according to the infra-red spectra [5]. This suggests that in addition to the E-2 type elimination, an intramolecular transfer takes place by allylic hydrogen.

Raynaud et al. reported carrying out ring-opening polymerizations of ethylene oxide initiated by heterocyclic carbene [15]. The reaction yields high molecular weight polymers. It is illustrated as follows:



where *R* can be a propyl or a tertiary butyl group.

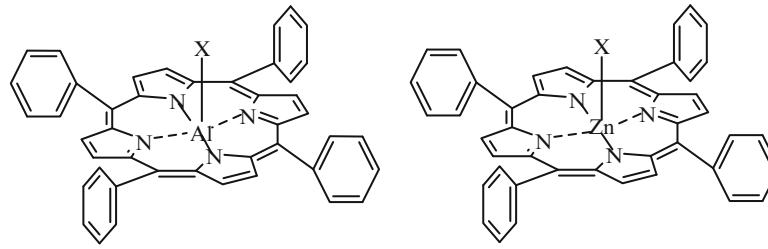


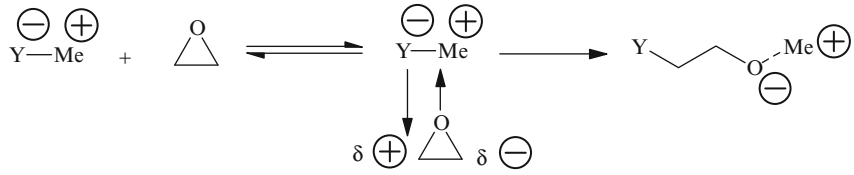
Fig. 5.1 Metalloporphyrin catalysts. X = methyl, methoxy, or other groups

5.3.3 *Polymerization by Coordination Mechanism*

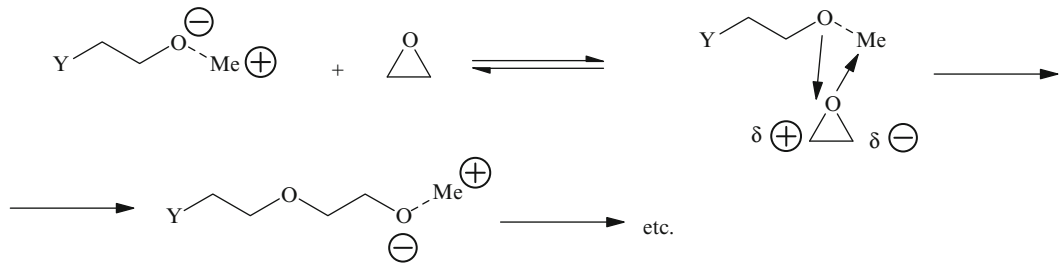
The coordination catalysts for these reactions are diverse. They can be compounds of alkaline earth metals, like calcium amide, or calcium amide-alkoxide. They can also be Ziegler–Natta type catalysts. These can be alkoxides of aluminum, magnesium, or zinc combined with ferric chloride. Others are reaction products of dialkylzinc with water or alcohol. They can also be bimetallic μ-oxoalkoxides, such as $[(RO)_2AlO_2]Zn$. Other catalysts are aluminum or zinc metalloporphyrin derivatives (see Fig. 5.1).

From propylene oxide these catalysts yield crystalline, isotactic polymers [16]. Living polymerizations with metalloporphyrin derivatives are difficult to terminate and are, therefore, called by some ***immortal*** [18]. Catalysts like, $(C_6H_5)_3$–$SbBr_2$–$(C_2H_5)_3N$ in combination with Lewis acids also yield crystalline poly(propylene oxide). Others, like pentavalent organoantimony halides are useful in polymerizations of ethylene oxide [19].

Polymerizations of epoxides by ***coordination*** mechanism result in high molecular weight products. The details of the reaction mechanism have not been fully resolved yet, but it is commonly believed to involve coordination of the monomers to electrophilic centers of the catalyst. This is followed by activation for an attack by the anion [2]. Such mechanism [1] can be illustrated by the following reactions:

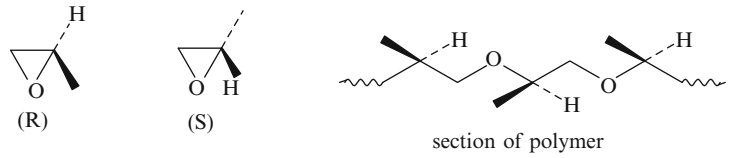


where Me means metal.

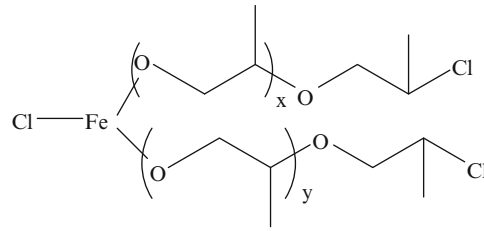


where, Me represents the metal catalyst.

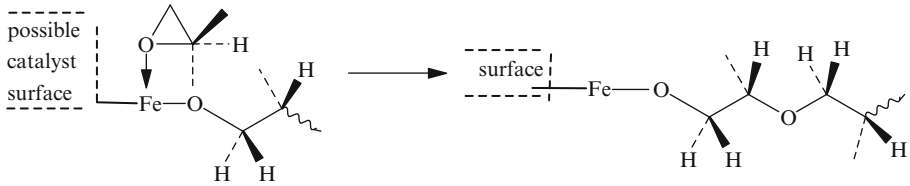
Ferric chloride polymerizes propylene oxide, a monomer with an asymmetric carbon atom, with retention of asymmetry in the backbone [3]. The products of polymerization contain either optically active polymers or racemic mixtures, depending upon the monomers used. When only a pure optical isomer monomer is used the products are crystalline polymers composed of the same optically active units:



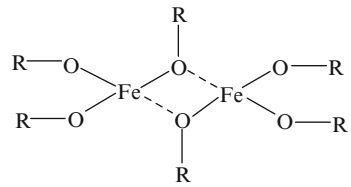
The polymers are fairly high in molecular weight, approximately 100 times greater than the products from KOH initiations. Propylene oxide initially reacts with ferric chloride to form an oligomer, a chloropolyalkoxide. The material contains approximately four or five propylene oxide repeat units. This forms two different halogen sites. It can be illustrated as follows:



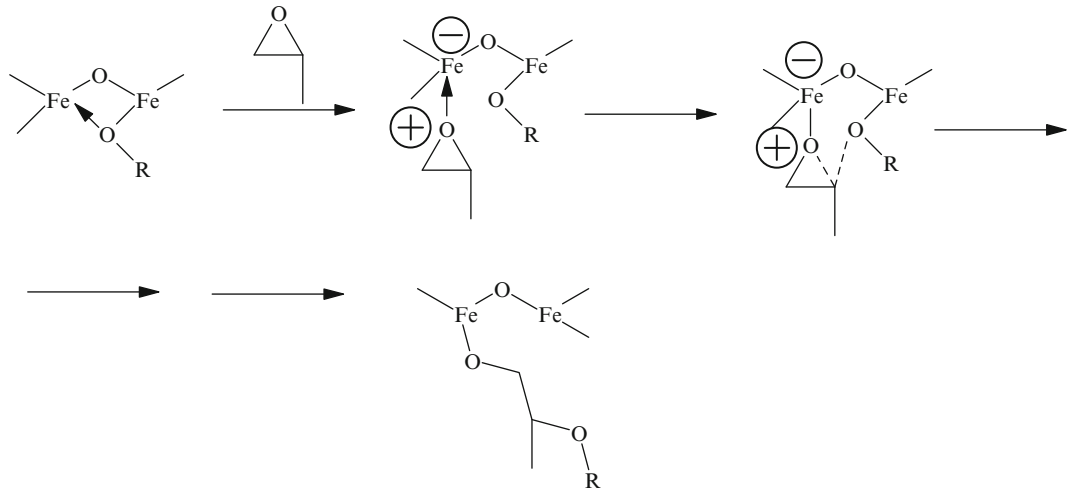
The above compound may be the catalyst or one closely related to it for forming stereoregular polymers. Water appears to play a role, because the proportion of crystallinity increases with addition of water. When water is added in a molar ratio of 1.8:1.0 of water to iron, the proportion of crystalline to amorphous fraction increases from 0.13 to 0.86. Price and Osgen [17] suggested that the polymerization proceeds in a step-growth mechanism as follows:



The solid surface of the catalyst causes the transition state to be more compressed. Steric repulsions between the incoming monomer and the ultimate unit are minimized if the incoming monomer molecule is forced to be ***trans*** to the methyl group of the previous unit. Such a conformational approach also results in minimum repulsion between the incoming monomer and the bulky growing polymer chain [18–20]. Also, ferric alkoxides are associated in nonpolar solvents. A dimer may have the following structure:



By comparison, intramolecular chelation can be expected to reduce the degree of association of the catalyst. Addition of water results in increased association after hydrolysis of the ferric alkoxide. This may explain the effect of promoting stereoregularity by addition of water [20]. The ferric alkoxide catalyst can also be made highly stereospecific by partial hydrolysis and still remain soluble in ether, the polymerization medium [21]. This led to a suggestion [22] that the catalyst may contain active Fe–O–Fe bonds. Such bonds would be formed from condensation of partially hydrolyzed alkoxide derivative. The monomer insertion between the iron–oxygen bonds can be illustrated as follows:

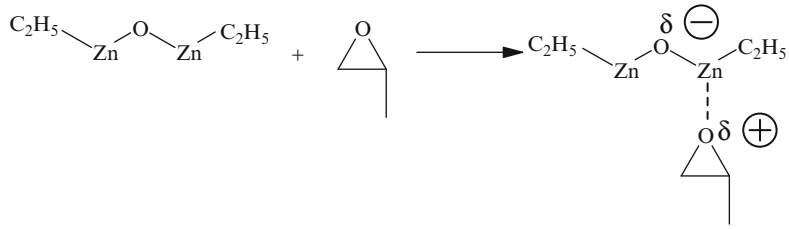


The forces of interaction between the iron atoms and the various oxygen atoms as shown above assure a *cis* opening of the epoxide ring. The mechanism of the reaction of the ferric alkoxide is an S_N2 type. There is, therefore, increased restriction on the conformation of the monomer unit as it approaches the reaction center [22].

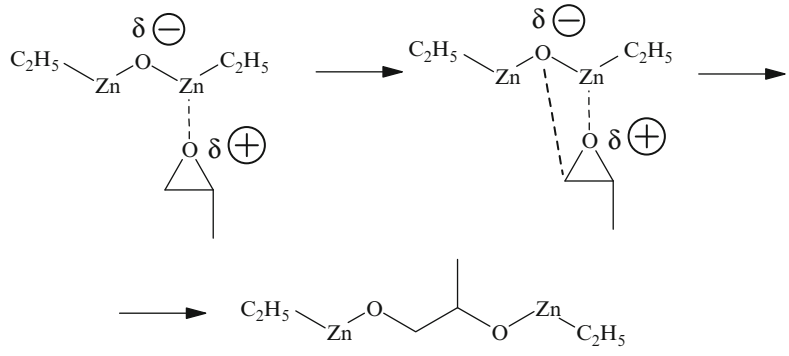
Many other coordinated anionic catalysts that are *metal alkoxides* or *metal alkyls* are also much more reactive in the presence of water or alcohols. The function of these co reactants is to modify the catalyst itself. For instance, diethylzinc combined with water in a ratio of 1:1 yields a very reactive species. The exact nature of the catalyst is still not fully established, however, the reaction product is pictured as follows [23, 24]:

$$C_2H_5 - Zn - O - Zn - C_2H_5$$

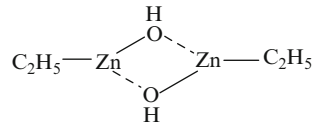
Several reaction mechanisms were proposed. One suggested pathway for propylene oxide polymerization pictures an initial coordination of the monomer with a cationically active center [25]:



The propagation is preceded by an intramolecular rearrangement:

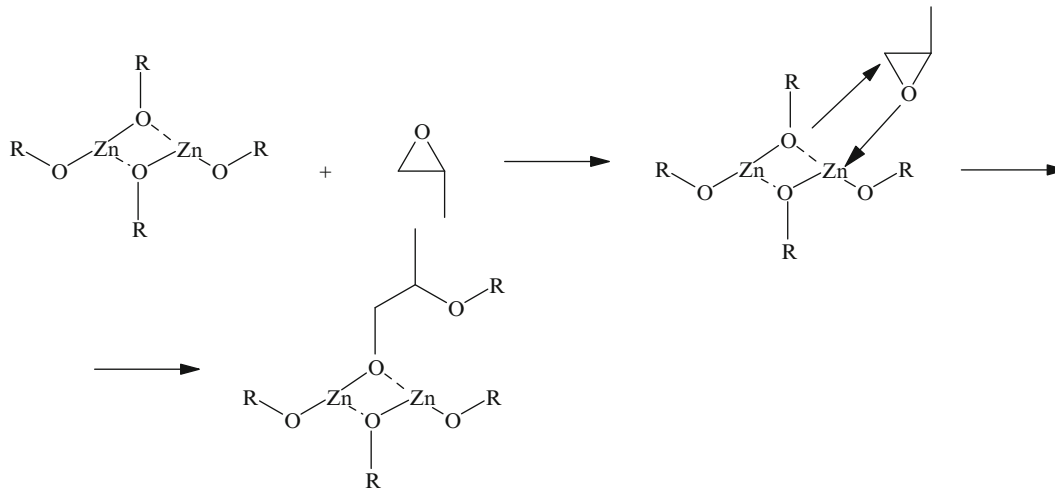


Another mechanism is derived from the structure of the diethylzinc–water catalyst [25] that is visualized as a dimer:



A similar structure pictured can be shown for diethylzinc–alcohol. The asymmetric induction is suggested to takes place during coordination of the monomer to the catalyst site. This is a result of indirect regulation that results form interactions between the monomer and the penultimate unit [25].

In yet another mechanism the initial coordination and subsequent propagation steps are pictured as follows [26]



While the detailed structures of most catalyst sites are still unknown, it was established that stereoselectivity does not come from the chirality of the growing chain end. Rather it is built into the catalyst site itself [27, 28]. Normal preparations of the catalysts give equal numbers of (*R*) and (*S*) chiral catalyst sites. These coordinate selectively with (*R*) and (*S*) monomers respectively in the process of catalytic-site control [23].

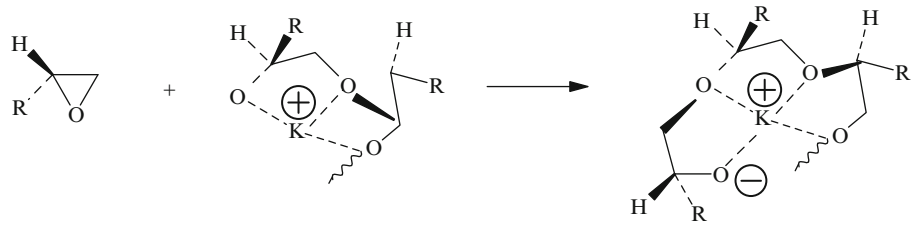
5.3.4 Steric Control in Polymerizations of Oxiranes

Cationic polymerizations of oxiranes are much less isospecific and regiospecific than are anionic polymerizations. In anionic and coordinated anionic polymerizations, only chiral epoxides, like propylene oxide, yield stereoregular polymers. Both pure enantiomers yield isotactic polymers when the reaction proceeds in a regiospecific manner with the bond cleavage taking place at the primary carbon.

In all polymerizations of oxiranes by cationic, anionic, and coordinated anionic mechanisms, the ring-opening is generally accompanied by an inversion of the configuration at the carbon where the cleavage takes place. A linear transition state mechanism involving dissociated nucleophilic species has been proposed [15]. Yet, there are some known instances of ring-opening reactions of epoxies that are stereochemically retentive. For instance, ring opening of 2,3-epoxybutane with $AlCl_3$ results in

formation of 3-chloro-2-butanol, where the *cis* and *trans* epoxides are converted to the *erythro* and *threo*-chlorohydrins. Inoue and coworkers [19] found, however, that polymerizations of *cis* and *trans* 2,3-epoxybutanes take place with inversion of configuration when aluminum 5,10,15,20-tetraphenylporphine and zinc 5,10,15,20-tetraphenyl-21-methylporphine catalysts are used. To explain the inversion, Inoue and coworkers proposed a linear transition state mechanism that involves a simultaneous participation of two porphyrin molecules [19]. One porphyrin molecule accommodates a coordinative activation of the epoxide and the other one serves as a nucleophile to attack the coordinated epoxide from the back side.

Potassium hydroxide or *alkoxide* polymerizes racemic propylene oxide with better than 95% regioselectivity of cleavage at the bond between oxygen and the carbon substituted by two hydrogens. The product, however, is atactic. Both (*R*) and (*S*) propylene oxides react at the same rate. This shows that the initiator is unable to distinguish between the two enantiomers of propylene oxide. When *t*-butyl ethylene oxide is polymerized by KOH it yields a crystalline product. This product is different in its melting point, X-ray diffraction pattern, and solution-NMR spectra from the typical isotactic polymers. It contains alternating isotactic and syndiotactic sequences [31]. It was suggested [34] that this may be a result of the configuration of the incoming monomer being opposite to that of the penultimate unit. Chelation of the paired cation ($K\oplus$) with the last and the next to the last oxygen is visualized. Geometry of such a chelate is dictated by the requirement that the penultimate *t*-butyl group be in an equatorial conformation. This makes it reasonable to postulate that the necessary preference for the incoming monomer is to be opposite to that of the penultimate unit [31]:

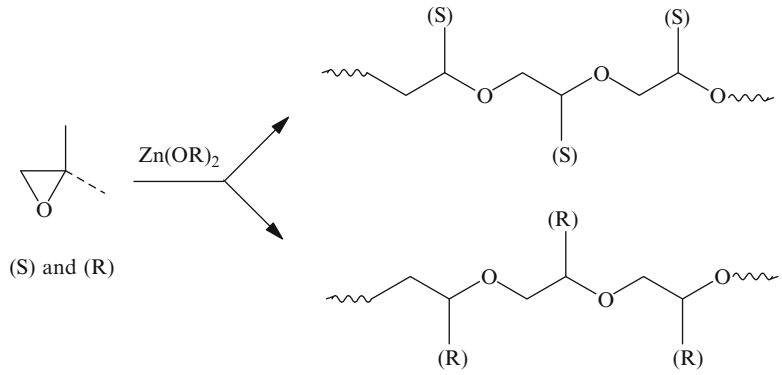


When phenyl glycidyl ethers are polymerized under the same conditions, the steric arrangement is all isotactic rather than isotactic–syndiotactic [31]. Price explained that on the basis of the oxygen in C_6H_6–O–CH_2 seeking to coordinate potassium ions in the transition state [31]. In the case of *t*-butylethylene oxide, on the other hand, the tertiary butyl group tends to be as far as possible away from the potassium ion [34]. This is supported by the observation that *p*-methoxy and *p*-methyl groups on phenyl glycidyl ether increase the crystalline portion of the polymer, while the *p*-chloro substituent decreases it [31].

Most stereoselective coordination catalysts polymerize propylene oxide to yield polymers that contain high ratios of isotactic to syndiotactic sequences. Large portions of amorphous materials, however, are also present in the same materials. These amorphous portions contain head to head units that are imperfections in the structures [29, 30]. For every head to head placement, one (*R*) monomer is converted to an (*S*) unit in the polymer [23]. This shows that at the coordination sites abnormal ring openings occur at the secondary carbon with an inversion of the configuration and results in head to head placements [23, 31]. Also, *erythro* and *threo* isomers units are present. The isotactic portion consists almost exclusively of the *erythro* isomer while other amorphous fraction contains 40–45% *erythro* and 55–60% *threo* [31]

All the above information is indirect evidence that a typical catalyst, such as $(C_2H_5)_2Zn$–H_2O contains isotactic and amorphous sites. The isotactic sites are very selective and coordinate either with (*R*) or with (*S*) monomers. The amorphous sites, on the other hand, coordinate equally well with both (*R*) and (*S*) monomers. In addition, there is little preference for attack on either the primary or the secondary carbons during the ring-opening reactions [23].

According to a Tsuruta mechanism [36] the first step in propylene oxide polymerization, with catalysts like zinc alcoholates, is the coordination of the ether oxygen onto a zinc atom. The second step is a nucleophilic attack at the oxirane ring by the alkoxy ion. Almost all the bond cleavage takes place at the CH_2–O bond. This results in retention of the steric configuration of the carbon atom at the C–H group. The next oxirane molecule repeats the process, coordinates with the same zinc atom and then undergoes the ring-opening reaction to form a dimer. Repetition of this process many times yields a high molecular weight polymer [36]:



The catalyst can also be ZnR_2–CH_3–OH.

Special catalyst complexes, like $[Zn(OCH_3)_2 \cdot (C_2H_5OCH_3)_6]$, form through carefully control of reaction conditions by adding 16 moles of methyl alcohol to 14 moles of diethylzinc in heptane under an argon atmosphere. X-ray analysis shows that two different structures [36]. One of them is a centrosymmetric complex of two enantiomorphic distorted cubes that share a corner Zn atom. The two would be equivalent if they were not distorted. Another structure, also centrosymmetric, consists of two enantiomorphic distorted structures that resemble "chairs without legs," where the surfaces share a common seat. Both types of complexes are active initiators for polymerization of propylene oxide. Each has two enantiomorphic sites for polymerization. Based on that knowledge, NMR spectra and GPC curves, Tsuruta suggested the following mechanism of a monomer coordinating with the catalyst [36] (see Fig. 5.2). The bonds at the central zinc atom are loosened and coordination takes place with methyl-oxirane molecule at the central atom. Cleavage at the O–CH_2 bond of the oxirane takes place by a concerted mechanism. If the bond loosening takes place at the *d* cube and the nucleophilic attack takes place at one of the methoxy groups on that cube then chirality around the central zinc will favor *L* monomer over the *D* monomer. This is the origin of the *l** catalyst site. If the bond loosening takes place in the *l* cube the catalyst site will have *d** chirality. Because the probability of bond loosening in the *d* cube is exactly the same as in *l* cube, an equal number of *l** and *d** sites should be expected to form. These two cubes become a source of *d** and *l** chiral nature [35].

5.4 Polymerization of Oxetanes

Oxetanes (or oxacyclobutanes) are preferably polymerized in solution to maintain temperature and stirring control. It is necessary to purify both the monomer and the solvent, because impurities interfere with attainment of high molecular weight.

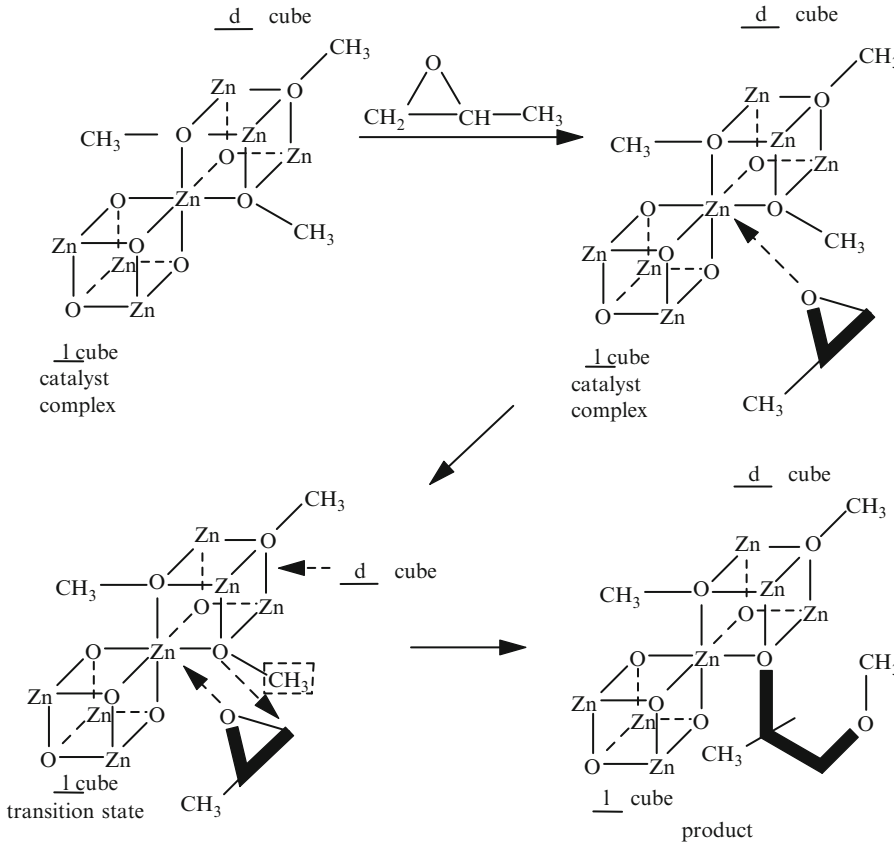


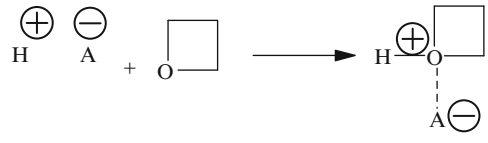
Fig. 5.2 Tsuruta mechanism

5.4.1 The Initiation Reaction

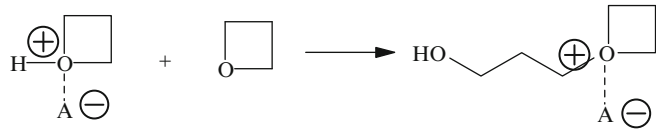
Theoretically, any Lewis acid can catalyze oxetane polymerizations. However, these acids differ considerably in their effectiveness. Boron trifluoride and its etherates are the most widely reported catalysts. Moisture must be excluded, as it tends to be detrimental to the reaction [35].

Chlorinated hydrocarbon solvents, like methylene chloride, chloroform and carbon tetrachloride, are common choices. The reactions are usually conducted at low temperatures and there are indications that the lower the reaction temperature the higher the molecular weight of the product

It was reported that when oxetane polymerizations are carried out with boron trifluoride catalyst in methylene chloride at temperatures between 0 and −27.8°C a cocatalyst is not required [32]. The product, however, is a mixture of linear polymer and a small amount of a cyclic tetramer. This is in agreement with an earlier observation that the polymerizations of oxetane are complicated by formations of small amounts of cyclic tetramers [33]. Other catalysts, like protonic acids, capable of generating oxonium ions, will also polymerize oxetane. Such acids are sulfuric, trifluoroacetic, and fluorosulfuric. The initiation reaction can be illustrated as follows:



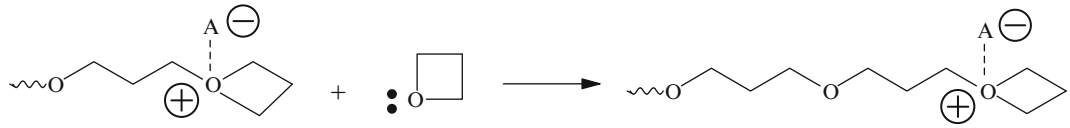
The adduct reacts with cyclic ether:



When complexes of Lewis acids with active hydrogen compounds initiate the polymerizations, such complexes acts as protonic acids. On the other hand, etherates initiate by forming oxonium ions and may involve alkyl exchange reactions with the monomer:

5.4.2 The Propagation Reaction

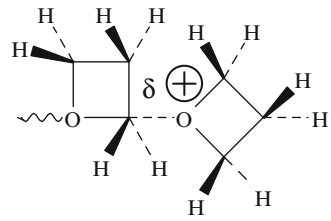
The propagation takes place via tertiary oxonium ions [37, 38]:



A cyclic oligomer forms in some instances in addition to the polymer [40]. For instance, in polymerizations with BF_3 in methylene chloride at low temperatures a cyclic tetramer forms, probably by a backbiting process [40].

The oxonium exchange reactions may occur with the polymer ether linkages as well as with cyclic tetramers that form, as shown above. The concentrations of the oxonium ions of the ether group on the polymer and on the cyclic tetramers, however, are very small [42]. Polymerizations with PF_5, on the other hand, or with $(C_2H_5)_3OPF_6$ either in bulk or in methylene chloride solutions, yield no significant amounts of cyclic oligomers [43].

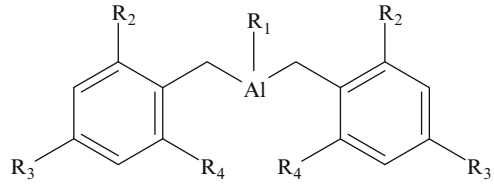
The activation energy of polymerizations of oxetane monomers is higher that that of tetrahydrofuran (see next section). This indicates that the orientation of the cyclic oxonium ion and the monomer is looser in the S_N2 transition state [42]:



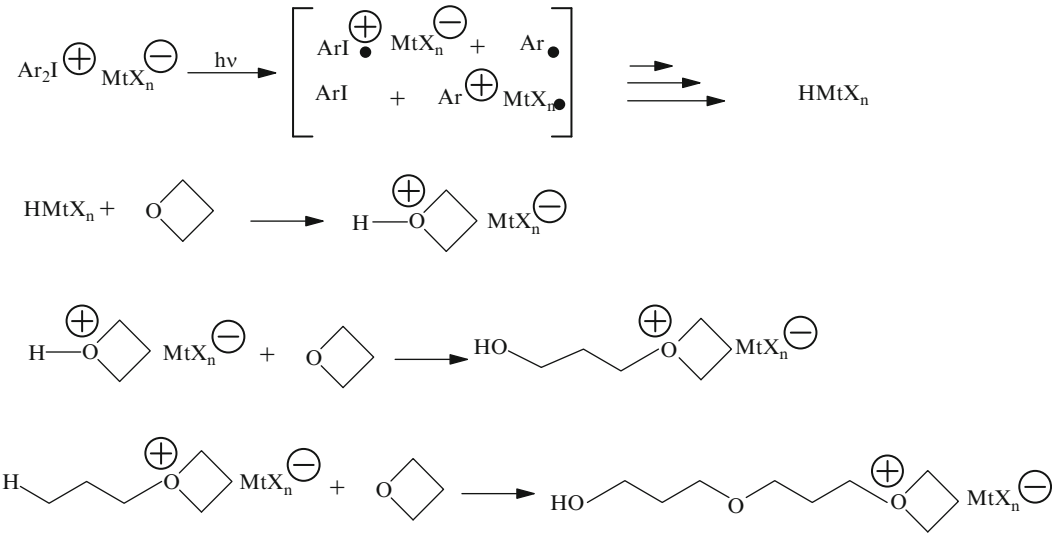
In principle, stereospecificity should be possible in substitute polyoxycyclobutanes, such as 2-methyl, 3-methyl, and others. The 2-methyl derivative however, yields amorphous polymers. This is due to the monomer's unsymmetrical structure [33] NMR studies of the microstructure of polymers from 3,3-dimethyloxetane [44] and 2-methyloxetane [43] led to no conclusions about the manner of ring opening. The predominant head to tail structures may result from attacks at either the methylene or the methine carbons next to the oxonium ions of the propagating species.

Oxetane compounds also polymerize with the aid of aluminum trialkyl–water acetylacetone catalysts [45, 46]. The reactions can take place at 65°C in heptane and yield very high molecular weight polymers. These polymerizations, however, are ten times slower that similar ones carrier out with propylene oxide, using the same catalyst. The reaction conditions and the high molecular weights of the products led to assumption that coordinated mechanisms of polymerizations take place [46].

Also, it was reported [218] that quaternary onium salts coupled wit bulky organoaluminum diphenolates initiate controlled (living) coordinate anion polymerizations of oxetane to give narrow molecular weight distribution polyethers The catalyst system consists of onium salts, such as quaternal ammonium phosphonium halides that are combined with sterically hindered methylaluminum diphenolates [47]



Crivello reported frontal photopolymerization of oxetane [48]. He proposed a mechanism for the polymerization that is shown in the following scheme:



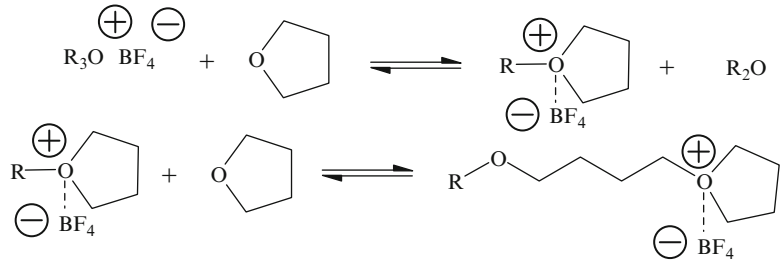
Crivello reported that only diaryliodonium salts were used as cationic photoinitiators in this study. Photo activation was carried out by UV irradiation prior to thermal initiation. Initiation was carried out using an electrically heated wire immersed in the monomer. The velocity of the resulting propagating front is quite high with the temperature of the front reaching 110°C.

5.5 Polymerization of Tetrahydrofurans

Lewis acids, carbon cations, salts of oxonium ions, and strong protonic acids initiate polymerizations of tetrahydrofuran. The reactions can be conducted in solution or without a solvent It was originally polymerized [49, 50] with a trialkyloxomum salt, $R_3O{\bullet}BF_4$.

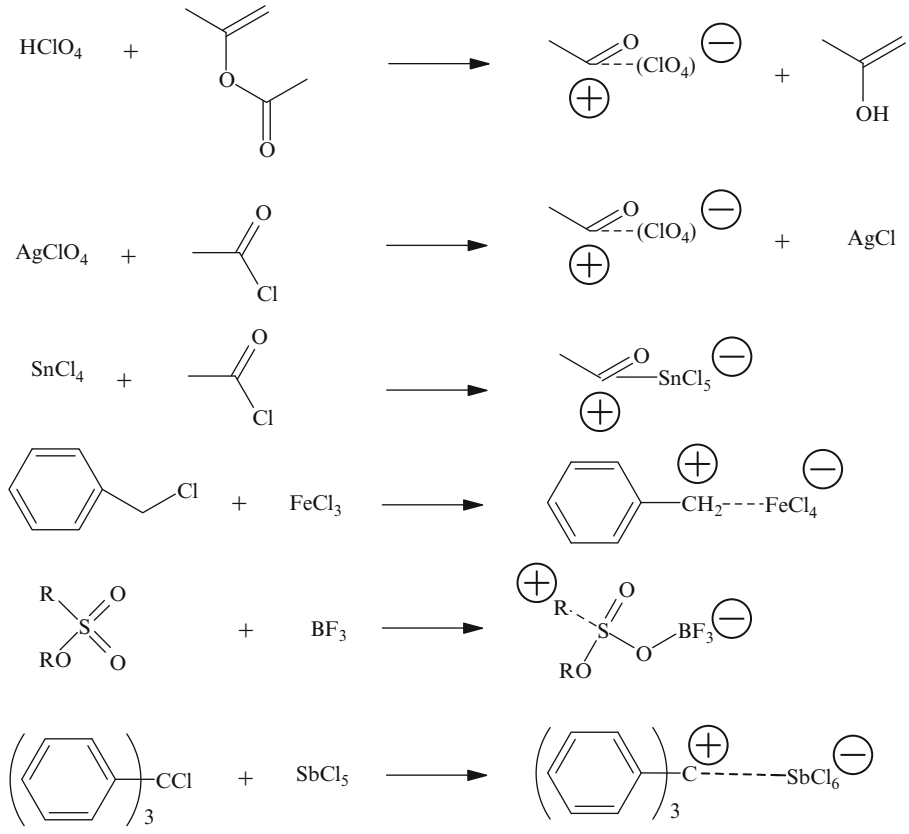
5.5.1 The Initiation Reaction

The initiations result from coordination of the cation catalysts with the oxygen of the monomers to form oxonium ions [48, 49]. This weakens the oxygen–carbon bonds and leads to ring openings after reactions with a second molecule of the monomer. New oxonium ions are generated in the process:



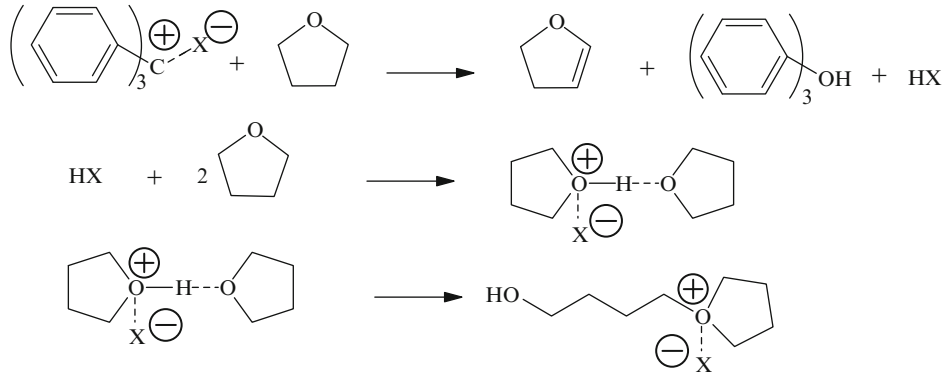
Some active oxonium salts are [48–50]: $[(C_2H_5O)_3O]^+$ $BF4^-$, $[(C_2H_5O)_3O]^+$ $SbCl_6^-$, $[(C_2H_5O)_3O]^+$ $FeCl_4^-$, and $[(C_2H_5O)_3O]$ $^+AlCl_4^-$

Examples of carbon cations that can initiate polymerizations of tetrahydrofuran, as well as some other cyclic ethers are:

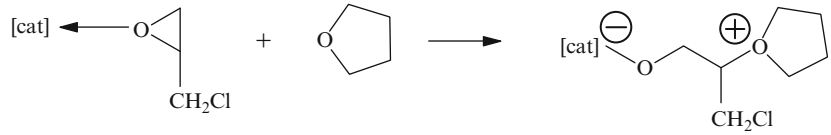


The initiation mechanisms, however, by many carbon cations as, for instance, by triphenylmethyl cations, are not straightforward. Initially, hydride ions are abstracted from the monomers to form triphenylmethanes [51–53]. Simultaneously, acids are released from the counterions. The acids

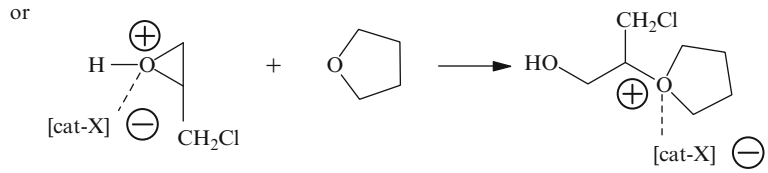
become stabilized by complexing with monomers. After that, the complexes react slowly with additional monomers to form the propagating oxonium ions. This makes the acids the real initiators::



Other initiators for tetrahydrofuran polymerizations also include Lewis acids in combinations with "promoters." These are complexes of Lewis acids, like BF_3, SnCL1, or $C_2H_5AlCl_2$ with epirane compounds like epichlorohydrin [42]. The small ring compounds are mote reactive toward many Lewis acids, or protonic acids, then tetrahydrofuran and act as promoters of the initiation reactions. The initiations in the presence of small quantities of oxirane compounds, for instance, can be illustrated as follows:



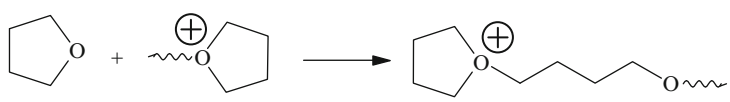
or



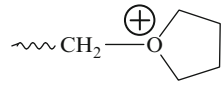
Strong Bronsted acids form when diaryliodonium salts. like BF_4^-, AsF_6^-, PF_6^- and SbF_6^- are reduced with compounds like ascorbic acid in the presence of copper salts. such acids also initiate the polymerizations of tetrahydrofuran, cyclohexene, and *s*-trioxane [54].

5.5.2 *The Propagation Reaction*

The propagation process is a succession of nucleophilic attacks by fn electrons on the oxygens of the monomers upon the α-carbons of the heteroatoms of the ultimate polymerizing species [1]:



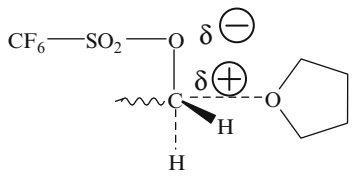
The products of these reactions are linear. Actually, this is common to polymerizations of many heterocyclics. The propagation reactions proceed by stepwise additions of monomer by S_N2 mechanism to the growing ends of the propagating chains. The NMR spectra of the growing chains only shows a presence of the oxonium ions [55, 56]:



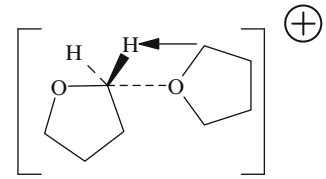
The oxonium ions could, in principle, be in equilibrium with minute quantities of carbon cations, $-CH_2^+$ that are more active. All evidence, to date, however, shows that in tetrahydrofuran polymerizations the presence of carbon cations is negligible in the propagation process [57]. Also, the rate constant for propagation of free macroions with the counterions is equal, within experimental error, to the rate constant for macroions–counterion pairs. This does not appear to depend upon the stricture of the anion studied. The above information, however, was obtained on large anions. With smaller anions, differences in the rates of propagation of macrocations and those of macroion–counterion pairs has not be ruled out.

An S_N2 attack requires that the reaction occur at the oxygen carbon bond. In such an attack steric requirements are less restricted than they are in an anionic polymerization. In addition, positive and negative charges in the macroion-pairs that contain the oxonium ions are dispersed and the anions are large. This means that the electrostatic interactions are less important in cationic polymerizations of this type than they are in anionic ones.

When the polymerization of tetrahydrofuran is carried out with the aid of CF_3SO_3H, both covalent and ionic species are present They can be detected during propagation by means of NMR spectroscopy. Both species exist in a mobile equilibrium. Solvent polarity, apparently, influences the position of such equilibria. In nitromethane, 95% of the growing chains are macroions. In carbon tetrachloride 95% of them are macroesters. In methylene chloride both species are present in the reaction mixture, approximately in equal amounts [58–62]. The propagation rate of macroions, however, is 10^2 times faster than that of the macroesters. As a result; chain growth even in carbon tetrachloride is still by way of the ions. The macroesters, therefore, can be considered as dormant species [59], or, as some suggest, even cases of temporary termination [59]. The much higher reactivity of the macroions is attributed to the contribution of the partially released strain in ionic species [49]. Macroions and macroesters can be illustrated as follows:



covalent



ionic

5.5.3 *The Termination Reaction*

The termination reactions in tetrahydrofuran polymerizations can depend upon the choice of the counterion, particularly if the reaction is conducted at room temperature [60]. In many reactions, the chains continue to grow without any considerable termination or transfer [63, 64]. Some refer to this process as "**living**" polymerization. thus in polymerizations of tetrahydmfuran [65] with PF_6^- or

SbF_6^- counterions the molecular weights of the products can be calculated directly from the ratios of the initiators to the monomers. The molecular weight distributions of the polymers from such polymerization reactions with PF_6^- and, SbF_6^- however, start out as narrow, but then broaden. This is believed to be due to transfer reactions with ether oxygen. It is supported by evidence that with SbF_6^- initiation, both termination and transfer reactions take place [65]. In addition, polymerizations of tetrahydrofuran, like those of the epoxides, can be accompanied by formations of some macrocyclic oligomers. This is often the case [66, 67] when strong acids are used as initiators. The proposed mechanism involves backbiting and chain coupling and results in linear polymers with hydroxyl groups and oxonium ions at opposite chain ends as well as some macrocycles.

The absence of linear oligomers is due to rapid reactions of the hydroxyl and oxonium ion end groups. This mechanism is quite general [67, 68] for ring-opening polymerizations of cyclic ethers initiated with string protonic acids. Substituted tetrahydrofurans generally resist polymerizations.

5.6 Polymerization of Oxepanes

Oxepanes are polymerized by various cationic initiators like $(C_2H_5)_3C^+BF_4^-$, $(C_2H_5)_3C^+SbCI_6^-$, BF_3-epichlorohydrin, and $SbCl_6$-epichlorohydrin [42].The reactions take place in chlorinated solvents, like methylene chloride. The rates of these reactions, however, are quite slow [42]. In addition, these polymerizations are reversible. The rates of propagation of the three cyclic ether, oxetane, tetrahydrofuran, and oxepane at 0°C fall is in the following order [42]:

$$\text{oxetane} > \text{tetrahydrofuran} > \text{oxepane}$$

At the same temperature oxetane is about 35 times as reactive as tetrahydrofuran, which in turn is about 270 times as reactive as oxepane. This cannot be explained on the basis of ring strain, nor can it be explained from considerations of basic strength. Saegusa suggested [42] that the differences in the propagation rates are governed by nucleophilic reactivities of the monomers. They are also affected by the reactivities of the cyclic oxonium ions of the propagating species and also by the steric hindrances in the transition states of propagation. Higher activation energy of oxepane is explained by increased stability of the seven-membered oxonium ion. The oxepane molecule has puckered structure, and the strain that comes from the trivalent oxygen is relieved by small deformations of the angles of the other bonds [42].

5.7 Ring-Opening Polymerizations of Cyclic Acetals

The cationic polymerizations of cyclic acetals are different from the polymerizations of the rest of the cyclic ethers. The differences arise from great nucleophilicity of the cyclic ethers as compared to that of the acetals. In addition, cyclic ether monomers, like epirane, tetrahydrofuran, and oxepane, are stronger bases than their corresponding polymers. The opposite is tree of the acetals. As a result, in acetal polymerizations, active species like those of 1,3-dioxolane, may exist in equilibrium with the macroalkoxy carbon cations and tertiary oxonium ions [69]. By comparison, the active propagating species in the polymerizations of cyclic ethers, like tetrahydrofuran, are only tertiary oxonium ions. The properties of the equilibrium of the active species in acetal polymerizations depend very much upon polymerization conditions and upon the structures of the individual monomers.

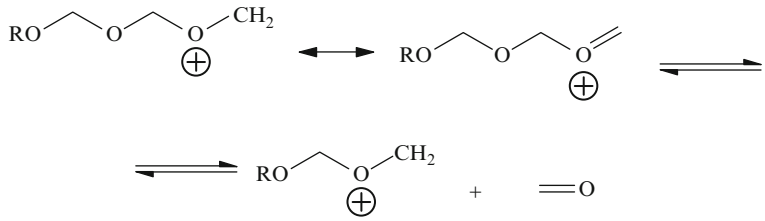
5.7.1 Polymerization of Trioxane

Trioxane is unique among the cyclic acetals because it is used commercially to form polyoxymethylene, a polymer that is very much like the one obtained by cationic polymerization of formaldehyde. Some questions still exist about the exact mechanism of initiation in trioxane polymerizations. It is uncertain, for instance, whether a cocatalyst is required with strong Lewis acids like BF_3 or $TiCl_4$.

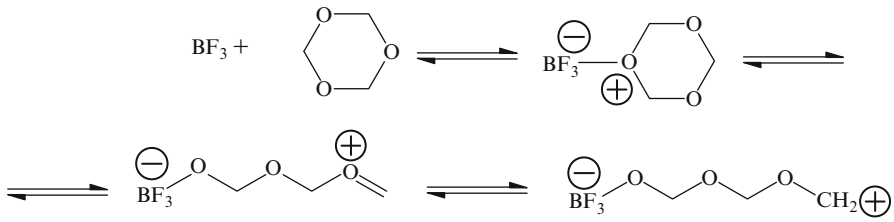
The cationic polymerization of trioxane can be initiated by protonic acids, complexes of organic acids with inorganic salts, and compounds that form cations [70]. These initiators differ from each other in activity and in the influence on terminations and on side reactions. Trioxane can also be polymerized by high-energy radiation [70]. In addition, polymerizations of trioxane can be carried out in the solid phase, in the melt; in the gas phase, in suspension, and in solution. Some of these procedures lead to different products, however, because variations in polymerization conditions can cause different side reactions.

Polymerizations in the melt above 62°C are very rapid. They come within a few minutes to completion at 70°C when catalyzed by ten moles of boron trifluoride. This procedure, however is only useful for preparation of small quantities of the polymer, because the exothermic heat of the reaction is hard to control.

Typical cationic polymerizations of trioxane are characterized by an induction period. During that period only oligomers and monomeric formaldehyde form. This formaldehyde, apparently, results from splitting the carbon cations that form in the primary steps of polymerization. The reaction starts after a temperature dependent equilibrium concentration of formaldehyde is reached [70].



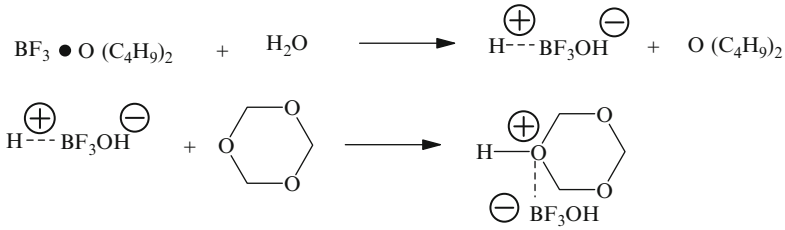
Several reaction mechanisms were proposed. One of them is based on the concept that Lewis acids, like BF_3 coordinate directly with an oxygen of an acetal. This results in ring opening that is induced to form a resonance stabilized zwiter ion [71]:



Resonance stabilizations of the adjacent oxonium ions lead to formations of carbon cations that are believed to be the propagating species. Propagations consist of repetitions of the sequences of addition of the carbon cations to the monomer molecules and are followed by ring opening. The above mechanism has to be questioned, however, because rigorously dried trioxane solutions in cyclohexane fail to polymerize with $BF_3{\cdot}O(C_4H_9)_3$ catalyst [72]. The same is true of molten trioxane [73]. It appears,

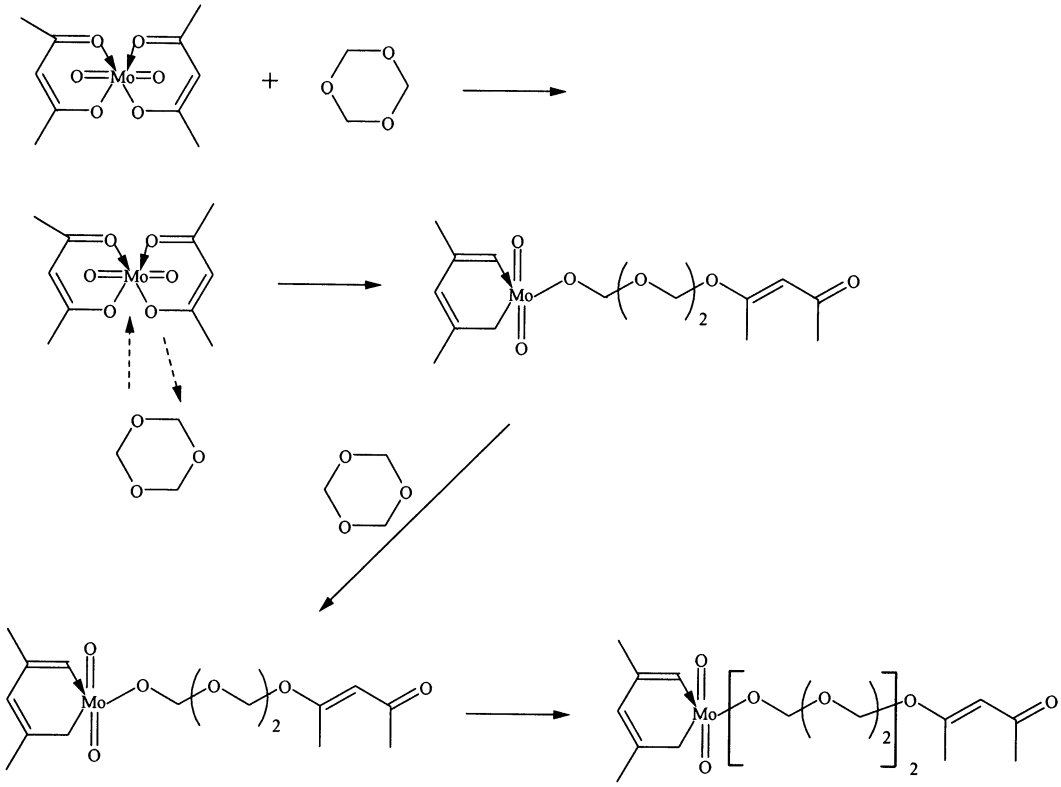
therefore, that BF_3-trioxane complexes don't form as suggested and do not result in initiations of the polymerizations. Additions of small quantities of water, however, do result in initiations of the polymerizations.

Another mechanism, is based on a concept that two molecules of BF_3 are involved in the initiation process [69]. This also appears improbable since without water BF_3 fails to initiate the reaction. the following mechanism, based on water as the cocatalyst was developed [73]:



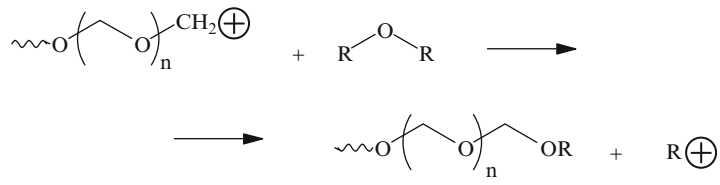
Chain growth in the reaction is accompanied by formations of tetraoxane and 1,3-dioxalane because of backbiting [71, 74].

Complex molybdenyl acetylacetones also act as catalysts for trioxane polymerization. The mechanism that is visualized involves formation of a coordinated intermediate [75]:

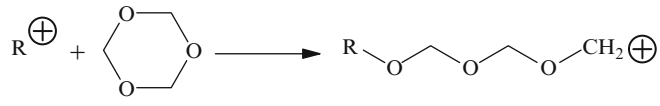


The termination mechanism and the catalyst requirement have not yet been fully explored.

Some transfer to water takes place during the reaction. As a result the polymer contains at least one terminal hydroxyl group [76]. Besides water, methyl alcohol and low molecular weight ethers also act as transfer agents [77].

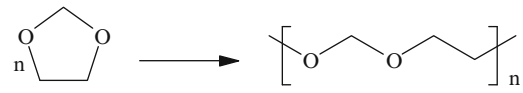


The new cation can initiate chain growth:

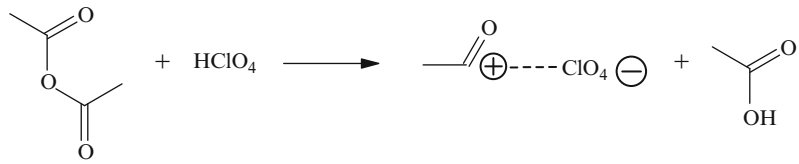


5.7.2 *Polymerization of Dioxolane*

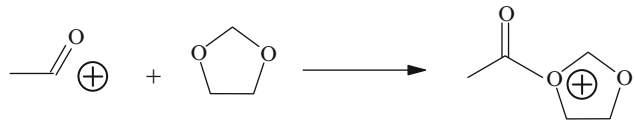
Polymerization of this cyclic monomer yields polymers that consists of strictly alternating oxymethylene and oxyethylene units [76]. the polymerization reaction can be induced by acidic catalysts, like sulfuric acid, boron trifluoride, *p*-toluenesulfonic, acid and phosphorous pentafluoride [76]:



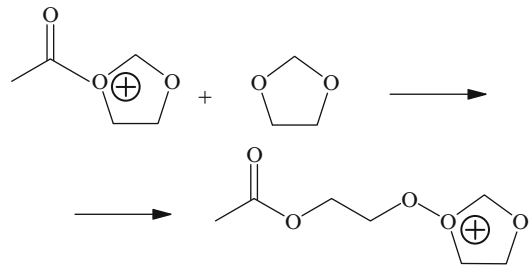
The polymers of molecular weight 10,000 or higher are tough solids that can he cold drawn. The following mechanism was proposed for the polymerizations that are initiated by reaction products of acetic anhydride with perchloric acid [78]:



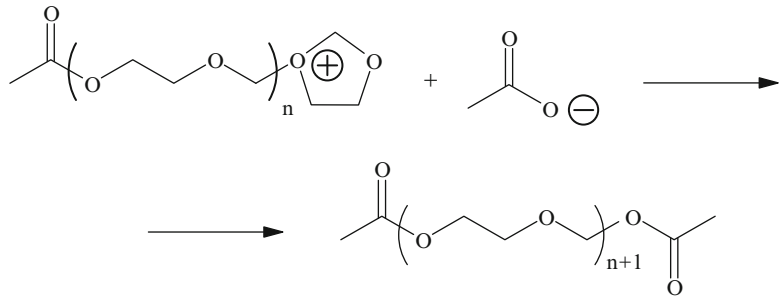
Initiation



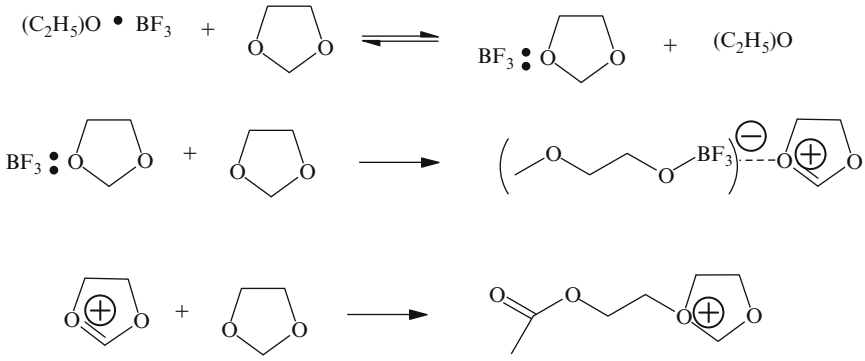
Propagation



Termination



Acetate groups are present at both end of the polymer molecules as shown above [78]. This was confirmed by analytical evidence. The initiation of dioxolane polymerization is pictured differently [79, 80]:

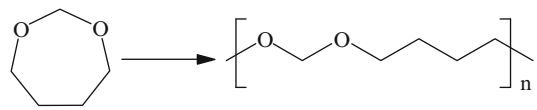


Chain cleavage can occur as a result of BF_3 complexation with an oxygen in a chain [80]:

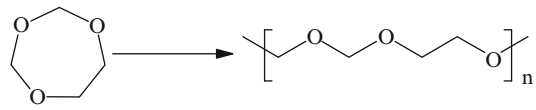
There is some disagreement about the nature of the end groups. and there are some speculations that the polymers might possess large cyclic structures. Nevertheless, polymerizations initiated with benzoyllium hexafluoroantimonate ($C_6H_5CO^+SbF_6^-$) and conducted at $-15°C$ in nitromethane or methylene chloride result in mostly linear polymers. The terminal end groups come from terminating agents that are deliberately added [81]. These polymerizations proceed without any appreciable amounts of transfer reactions, affecting the DP.

5.7.3 *Polymerization of Dioxopane and Other Cyclic Acetals*

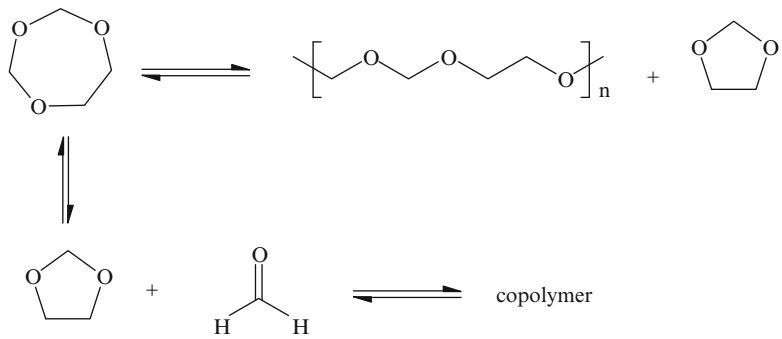
Polymerization of six membered cyclic formals has, apparently not been explored [1]. Polymerization of 1,3-dioxopane can be initiated by camphor sulfonic acid [82, 83]:



1,3-trioxopane, a product of condensation of trioxane with ethylene oxide, can be polymerized by cationic mechanism both in solution and in bulk [84]:

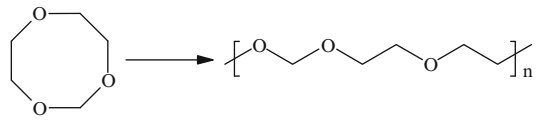


Polymerizations, carried out with boron trifluoride catalyst in dichloroethane solvent result in several reactions that occur simultaneously [84]:



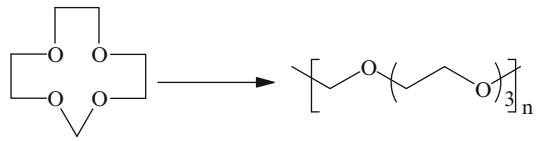
At low temperatures the amount of dioxolane that forms in the above reaction decreases considerably and can become zero.

Ring-opening polymerizations of trioxocane result in the following polymer [84, 85]:



So far, the nature of the end groups has not been established. Nor has it been shown that a macrocyclic structure does not form.

1,3,6,9-tetraoxacycloundecane (triethylene glycol formal) can be polymerized can be polymerized by several cationic initiators in solution or in bulk at varying temperatures from −30 to +150°C [84]:



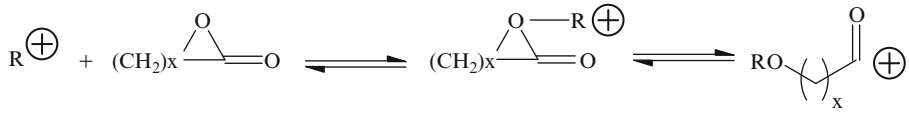
5.8 Polymerization of Lactones

Polymerization of lactones can be carried out by three mechanisms, namely, cationic, anionic, and coordinated one. Often, the mechanism by which a specific lactone polymerizes depends upon the size of the ring.

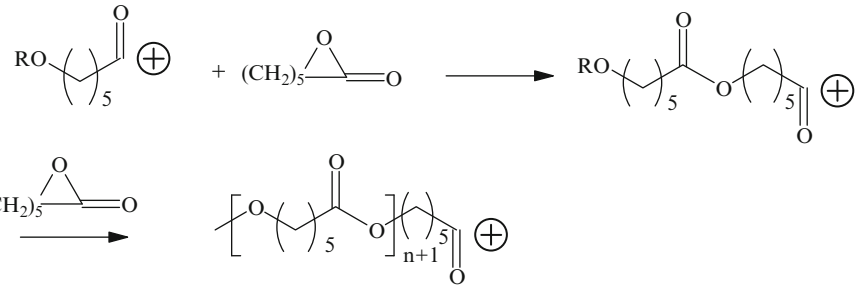
5.8.1 Cationic Polymerization

Cationic polymerizations of lactones has been carried out with the help of alkylating agents, acylating agents, Lewis acids, and protonic acids. Various reaction schemes were proposed to explain the

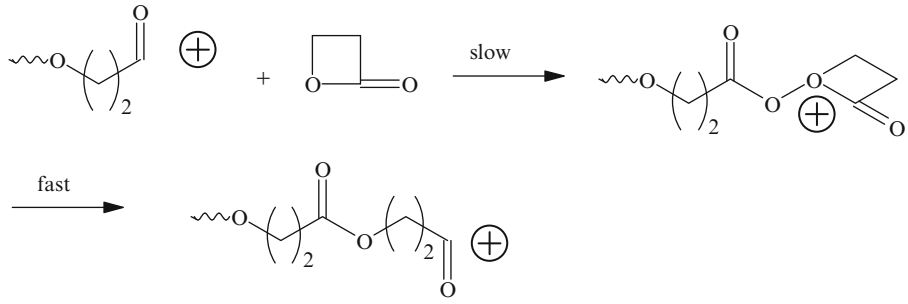
cationic mechanism. They tend to resemble the schemes suggested for the polymerization of cyclic ethers [86, 87]. The initiation step involves an equilibrium that is followed by a ring-opening reaction:



The propagation consists of many repetitions of the above step:

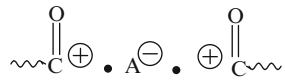


The polymerization of propiolactone in methylene chloride with an antimony pentachloride-dietherate catalyst was investigated [88]. The results show that the concentration of the active centers is dependent upon catalyst concentration and upon the initial concentration of the monomer. They also support the concept that opening of the lactone rings includes initial formation of an oxonium ions [88]:



Because the carbonyl oxygen is the most basic of the oxygens in the lactone molecule, a reverse reaction is

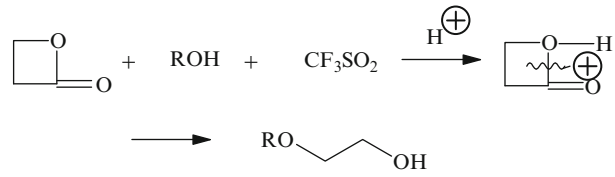
Conductivity measurements during polymerizations of β-propiolactone with antimony pentafluoride-etherate or *p*-toluenesulfonic acid show [89] that ion triplets form during the reaction. These are:



The triplets appear to be active centers throughout the course of the polymerizations. In addition, most of the growing chain ends exist as ion pairs, depending upon the concentration of the monomer [89].

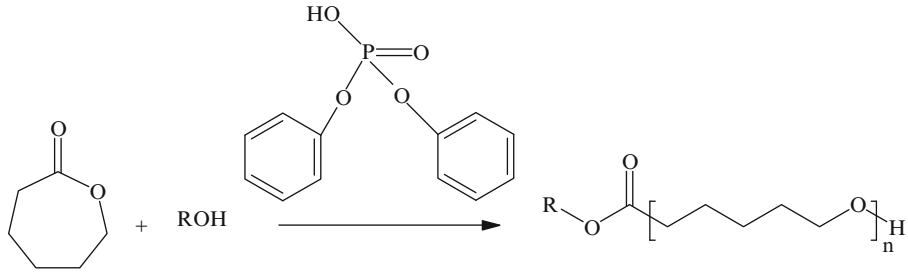
Bourissou et al. reported recently controlled cationic polymerization of lactones using a combination of triflic acid with a protonic reagent as the initiators [90]. The reaction was carried out in CH_2Cl_2. Results indicated that the process is controlled is a linear relationship between the molecular

weight of the product and the monomer to initiator ratio as well as to monomer conversion. The process is believed to proceed by protonation of the lactone by triflic acid and then followed by a nucleophilic attack by the initiating alcohol:



It is believed that the controlled cationic ring-opening polymerization proceeds by an "activated anionic mechanism" as suggested by Penczek [91]. According to his suggestion, the acid activates the cyclic ester and the alcohol subsequently initiates the polymerization.

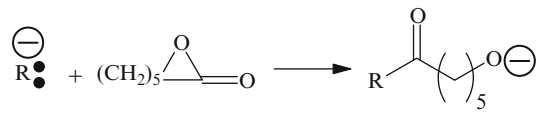
Kakuchi and coworkers reported controlled/living cationic ring-opening polymerizations of δ-valerolactone and ε-caprolactone with the aid of diphenyl phosphate [89]. The reaction was illustrated as follows:



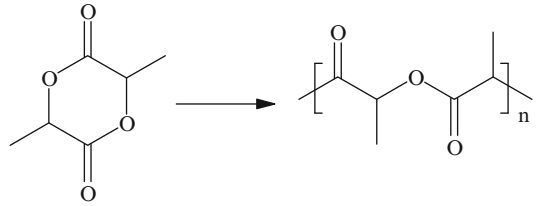
The ring-opening polymerization of δ-valerolactone and ε-caprolactone was carried out using 3-phenyl-1-propanol as the initiator and diphenyl phosphate as the catalyst in toluene at room temperature. They reported that the reaction proceeded homogeneously to yield poly(δ-valerolactone) and poly(ε-caprolactone) with narrow polydispersity indices. Analyses indicated a presence of residues of the initiator.

5.8.2 *Anionic Polymerization of Lactones*

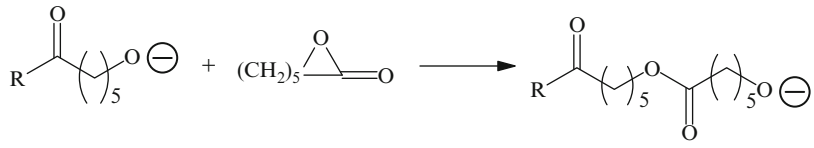
In anionic polymerizations the initiations result from attacks by bases upon the carbonyl groups:



Common initiators are Li and K alkoxides. In addition to that, it was reported that phosphazene bases can be used to carry out polymerizations of cyclic esters [92]. Also, commercially available materials, like *tert*-butoxybis(dimethylamino)methane and tris(dimethylamino)methane yield high molecular weight polylactic acid by ring-opening polymerization with narrow molecular weight distribution:



The propagations take place by a similar process:

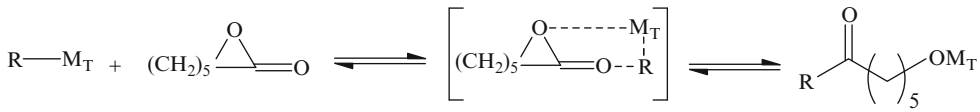


These steps repeat themselves until the chains are built up. Anionic polymerizations can yield optically active polymers. This was observed in formations of poly(α-methyl, α-ethyl-β-propiolactone) [193] that contains asymmetric carbon atoms.

5.8.3 *Polymerization of Lactones by Coordination Mechanism*

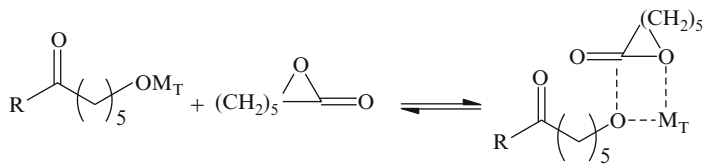
The mechanism of coordination polymerization was pictured by Yong, Malzner, and Pilato [90] as being an intermediate between the above two modes of polymerization (a cationic and anionic one):

Initiation



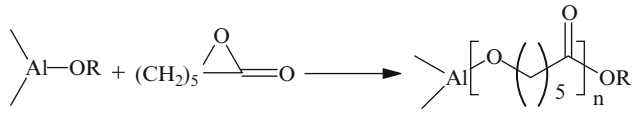
where, M_T means metal.

Propagation



The above shown mechanism, however, is incorrect when caprolactone is polymerized with tin compounds [95]. Yet, it appears to be correct for polymerizations of propiolactones with an ethylzinc monoxide catalyst [95].

The bimetallic oxoalkoxides are useful catalysts for the polymerizations of ε-caprolactone. The general course of the reaction is quite similar to one for oxiranes. A typical coordination mechanism is indicated from kinetic and structural data [97]. The molecular weight increases with conversion and the reaction exhibits a "living" character, because there is a linear relationship between DP and conversion. When the monomer is all used up, addition of fresh monomer to the reaction mixture results in increases in DP. By avoiding side reactions it is possible to achieve high molecular weights (up to 200,000) with narrow molecular weight distribution ($M_w/M_n \geq 1.05$) [97]. The reaction proceeds through insertion of the lactone units in the Al–OR bonds. The acyl–oxygen bond cleaves and the chain binds through the oxygen to the catalyst by forming an alkoxide link rather than a carboxylate one:

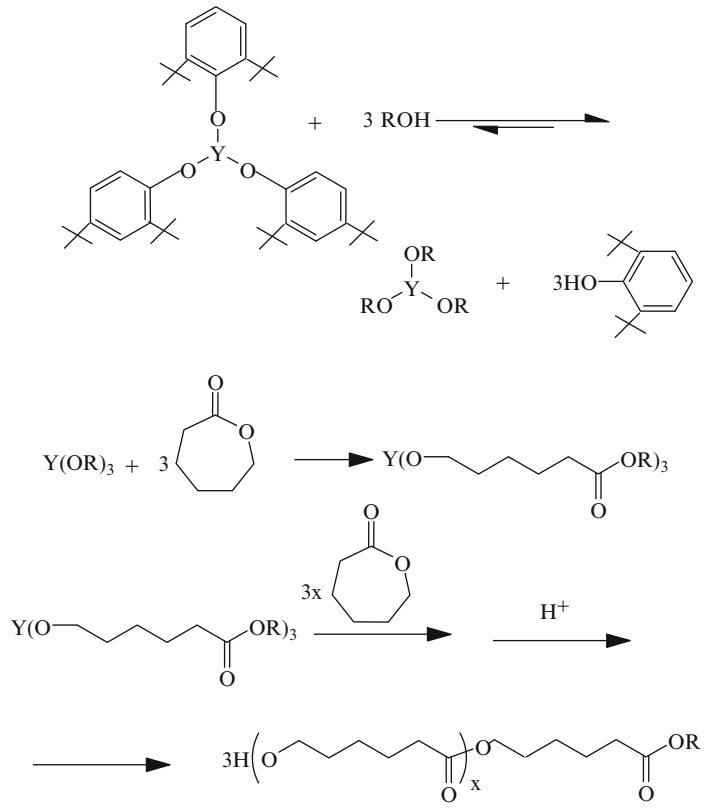


There are potentially four active sites per trinuclear catalytic molecule. The number of actual sites, however, depends upon the aggregation of the oxoalkoxides. Two different types of OR groups exist, depending upon the bridging in the aggregates. Only one is active in the polymerization. This results in a catalytic star-shaped entity. The fact that the dissociated catalysts generate four growing chains per each $Al_2(CH_2)_5CO_2(OR)_4$ molecule [97] tends to confirm this.

The commercially available aluminum triisopropoxide was reported to be a very effective initiator for the "living" ring-opening polymerizations of ε-caprolactone, lactides, glacolide, and cyclic anhydrides [98]. Based on kinetic and structural data, the ring-opening polymerization is believed to take place by a coordination-insertion mechanism. While the molecules of aluminum triisopropoxide are coordinatively associated in toluene, in the presence of lactones single isolated monomeric species form and are believed to remain unassociated during the propagation reaction [98].

Actually, ring-opening polymerizations of ε-caprolactone were achieved by various catalysts. Only a few, however, initiate "living" polymerizations. Among these are the aluminum alkoxides described above, bimetallic μ-alkoxides [99], porphynatoaluminum [100], mono(cyclopentadienyl) titanium complexes [101], and rare earth alkoxides [102, 103]. Examples of rare earth alkoxides are Ln, Nd, Y, or Nd isopropoxy diethyl acetoacetates and $(C_5H_5)_2LnOR$ and $[C_5(CH_3)_5]_2LnCH_3$ (donor) complexes. It was suggested that the steric effect of bulky groups of these catalysts is to suppress an interfering transesterification reaction by screening linear polymeric chains from the active centers during the reactions and yield "living" polymerizations [104]. These catalysts also are useful in formation of various block copolymers of lactones with other monomers [104, 105]. Among other lactones that were polymerized with the help of such rare earth catalysts are lactide [106–108], δ-valerolactone [109], β-propiolactone [109], and β-butyrolactone [107].

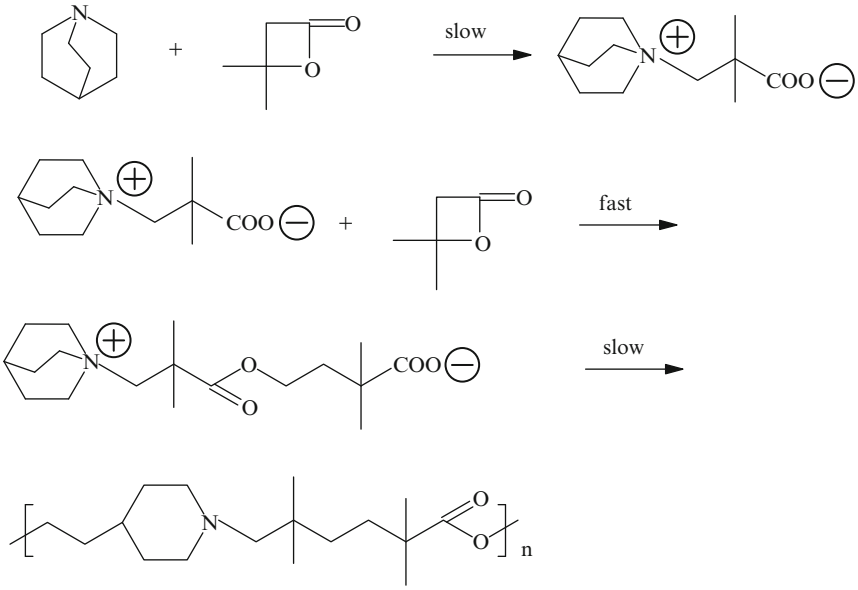
Polymerization of ε-caprolactone with a catalyst system consisting of tris(2,6-di-*tert*-butylphenoxy) yttrium and 2-propanol is first order with respect to the monomer and initiator [105]. This led to the conclusion that the reaction proceeds via a three-step mechanism that can be illustrated as follows [105]:



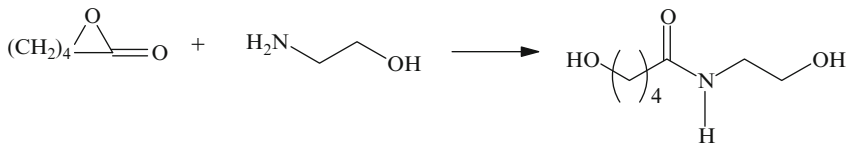
It was also reported that "living" ε-caprolactone polymerization can be carried with bis(acryloxy-) lanthanide (II) complexes based on samarium [110]. Thus, $(ArO)_2Sm(THF)_4$, (where ArO = 2,6-di-*tert*-butyl-4-methyl-phenoxy) yielded 98% conversion in toluene at 60°C in 1 h. The central ions and ligands appear to have an effect on the activity of the catalyst [110].

5.8.4 Special Catalysts for Polymerizations of Lactones

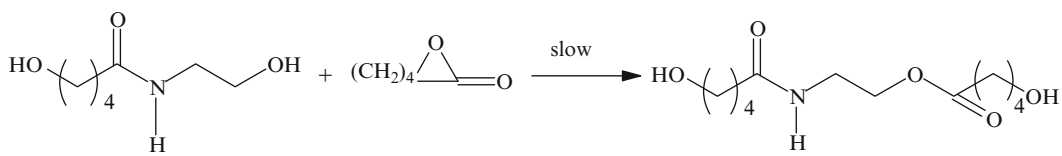
Some lactones can polymerize in the presence of compounds like alcohols, amines, and carboxylic acids without additional catalysts. The reactions, however, are slow and yield only low molecular weight polymers [95]. Exception is polymerizations of pivalolactone in the presence of cyclic amines that yield high molecular weight polyesters at high conversion [111]. The initiating steps result from formations of adducts, amine-pivalate betaines:



The above reaction appears to be restricted to highly strained lactones and may not work with larger lactones [95], For instance, when polymerization of δ-valerolactone is initiated with ethanolamine at temperatures up to 200°C there is initially a rapid reaction between the amine group and the monomer:



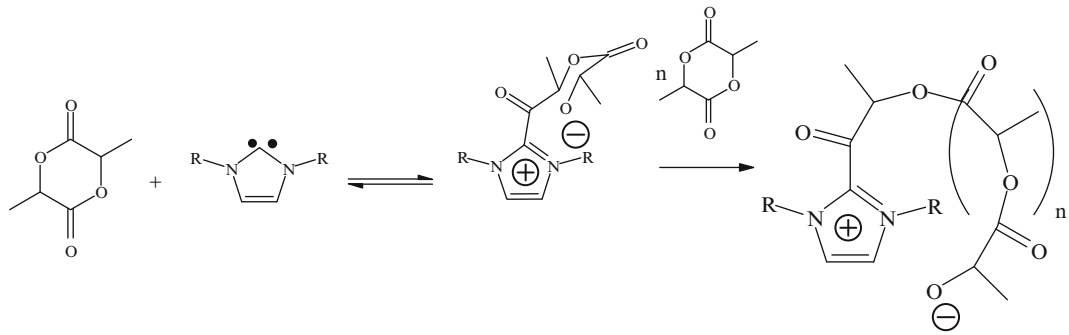
The subsequent reactions, however, are slow:



It was suggested that initiators, like dibutylzinc, that lack active hydrogens should be placed into a special category [96]. They can initiate polymerizations of some lactones. One of them is ε-caprolactone. Polymers form that are inversely proportional in molecular weights to the catalyst concentrations [112]. The same is true of stannic tetraacrylate. High molecular weight poly(ε-caprolactone), as high as 100,000 forms. Addition of compounds that may serve as source of active hydrogens is not necessary [95]. This group of initiators also includes dimethylcadmium, methylmagnesium bromide, and a few others that are effective in polymerizations of δ-valerolactone, ε-caprolactone, and their alkyl substituted derivatives. The polymers that form are high in molecular weight, some as high as 250,000 [113].

Another group consists of zinc and lead salts, stannous esters, phosphines, and alkyl titanates. This group does require additions of compounds with active hydrogens. Such additives can be polyols, polyamines, or carboxylic acid compounds [95]. Molecular weight control is difficult with the catalysts belonging to the first group. This second group, on the other hand, not only allows control over the molecular weights, but also over the nature of the end groups [95].

Weymouth and coworkers carried out kinetic and mechanistic studies of heterocyclic carbene mediated zwitterionic polymerization of cyclic esters [96]. Based on their results they proposed the following ring-opening mechanism:



From the kinetic studies they were able to conclude that in the heterocyclic carbene initiated polymerization of lactide, the rate of initiation is slower than the rate of propagation. Also, the rate of propagation is much faster than chain termination via cyclization.

5.9 Polymerizations of Lactams

Polymerizations of lactams produce important commercial polymers. The polymerization reactions, therefore, received considerable attention. Lactam molecules polymerize by three different mechanisms: cationic, anionic, and a hydrolytic one (by water or water releasing substances).

The lactam ring is strongly resonance stabilized and the carbonyl activity is low. Nevertheless, the ring-opening polymerizations start with small amounts of initiators through *trans*-acylation reactions. Fairly high temperatures, however, are needed, often above 200°C. In all such reactions, one molecule acts as the acylating agent or as an electrophile while the other one acts as a nucleophile and undergoes the acylation.

Generally, the initiators activate the inactive amide groups causing them to react with other lactams through successive transamidations that result in formations of polyamides. Both acids and bases catalyze the transamidation reactions. The additions of electrophiles affect increases in the electrophilicity of the carbonyl carbon of the acylating lactam. The nucleophiles, on the other hand, increase the nucleophilic character of the lactam substrate (if they are bases).

All initiators can be divided into two groups. To the first one belong strong bases capable of forming lactam anions by removing the amide proton. This starts the anionic polymerization reaction. To the second one belong active hydrogen compounds capable of protonating the amide bond and thereby affecting cationic polymerization [114].

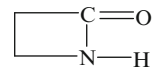
Side reactions are common in lactam polymerizations. Their nature and extent depends upon the concentration and character of the initiators, the temperatures of the reactions, and the structures of the lactams. When cationic polymerizations of lactams are initiated by strong acids, strongly basic amidine groups can be produced. These groups bind the strong acids, inactive the growth centers, and decrease the rate of polymerization. Use of strong bases to initiate polymerizations of lactams possessing at least one α-hydrogen also result in side reaction. Compounds form that decrease the basicity of lactams and polyamides and slow the polymerizations. Also, side reactions give rise to irregular structures, namely branching.

The ring-opening polymerization reactions depend upon thermodynamic and kinetic factors, and on the total molecular strain energies of the particular ring structures. Six-membered δ-valerolactam is the most stable ring structure and most difficult to polymerize. Also, presence of substituents increases the stability of the rings and decreases the ability to polymerize.

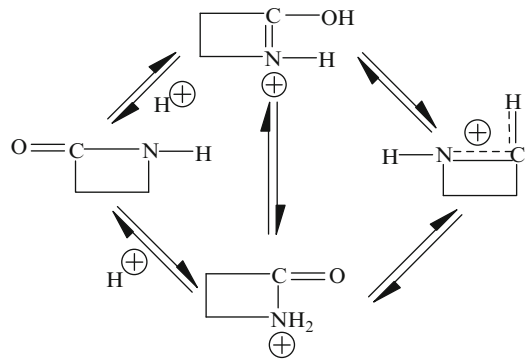
5.9.1 Cationic Polymerization of Lactams

The catalysts for cationic polymerization can be strong anhydrous acids, Lewis acids [115], salts of primary and secondary amines, carboxylic acids, and salts of amines with carboxylic acids that split off water at elevated temperatures [114]. The initiators react by coordinating with and forming rapid pre equilibrium lactam cations. These cations are the reactive species in the polymerizations. Initiations of this type are also possible with weakly acidic compound, but such compounds are not able to transfer protons to the lactam. They are capable, however, of forming hydrogen bonds with the lactams. The high reactivity of the lactam cations may be attributed to the decreased electron density at the carbonyl carbon atoms. This makes them more subject to nucleophilic attacks [114].

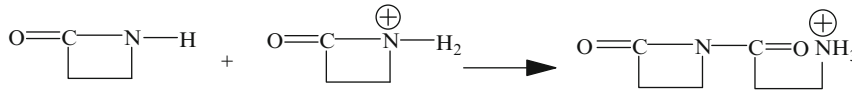
Protonations of the amides occur at the oxygens [116], but small fractions of N-protonated amides are also presumed to exist in tautomeric equilibrium. To simplify the illustrations, all lactams will be shown in this section as:



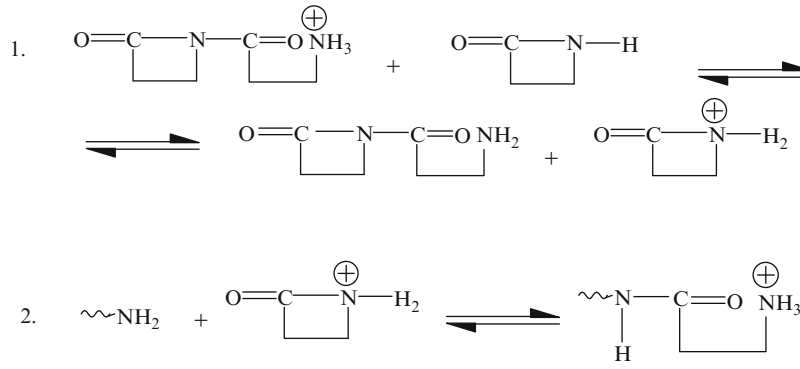
So, while the above structure commonly represents propiolactam, in this section it can mean any lactam, like a caprolactam, valerolactam, etc. Thus, the equilibrium can be shown as follows:



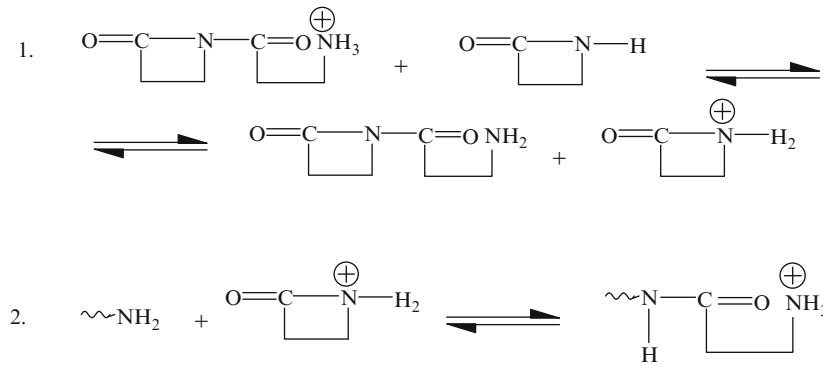
In a reaction mixture where the initiators are strong acids the strongest nucleophiles are the monomers. Acylations of the monomers with the amidinium cations result in formations of aminoacyllactams [113]:



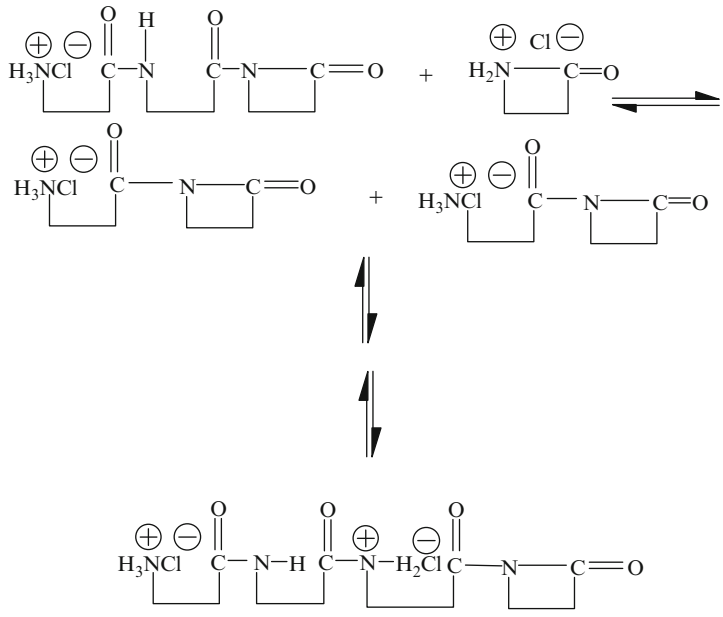
Acylation of these amine groups by molecules of other protonated lactams results in the monomers becoming incorporated into the polymers [117]. The growth centers are preserved and a molecule of lactam is protonated. This occurs in two steps [117]:



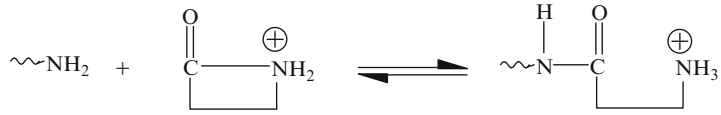
These reactions attain equilibrium quickly. Aminolyses of acyllactams, that are the reverse of the initiation reactions, precede rapidly [117–119]. Aminolyses of aminoacyllactams actually contribute to the propagation process [120, 121]:



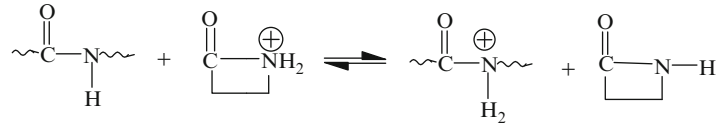
These reactions attain equilibrium quickly. Aminolyses of acyllactams, that are the reverse of the initiation reactions, precede rapidly [117–119]. The reaction, therefore, proceeds as follows [120, 121]:



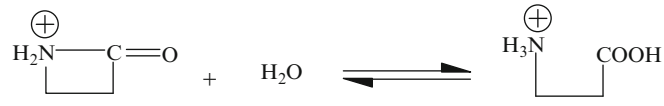
The above reaction results in the destruction of the equilibrium and a regeneration of the strongly acidic amide salt. Total lactam consumption results from repetitions of the above sequences and formations of new aminoacyllactam molecules [113–121]. Initiations of polymerizations with acid salts of primary and secondary amines result in chain growths that proceeds predominantly through additions of protonated lactams to the amines [113]:



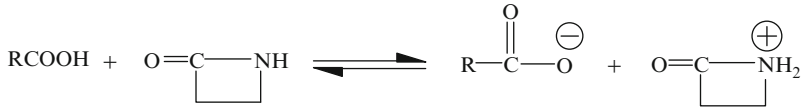
The rate at which the initiating amines are incorporated is proportional to the basicity. As the conversion progresses the concentration of protonated lactams in the reaction mixture decreases while that of the protonated polymer amide groups increases. The latter takes part in the initiation reactions with lactam molecules and in exchange reactions with polymer molecules [113]:



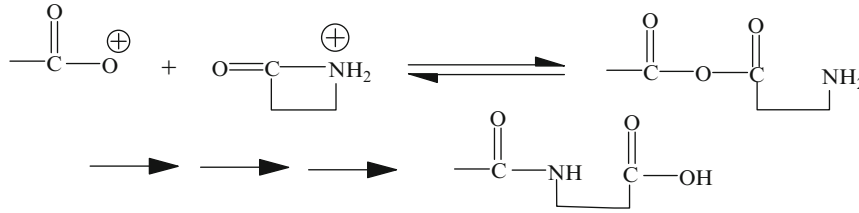
In each of the initiation steps the strongest nucleophile present reacts with the lactam cation. When strong anhydrous Bronsted acids initiate the polymerizations, the free lactams are acylated first with the formation of aminoacyllactams. When the polymerizations are initiated by amine salts, the initial steps are conversions of the amines to the amino acid amides. On the other hand, hydrolytic polymerizations start formations of unsubstituted amino acids [122]:



When weak carboxylic acids or acids of medium strength initiate lactam polymerizations at anhydrous conditions, there is an induction period [123]. In addition, the rates of these reactions are proportional to the pK_a of the acids [105]. It appears that different reaction mechanisms are involved, depending upon the acid strengths [113]. The nucleophiles are present in equilibrium:

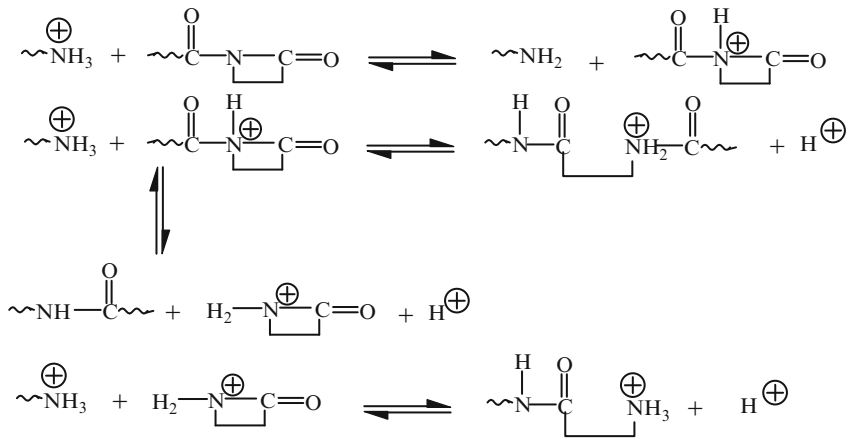


The acylation of the carboxylate anions is assumed to lead to formations of mixed anhydrides of the acids with amino acids [124] and subsequent rearrangements:

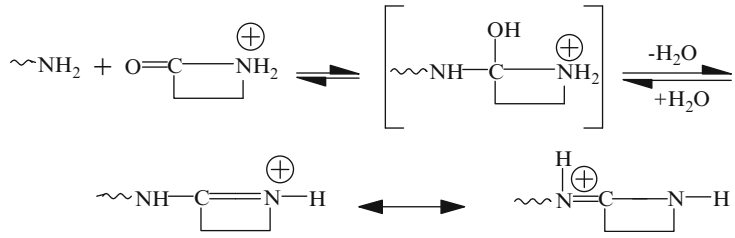


When strong acids, however, initiate the polymerizations, the strongest nucleophiles present are the lactam amide groups that undergo acylations. As a result, the acids are not incorporated into the polymers.

The propagation steps in cationic polymerizations of lactams occur by transamidation reactions between lactam rings and the ammonium groups formed during the steps of initiation. It is believed that during the reaction proton transfers take place first from the amine salts to the lactams or to the acyllactams to form cations. These in turn acylate the free amines that form with the regeneration of ammonium groups:



The propagation step is very rapid when aminolysis takes place at the carbonyl group of the activated acid derivative (like acyllactam or an acid chloride). It is slower, however, if it involves an amide group of the monomer [114]. As is typical of many carbonyl reactions, acylations are followed by eliminations [125]:

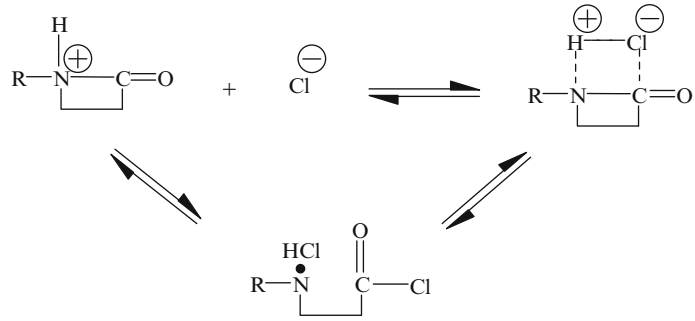


The above water elimination reaction results in formations of amidines. Acylamidinium ions can also result from dehydration of the tetrahedral intermediates during the reactions of amino groups with acyllactams. Such groups could also be present within the polymer molecules. The water that is released in these reactions hydrolyzes the acyllactams, acylamidine salts, and lactam salts to yield carboxylic acids [114].

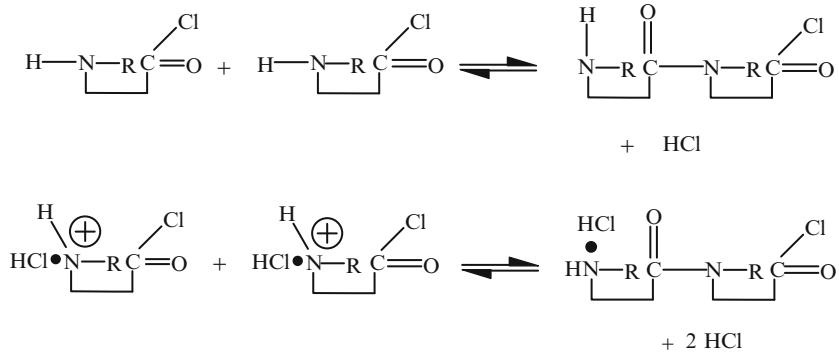
In the cationic polymerization of lactams the ammonium and amidinium groups form N-terminal chain ends. The C-terminal chain ends are in the form of carboxylic acid groups or alkylamide residues. This is important, because the nature of the end groups and their reactivity determine the steps that follow in the polymerizations. This means that the different types of cationic polymerizations of lactams are the results of the different end groups that form during the initiation steps. Formation of amidines increases with increasing acidity and concentration of the initiator and with an increase in the temperature:

When strong acids or amine salts initiate the polymerizations, almost all amine salt groups become converted to amidine salts shortly after the start of the initiation reaction [108]. Formation of amidinium salts leads to a decrease in the reaction rate because they initiate polymerizations of lactams less effectively than do ammonium salts [125, 126]. Lewis acids act in a similar manner, unless a co-reactant is present, like water. In that case, the Lewis acids are transformed into protonic acids and the polymerizations proceed as if they were initiated by protonic acids [114].

N-substituted lactams can generally not be polymerized. Some exceptions, however, are known when cationic mechanisms are employed [122] and when strong carboxylic or inorganic acids are used as initiators. In such cases the anions of the initiating acids, like Cl^-, react with the lactam cations to yield amino acid chlorides [114]:

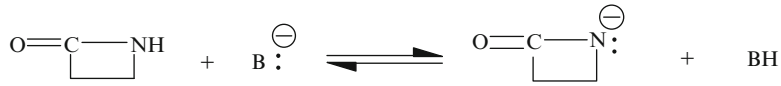


Only the more strained four-, eight- and nine-membered N-substituted lactams have so far been shown to be capable of polymerizations [113]. The 2,2-dimethylquinuclidone is highly strained and undergoes polymerizations at room temperature [127]. The propagation reaction of substituted lactams can be illustrated as follows [122]:

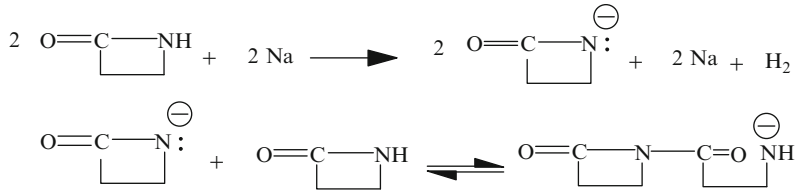


5.9.2 *Anionic Polymerization of Lactams*

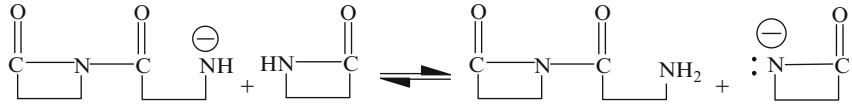
The anionic polymerizations of lactams are initiated by strong bases [128] capable of forming lactam anions:



Such bases can be alkali metals, metal hydrides, organometallic compounds, and metal amides. The initiation step of ring-opening amidation can be shown as follows:

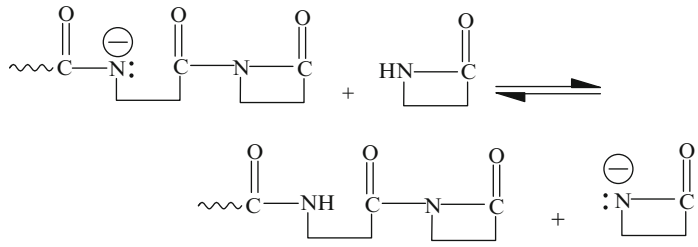


The primary amine anions abstract protons very rapidly from other molecules of lactams to form amino-acyllactams [130]:

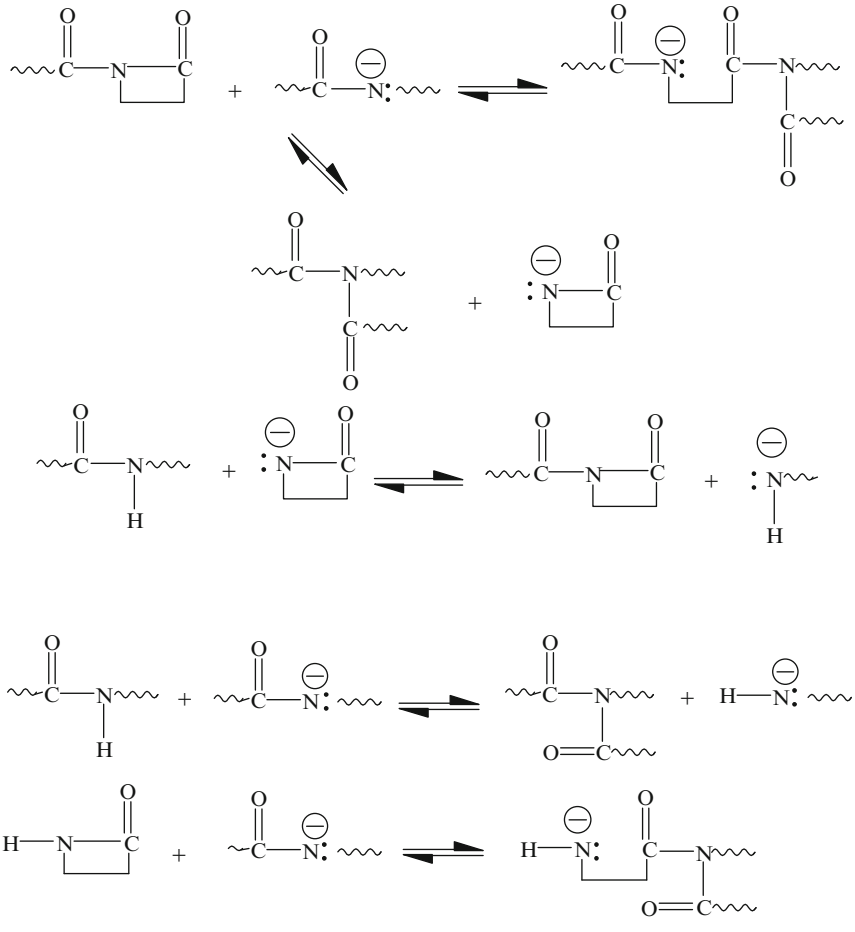


In these reactions, the propagation centers are the cyclic amide linkages of the N-acylated terminal lactam rings. Acylation of the amide nitrogens have the effect of increasing the electron deficiencies of these groups. This in turn increases the reactivities of the cyclic amide carbonyls toward attacks by the nucleophilic lactam anions [115]:

Very rapid proton exchanges follows. This results in equilibrium between the lactam and the polymeric amide anions [129]:



The polymer amide anions can undergo acylation by acyllactam groups with accompanying ring opening or with formation of lactam anions. In the first instance, it is an alternate path of propagation with formation of imide groups:



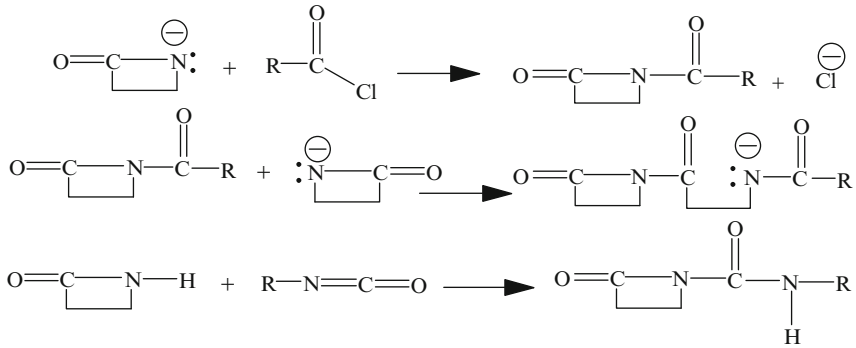
The acylation reactions shown above are much faster than the initiation reactions [129, 131] As a result, there are induction periods in anionic polymerizations of lactams [113]. In addition, steep increases in molecular weights take place at the beginning of the polymerizations. Bimolecular aminolyses may contribute to that, though their contributions to the total conversions are negligible [113].

The overall rates of polymerizations depend on the concentrations of acyllactams and diacylamine groups as well as on the lactam anions. The latter result form dissociations of the lactam salts, depending upon the nature of the metal:

where Me means metal The alkali metals can be rated in the following order with respect to rates of initiations and propagations [113, 132]:

$$\mathrm{Li}<\mathrm{Na}<\mathrm{K}<\mathrm{Ca}$$

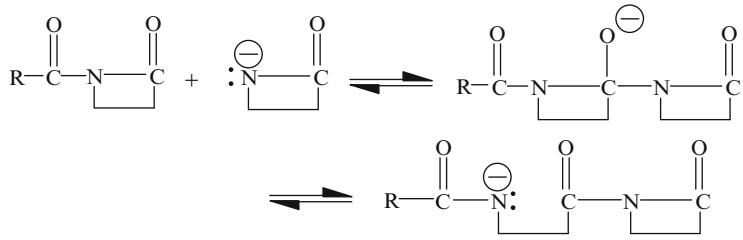
Additions of *activators* or cocatalysts, such as acyl halides, anhydrides, or isocyanates, can result in elimination of the induction period. These additives insure formations of stabilized adducts:



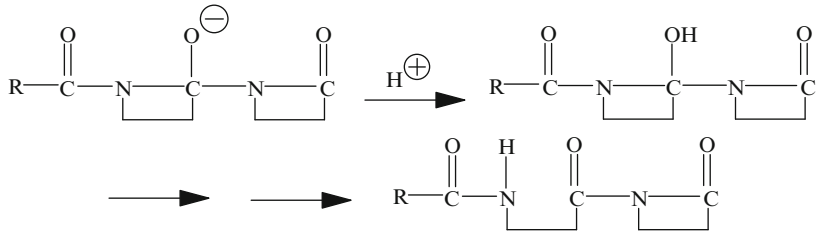
The structures of the activators can determine the rates of addition to the first lactam anion [113]. If, for instance, the acyl group is large, as in pivaloylcaprolactam, the decrease in the rate can be merely due to steric hindrance [113, 129]. On the other hand, substituents like the benzoyl group increase the rates of additions to the first lactam anions [113, 129]. In addition, the structures of the activators can also affect the course of the polymerization. This is because they become incorporated at the end of the polymeric molecules and may influence the basicity during the polymerization reactions.

Polymerizations in the presence of acylating agents are often called *activated* polymerization. If the acylating agents are absent from the reaction mixture the reactions may be called *nonactivated*. Sometimes the terms *assisted* and *nonassisted* are used instead.

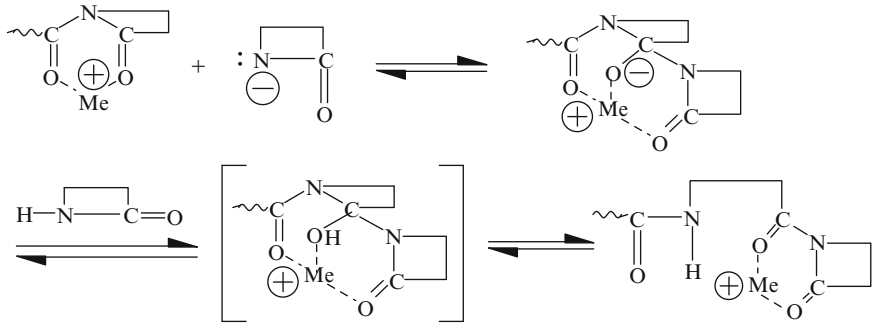
Several reaction mechanisms were offered to explain the mechanism of anionic ring-opening polymerizations of lactams. One mechanism is based on nucleophilic attacks by the lactam anions at the cyclic carbonyl groups of N-acylated lactams. This leads to formations of intermediate symmetrical mesomeric anions that rearrange with openings of the rings [133, 134]:



Champetier and Sekiguchi concluded that the intermediate anions are neutralized first by protons from the lactams or from the polymer amide groups. The neutral molecules subsequently rearrange with the openings of the penultimate units [135, 136].

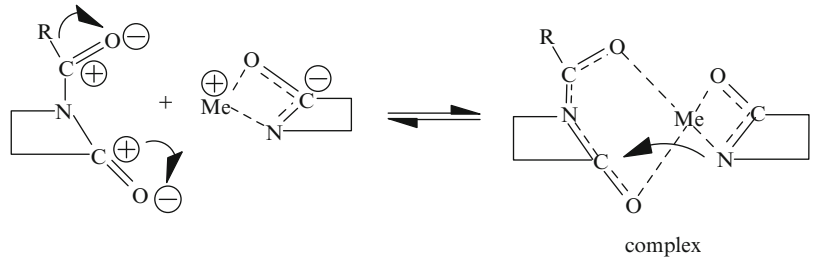


They also felt that the acylating strength of the acyllactams is enhanced by coordination of the cations with the imide carbonyl groups [135, 136]. This is based on an assumption that the incorporations of the lactam units proceed through additions of lactam anions. Protonations and subsequent rearrangements follow [135, 136]. This type of chain growth is termed *lactomolytic* propagation [137]:



The mechanism implies that the alkaline cation is fixed to the imide group and that a nucleophilic attack (that is the rate-determining step) by the lactam anion takes place on the endocyclic carbonyl group of the imide to give a "carbinolate" anion. Proton exchange takes place between this intermediate and a lactam monomer. Intramolecular rearrangement results in ring opening of the unit that is now in the penultimate position.

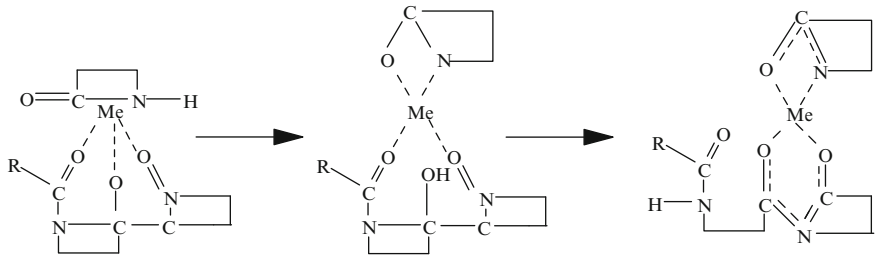
In anionic activated polymerization of ε-caprolactam chain growth involves both free anions and ion pairs [138]. Quantum-chemical calculations suggest that in the alkali metal lactamate molecule the negative charge is delocalized between the oxygen and the nitrogen heteroatoms. This led to a suggestion by Frunze et al [138]. that the acts of initiation are formations of activated intermediate chelate type complexes between the activators and the catalyst molecules [138]:



complex

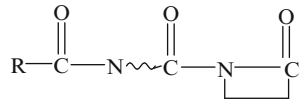
where Me is a metal like Li, K, Cs, etc.

The carbinol fragment of the resulting complex, shown above, undergoes an intramolecular rearrangement. It leads to opening of the heterocyclic ring and to growth of the polymer chain by one unit:

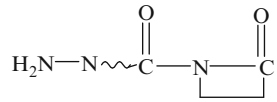


The Frunze et al. mechanism [138] has much in common with the "alkali lactomolytic" mechanism of Champetier and Sekiguchi [135], except for the formation of the above shown complex. Frunze et al. also believe that probably a single mechanism exists for the anionic polymerization of lactams that they describe as *ion-coordinative* [138]. The contributions of various mechanisms via ion pairs or via free ions depend upon the nature of the alkali metal counterion and upon their capacity to coordinate with electron donating compounds (activator and monomer). The growth of ion pairs may mainly be expected from a lithium counterion, while growth by free anions may be expected from potassium or cesium

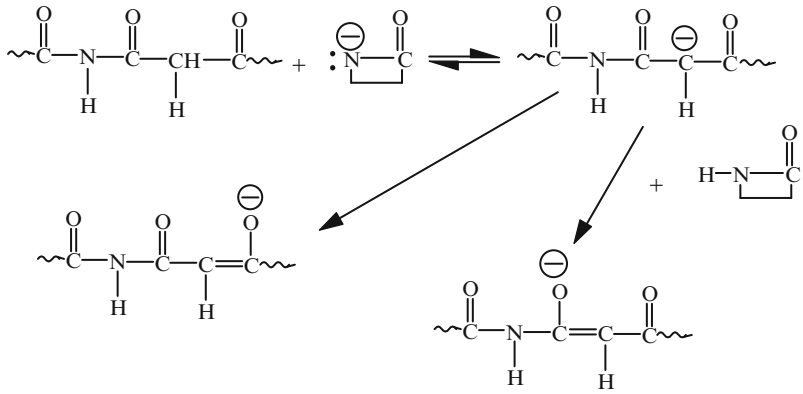
The products of anionic lactam polymerizations can vary, depending upon reaction conditions such as the temperatures, and upon the structures of the lactams themselves. Thus, five-, six-, and seven-membered lactams polymerize at different temperatures and the products differ in molecular weights. For instance, α-pyrrolidone polymerizes readily at 30°C to a polymer of a molecular weight of 15,000, while ε-caprolactam requires 178°C to form polymers of that size or larger [137]. A third lactam, α-piperidone is hard to polymerize to a high molecular weight polymer in good yields [137]. The regular molecules that form in activated anionic polymerizations, as already shown, are [139]:



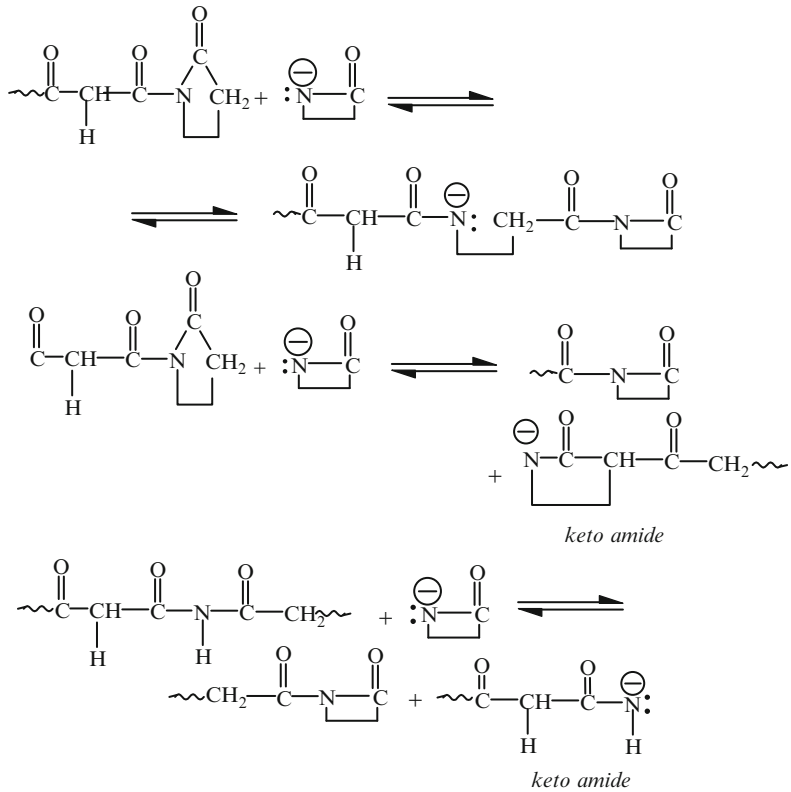
while those activated by lactam anions, are:



At higher polymerization temperatures, however, side reactions occur. Among them are Claisen type condensations. They lead to two type of N-acylated β-keto imide structures and take place readily above 200°C. Formation of these imides decreases the concentration of lactam anions:



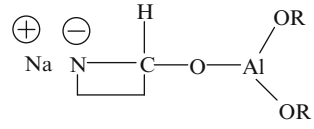
Cyclic keto imides as well as linear ones can yield active species through acylation of lactam anions. This results in formations of growth centers and keto amides:



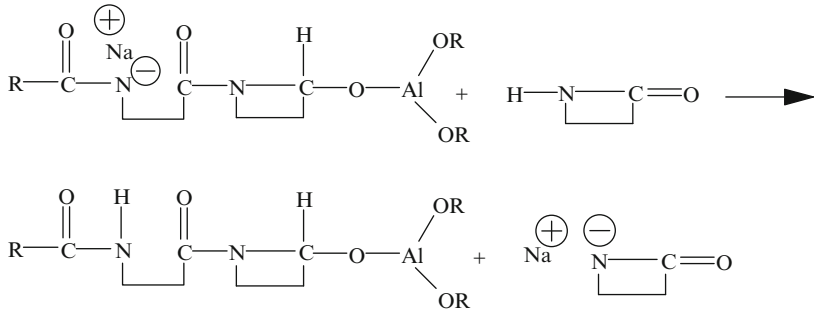
The acidity of keto amides with α-hydrogen atoms is much greater than that of the monomers or of polymer amide groups. Any formation of such structures, therefore, decreases the concentration of lactam anions.

Side reactions give rise to a variety of irregular structures that may be present either in the backbones, or at the ends of the polymer molecules, or both. Formation of branches in anionic polymerizations occurs in polymerizations of ε-caprolactam [140, 141]. This lactam and higher ones polymerize at temperatures greater than 120°C. Above 120°C the β-keto-amide units and possibly the *n*-acyl-keto-amide structures are preserved. They may, however, be potential sites for chain splitting later during polymer processing that takes place at much higher temperatures [142].

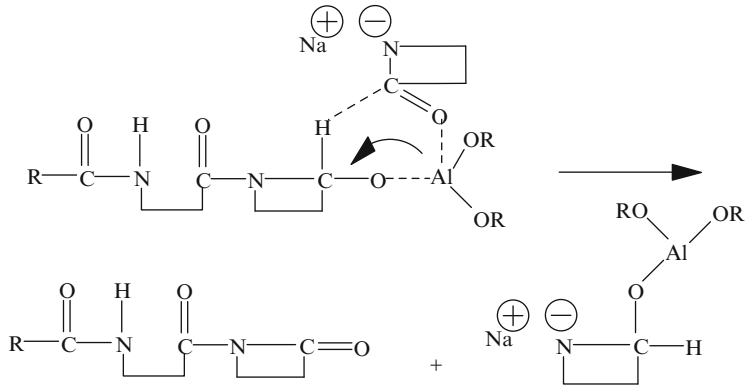
A new group of catalysts, metal dialkoxyaluminum hydrides, for anionic polymerizations of lactams, were reported recently [143]. A different anionic mechanism of polymerization apparently takes place. When ε-caprolactam is treated with sodium dialkoxyaluminum hydride, a sodium salt of 2(dialkoxyaluminoxy)-1-azacycloheptane forms:



Such compound differs in nucleophilicity from activated monomers. These salts are products of deprotonation of lactam monomers at the amides followed by reduction of the carbonyl functions. It is postulated that during lactam polymerizations, after each monomer addition, the active species form again in two steps [143]. In the first one proton exchanges take place:



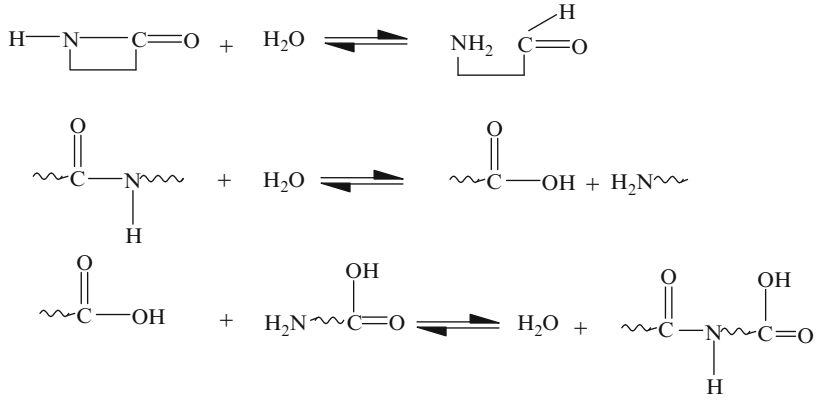
in the second step hydrogen and dialkoxyaluminum group are transferred:



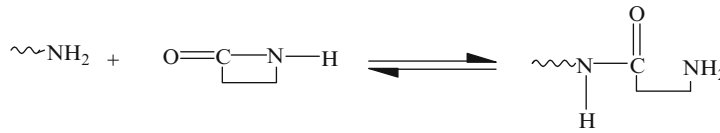
The third step is propagation. It consists of addition of a unit to the chain end and takes place upon reaction of the terminal acyl lactam with a sodium salt of 2(dialkoxyaluminoxy)-1-azacycloheptane shown above [143].

5.9.3 *Hydrolytic Polymerization of Lactams*

This polymerization can be looked upon as a special case of cationic polymerization. It is particularly true when weak acids are added to the reaction mixture, as is often the case in industrial practice. In hydrolytic polymerizations of lactams initiated by water, the hydrolysis–condensation equilibria determine the concentrations of the amine and the carboxylic acid groups. Both functional groups participate in the propagation reactions:



The concentration of these groups also determines the molecular weights of the final products [118–128]. This type of equilibria also occurs in polymerizations initiated by amino acids or by salts of carboxylic acids formed with primary and secondary amines. In the hydrolytic polymerizations of caprolactam the above reactions involve only a few percent of the total lactam molecules present [144, 145]. The predominant propagation reaction is a step-growth addition of lactam molecules to the end groups. It is acid catalyzed [144, 145]:



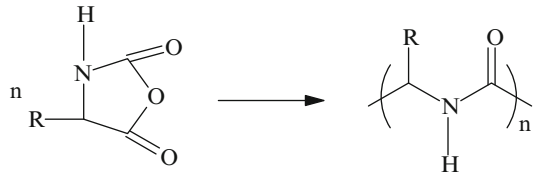
The exact mechanism of this addition is uncertain. It was postulated that the addition steps are through reactions of neutral lactam molecules with ammonium cations [146–148]. Others felt, however, that the lactam molecules add to the undissociated salts [149].

Hydrolytic polymerizations are the smoothest of all three types of polymerization reactions because the growing species are less activated than in either cationic or anionic polymerizations. Many commercial processes utilize it in ε-caprolactam polymerizations. Formation of irregular structures, however, and even crosslinked material was detected. In addition, at elevated temperatures deamination and decarboxylation of polycaprolactam can take place [150] Such reactions can result in formations of ketones and secondary amine groups. The ketones, in turn, can react with amines and form Schiff bases. This leads to branching and crosslinking.

In industrial preparations most of the water used to initiate the polymerizations is removed after conversions reach 80–90% in order to attain high molecular weights. The final products contain about 8% of caprolactam and about 2% of a cyclic oligomer [150]. These are removed by vacuum or hot water extraction. The material is then dried under vacuum at 100–200°C to reduce moisture to about 0.1%.

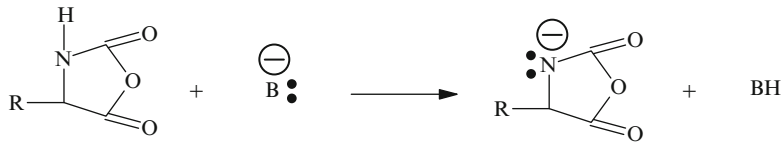
5.10 Polymerization of *N*-Carboxy-α-Amino Acid Anhydrides

The polymerizations of these anhydrides (or substituted oxazolidine-2,5-diones) can be carried out with basic catalysts to yield polyamides:

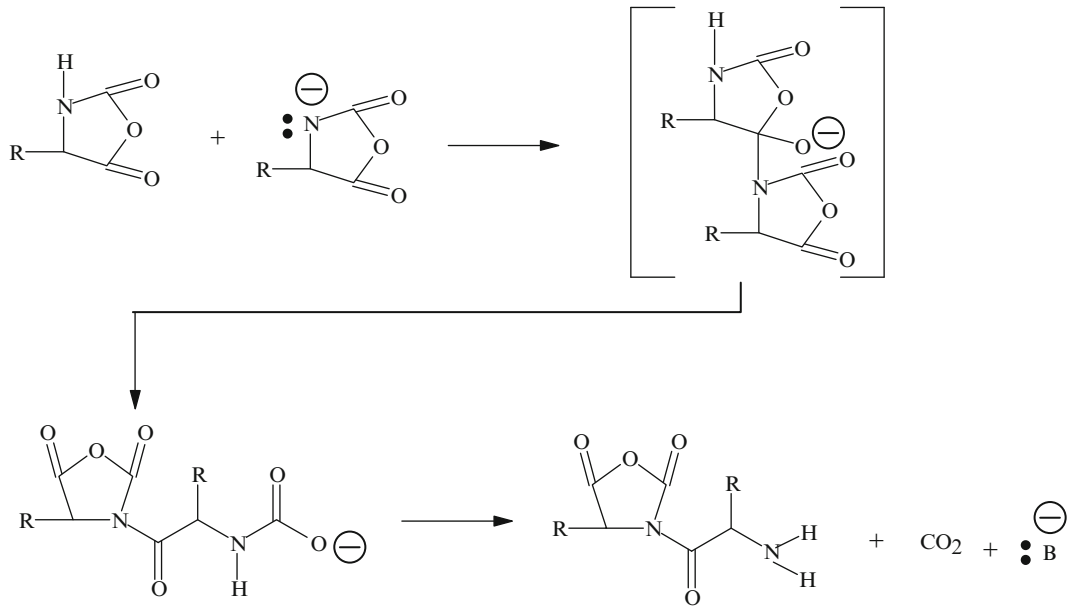


These polymerization reactions are important to biochemists because the products are poly(α-amino acid)s and resemble the building blocks of naturally occurring polyamides.

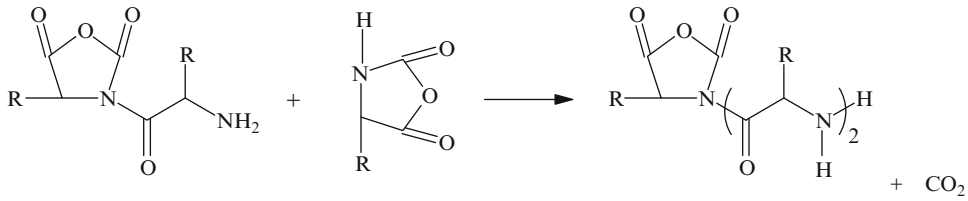
When the polymerization is initiated with strong bases, the initiating step is hydrogen abstraction from the anhydride by the base. This results in formation of *activated* species:



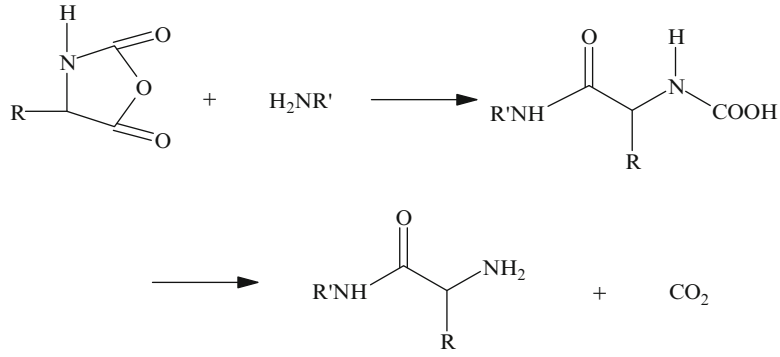
The reaction then proceeds by the *activated mechanism*. The initiation reaction was pictured by Ballard and Bamford [151] as follows:



Each propagation step consists of an addition of one unit of the anhydride and an accompanying loss of carbon dioxide:

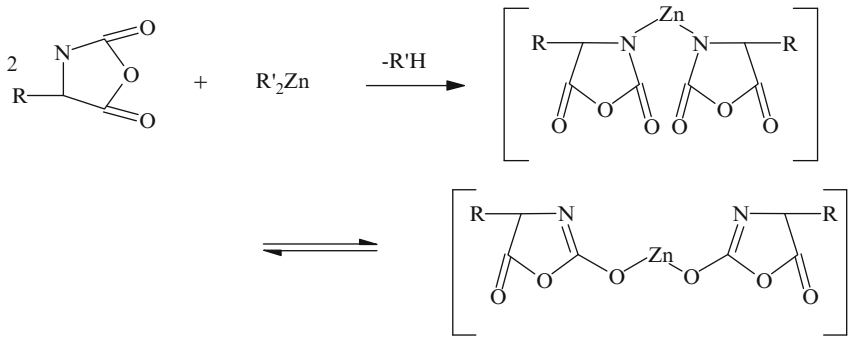


When the reaction is initiated by primary amines, the first step is a nucleophilic attack by the amine on the C_3 of the anhydride [151–153]. The carbon dioxide that is released comes from the C_2 carbonyl group. The propagation proceeds by addition of terminal amine groups to the C_3 carbonyl groups of the monomers [151–153]:

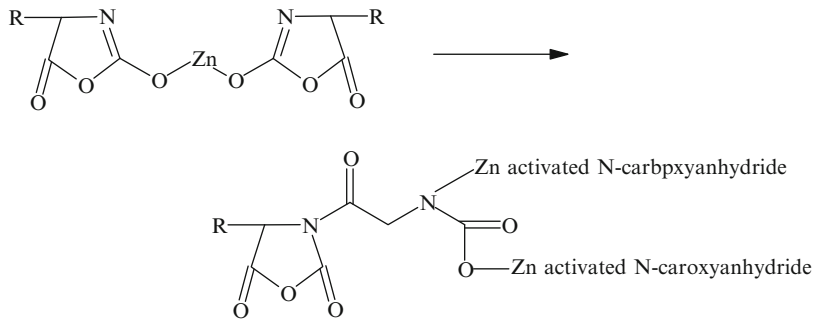


The polymerization rate depends upon the concentration of the amine and the monomer. The degree of polymerization is often but not always equal to the ratio of the monomer to the amine [154]. It means that the reaction may be similar to but not identical to a living type polymerization. In addition, the molecular weight distribution curve may be broadened or bimodal. This may be due to some chemical termination reactions. These can be intramolecular reactions of the terminal amine group with some functional group in the side chain and lead to formation of hydantoic acid end groups [154]. It may also be due to physical termination from precipitation of the product.

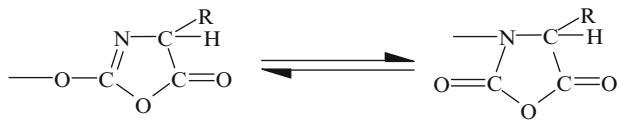
Dialkylzinc initiated polymerizations apparently take place by a different mechanism. The first step is pictured by Makino, Inoue, and Tsuruta as a hydrogen abstraction by dialkylzinc from NH [155]. This is similar to the reaction with a base shown earlier. The second stage of initiation, however, is a reaction between two molecules of the activated carboxyanhydrides, and formation of zinc carbamate [155]:



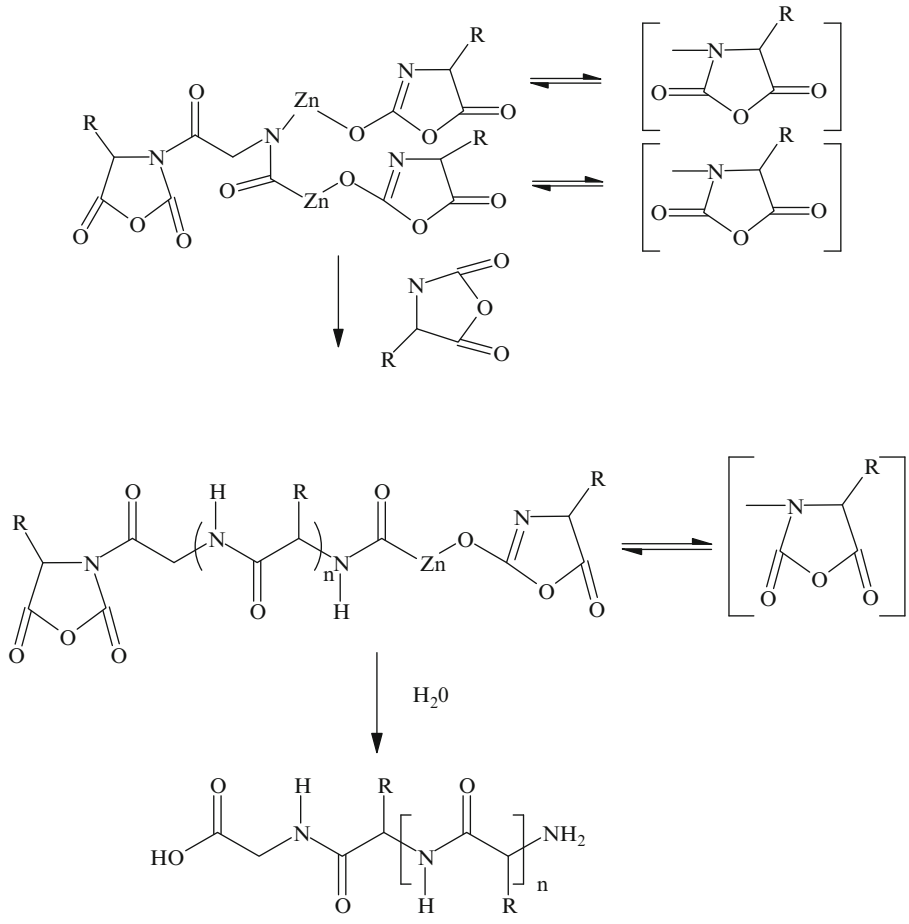
The propagation is a carbonyl addition of the zinc carbamate to the activated *N*-carboxyanhydride to form a mixed anhydride. The mixed anhydride then changes into an amide group with elimination of carbon dioxide [155]:



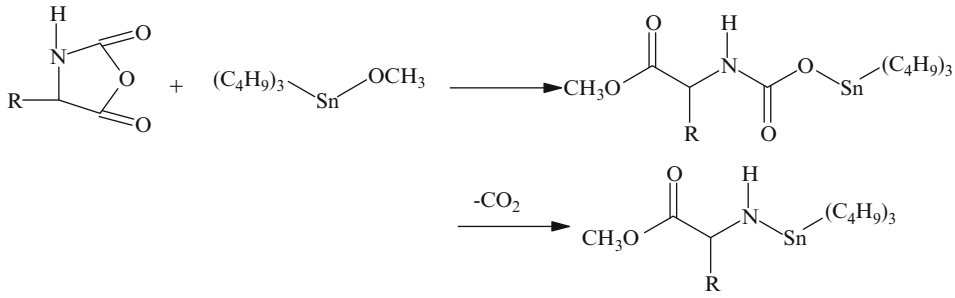
where, the activated *N*-carboxyanhydride portion is [155]:



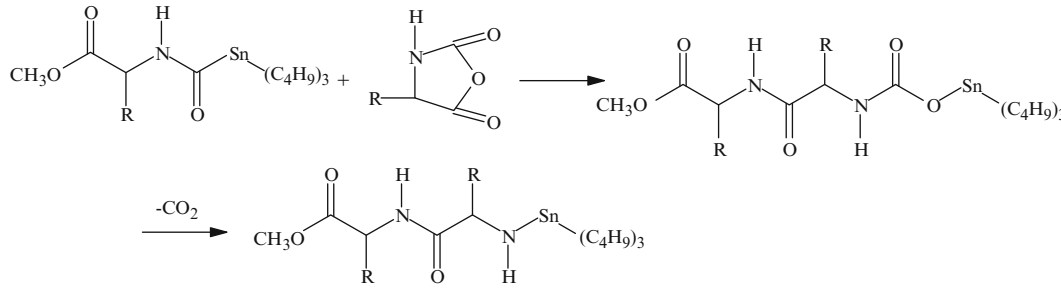
The complete reaction can be illustrated as follows:



Organotin compounds are also active as catalysts in the polymerizations of *N*-carboxyanhydrides [156]. The mechanism of the reaction was postulated by Freireich, Gertner and Zilkha [156] to consist of addition of the organotin compound to the anhydride and formation of organotin carbamate. It subsequently decarboxylates and leaves an active –N–Sn– group that adds to another molecule of *N*-carboxyanhydride. This process is repeated in every step of the propagation [156]:



Propagation



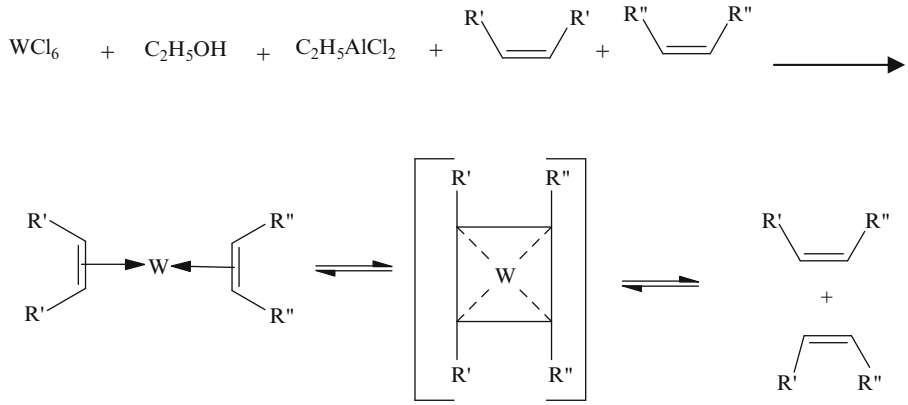
When *N*-carboxyanhydride polymerizations are initiated by secondary amines with small substituents, the amines act as nucleophiles, similarly to primary amines [157]. Secondary amines with bulky substituents, however, produce only *N*-carboxyanhydride anions. The same is true of tertiary amines. These anions in turn initiate polymerizations that proceed by the "active monomer mechanism."

Messman and coworkers did a mechanistic study of α-amino acid carboxy anhydride polymerization [158] They polymerization in high vacuum with polymerization at atmospheric The conclusion of their work was that poly(*O*-benzyl-L-tyrosine) prepared in vacuum yields a polymer by normal amine mechanism with minimum termination. By contrast when the reaction was not carried out at high vacuum, there were several termination products.

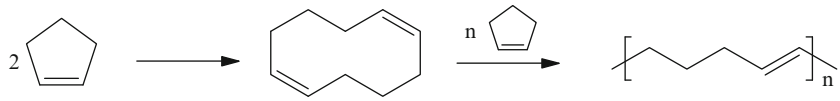
5.11 Metathesis Polymerization of Alicyclics

Ring-opening polymerizations of alicyclics by Ziegler–Natta type catalysts resulted from general studies of olefin metathesis [158–160]. These interesting reactions can be accomplished with the aid of many catalysts. The best results, however, are obtained with complex catalysts based on tungsten or molybdenum halides. One such very good catalyst forms when tungsten hexachloride is combined in right proportions with ethylaluminum dichloride and ethanol.

Several reaction mechanisms were proposed to explain the course of olefin metathesis. Most of the evidence supports a carbene mechanism involving metal complexes, originally suggested by Harrison and Chauvin [160–163]. A typical metathesis reaction of olefins can be illustrated as follows:

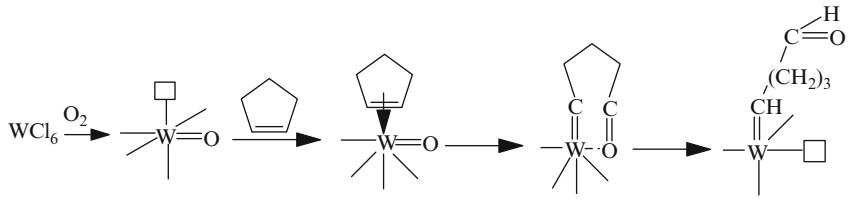


When this reaction is applied to cyclopentene, a high molecular weight polymer forms [164]:

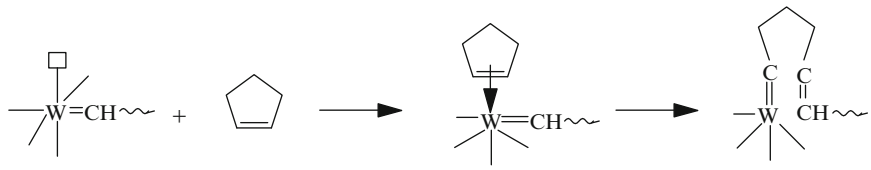


Tungsten hexachloride can apparently also act as a catalyst without the aluminum alkyl. In that case it is believed to be activated by oxygen [166].The propagation reaction based on the tungsten carbene mechanism can be shown as follows [162]:

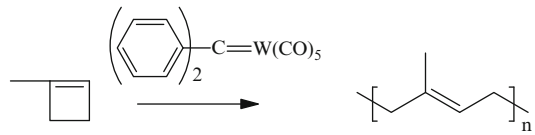
Initiation



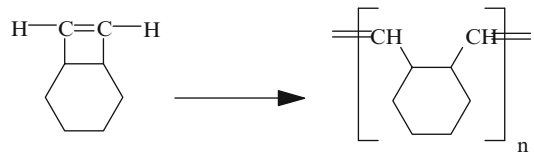
Propagation



It is significant that metal carbenes can act as catalysts for this reaction. Thus, a carbene $(C_6H_5)_2$–C=$W(CO)_5$ will polymerize 1-methylcyclobutene to yield a polymer that is very similar in structure to *cis*-polyisoprene [162]:

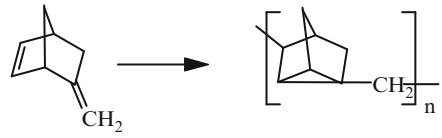


This carbene also yields high molecular weight linear polymers from bicyclo[4.2.0]octa-7-ene monomer [167]:

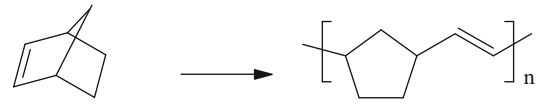


The same product can also be obtained with $WCl_6/Sn(CH_3)_4$ catalyst. The molecular weight of the product, however, is lower [167].

Some cycloolefins can undergo either a regular cationic polymerization or a metathesis one, depending upon the catalyst. One of them is norbornene and its derivatives. For instance, 5-methylene-2-norbornene polymerizes by a cationic mechanism with a 1:1 combination of tungsten hexachloride with tetraalkyltin. A 1:4 combination of a tungsten halide with either $C_2H_5AlCl_2$, or $MoCl_5$, or $TiCl_4$, or other acidic catalysts [166] yields the same product. The polymer that forms has the repeat units:



On the other hand, metathesis type polymerizations of norbornene takes place with WCL_6–$[(C_2H_5)_3Al]_{1.5}$ or WCl_6–$(CH_3)_4Sn$ to yield [166]:

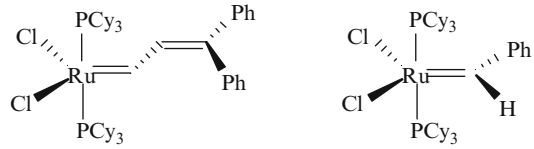


The product, poly[1,3-cyclopentylenevinylene], is a commercial synthetic specialty rubber, with a trade name of *Norsorex*. Reports in the literature show that there may be more than one mechanism of termination [160, 165]. One may be by formation of cyclopropane rings. This is a typical reaction of carbenes [160]. Another one, by a reduction of the transition metal and formation of free radicals [160]:

Still another way may be by hydrogen migration in the carbene complex [151]:

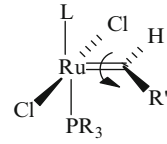
The chemistry of metathesis polymerization has been applied to preparation of unsaturated polycarbonates [168].This is a case of an acyclic diene metathesis. It takes place when Lewis acid free-catalysts are employed [169]. An example of one such catalyst is $Mo[CHC(CH_3)_2Ph](N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$. One interesting point about this process is that unconjugated dienes are polymerized to high molecular weight linear polymers without formations of any cyclic structures.

The ring-opening catalysts described above show sensitivity towards oxygen and moisture. Catalysts, however, that are based on ruthenium and osmium, often referred to as ***Grubbs catalysts***, exhibit good stability towards oxygen and moisture [170]. Examples of such catalysts are $RuCl_3$(hydrate), $OsCl_3$(hydrate), and ruthenium benzylidine catalyst, like $(Cyclohexyl_3P)_2Cl_2$ Ru=CH–CH=CPh and $(Cyclohexyl_3P)_2$Ru=CHPh [170]. They can be illustrated as follows:



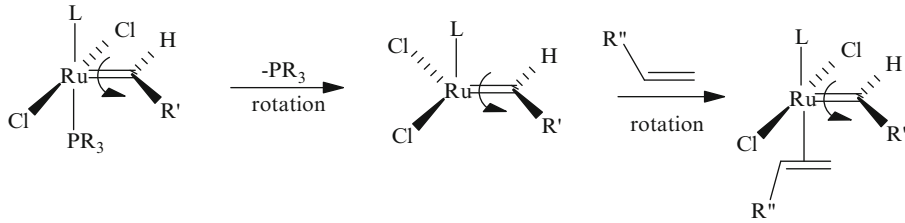
These materials require a small amount of solvent for activation.

A second generation of the Grubbs catalyst has a higher metathesis activity. It can be illustrated as follows:



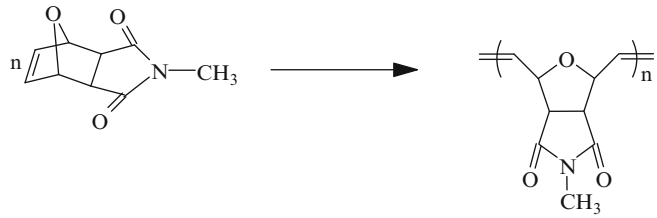
In the first generation, L is PR_3, as shown above, but in the second generation L is N-heterocyclic carbene, R is a cyclohexyl group, and R′ is a phenyl group.

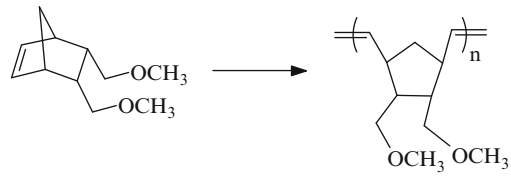
The discrepancy between the two catalysts was elucidated by Truhlar et al. [170] with aid of a computational density functional method named Mo6-L. They found that the benzylidine ligand in both catalysts rotates and serves as a toggle switch to trigger the metathesis reaction. The rotation precedes dissociation in the Grubbs 1 catalyst but occurs in synchronization with the dissociation in the Grubbs 2 catalyst [170].



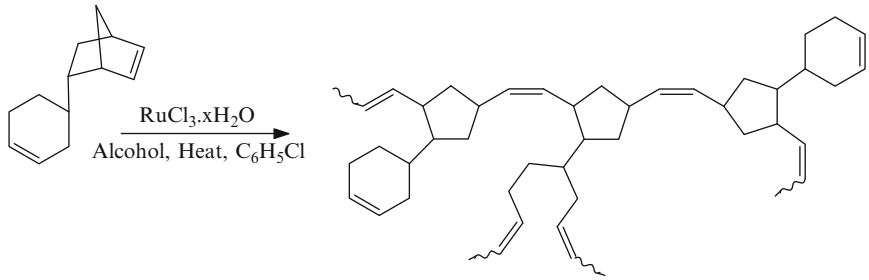
When the olefin substrate coordinates to ruthenium in the Grubbs 1, the catalyst must overcome electronic effects stemming from the rotation, a barrier that is lower in Grubbs 2.

Following are examples of polymerization reactions that were carried out with Grubbs catalysts [170]:



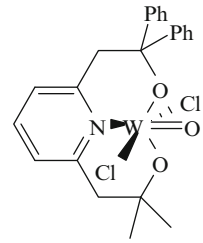


Another example, using a different ruthenium catalyst is polymerization of cyclohexenyl norbornene to form high molecular weight products [171]:



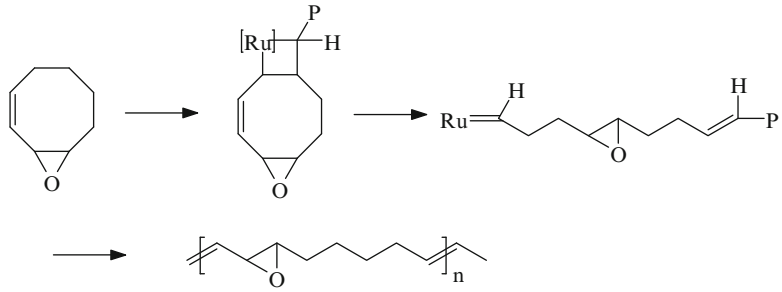
The versatility of these catalysts was further illustrated, when ring-opening metathesis polymerizations of norbornene were carried out in liquid carbon dioxide at high pressure, using Ru $(H_2O)_6$–$(Tos)_2$. The product was reported to be *cis*-ditactic polynorbornene [172]. It should be noted, however, that stereoselective polymerizations of norbornene are not confined to these catalysts only.

For instance, polymerization of norbornene with a tungsten based catalyst, combined with $(C_2H_5)_3Al$ as the co-catalyst,



was reported to have yielded at −78°C, 92% *cis* polymer [173].

Nevertheless, the Grubbs catalysts are very versatile and have made a great impact on polymer chemistry. Following are additional examples of use of Grubbs catalysts. One of them is ruthenium catalysts based on $[RuCl_2(arene)]$ dimers, with ligands of durene or *p*-cymene. They were formed by addition of tricyclohexylphosphine and activated with (trimethylsilyl)diazomethane [174]. These catalysts show good functional compatibility in preparation of a variety of polyoctenamers with epoxide, acid, ether, ester, acetal and bromine functionalities.[236] The following illustration serves as an example [174]:

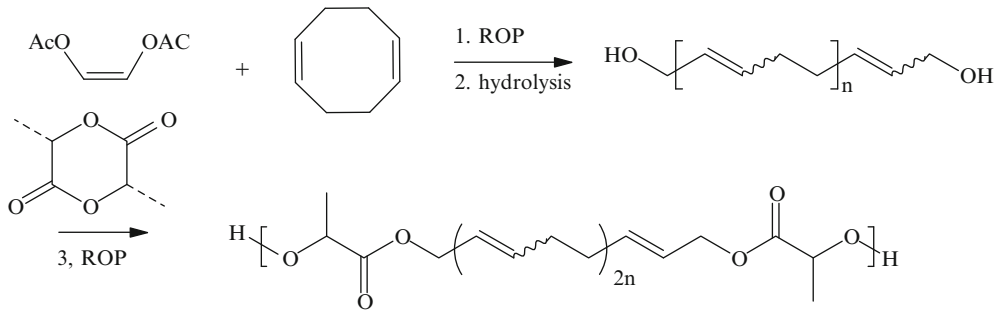


In addition, it was shown that some ring-opening metathesis polymerizations exhibit the characteristics of living polymerizations. Thus, the polymerization of cyclobutene with a tungsten catalyst $[W(CH\text{-}t\text{-}C_4H_9)(NAr)(O\text{-}t\text{-}C_4H_9)_2]$ (Ar = 2,6-diisopropyllphenyl), was shown to fit the category of living polymerization and was used to form block copolymers [175, 176]. Similarly, some substituted cyclobutanes were polymerized in a living manner using a molybdenum catalyst, $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ [Ar = 2,6-diisopropylphenyl] in combination with $PPhMe_2$ [177]. Also, bicyclo[3.4.0]heptene polymerization was found to be a living one when a ruthenium catalyst, $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ was used [178].

Polymers that contain pendant carbazole groups can exhibit photoconductivity (see Chap. 10). Formation of block copolymers with pendant carbazole groups was reported via a living ring-opening metathesis polymerization using a ruthenium catalyst [179]. In addition, what appears to be a first example of a homogeneous living polymerization in water was reported recently [180]. The reaction was carried out in the presence of a Bronsted acid using alkylidine ruthenium complexes. Water-soluble monomers polymerized quickly and quantitatively in the absence of surfactants or organic solvents. These polymerizations were found not to be living, however, when the Bronsted acid was absent [180]. It was suggested that the function of the acid is to eliminate hydroxide ions and to enhance the catalyst activity by protonating the phosphine ligands [2180].

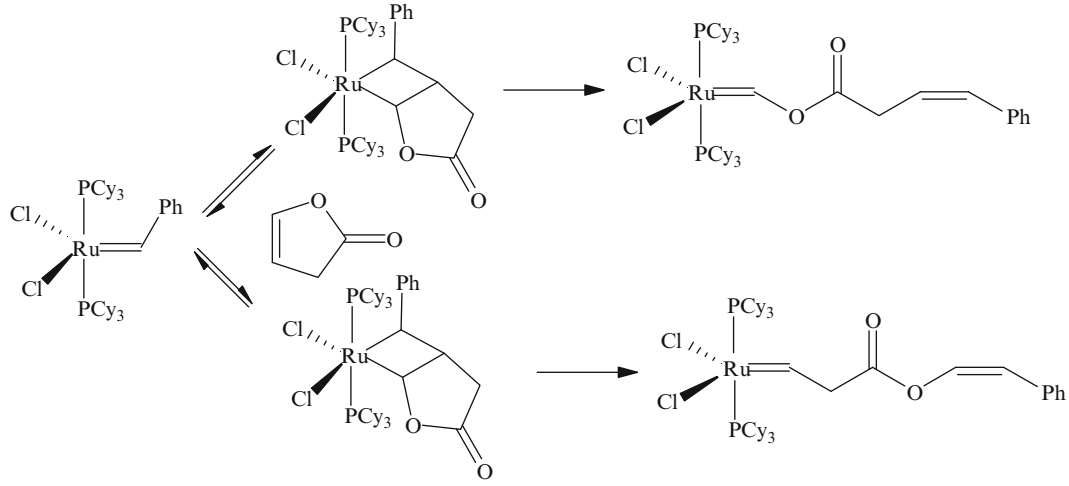
Yong and Swager [181] reported ring-opening metathesis copolymerizations of calixarene containing monomers with cyclooctene and norbornene to yield high molecular weight transparent elastic polymers.

Pitet and Hillmyer [182] combined metathesis ring-opening polymerization with cyclic ester ring-opening metathesis polymerization to form triblock AABA copolymers of cycloocatadiene and D,L-lactide.



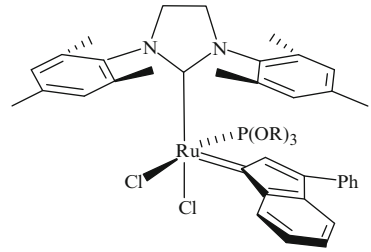
The product is a terpolymer with a soft midblock component with hard blocks at the end. As a result the polymer is a strong and tough material.

Ruthenium catalysts are reactive only towards olefins. As a result, it is possible to introduce functional groups into the monomer prior to polymerizations. This was demonstrated by Hilf and Kilbinger [183] They demonstrated that small ring vinyl lactones and carbonates are efficient quenchers for the olefin metathesis polymerization. The slow kinetics of the reaction can be overcome by an excess of the reagent. The rapid termination of the polymerization reaction yields highly functionalized polymers with narrow molecular weight distribution:



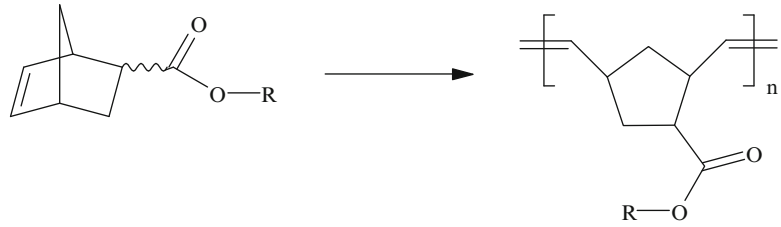
Metathesis type catalysts can also polymerize substituted acetylenes. This is discussed in Chap. 10.

A class of olefin metathesis catalysts that contains phosphite ligands has advantages over current catalysts for some challenging reactions, such as ring-closing metatheses of hindered dienes. Cazin et al. [184] modified an existing ruthenium indenylidene metathesis catalyst with triisopropyl phosphite groups to form *cis* and *trans* phosphite complexes.



The catalysts, that they call *cis*- and *trans*-Caz-1, promote a difficult tosylamine ring-closing with 100% conversion, compared with about 60% achieved by existing catalysts. And a considerably smaller amount of Caz-1 is needed to promote ring-closing metathesis of hindered dienes than is required for current catalysts. The Caz-1 catalysts also show unusually good stability and longevity in reactions [184].

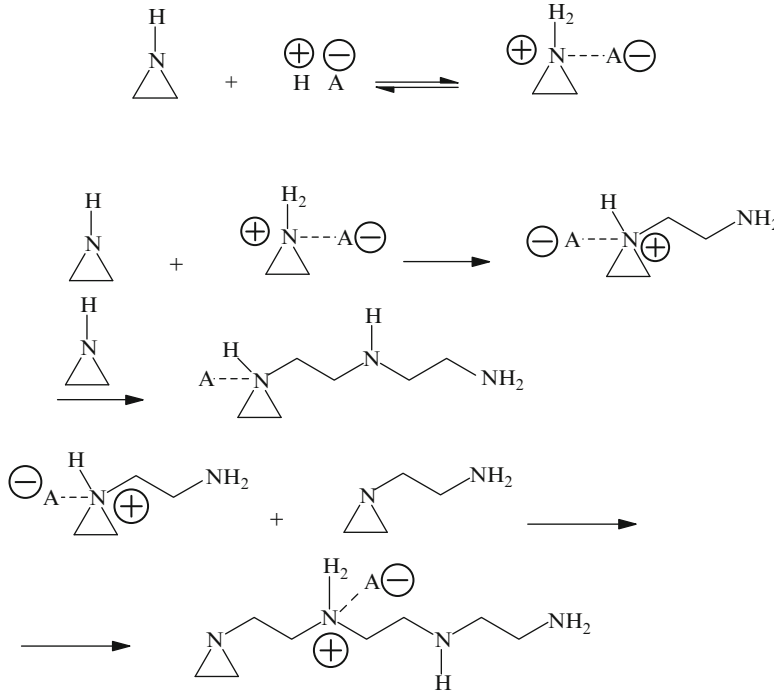
Wathier, Stoddart, and Grinstaff reported using the Grubs catalyst to form high molecular weight polymers, poly(ethyl-5-norbomene-2-carboxylate) and poly(methyl-5-oxanorbomene-2-carboxylate) carrying ester functions. The preparations were illustrated as follows [185]:

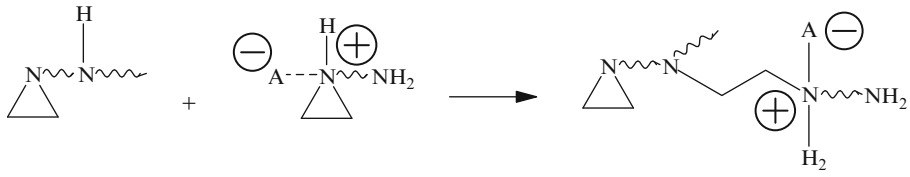


The authors point out that synthesizing high molecular weigh polymers with the aid of the Grubbs' catalyst can be difficult. Small changes in the structure of the monomer (i.e., oxa-norbornene vs. norbornene) can lead to drastic change in polymerization outcomes. On the other hand, the polymerization of norbornene with Grubbs' catalyst can lead to high molecular weight polymers with relatively narrow molecular weight distribution [185].

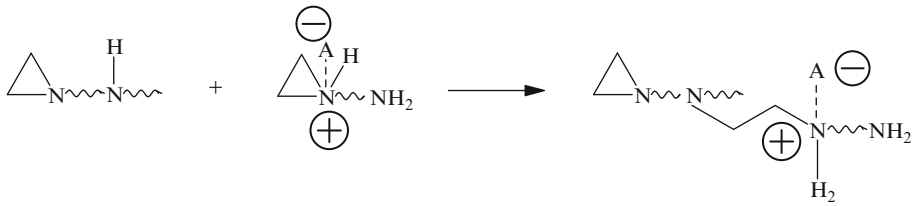
5.12 Polymerization of Cyclic Amines

The cyclic amines or imines (aziridines) polymerize only with acidic catalysts [186]. This reaction can be illustrated as follows:



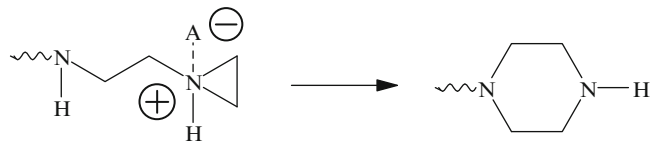


The high degree of strain in the three-membered rings causes very rapid polymerizations. A variety of cationic species act as efficient catalysts for such reactions. The propagating species are iminium ions and the propagation steps result from nucleophilic attacks by the monomers on the ions, as shown above. Branches form due to reactions of secondary amine groups with the iminium centers. They can also result from attacks by the imine end groups of inactive polymer chains on the iminium centers of the propagating species. As the reaction progresses, it slows down



because the protons become equilibrated with various amines [185]. The polymer is also extensively cyclized due to intramolecular nucleophilic attacks of primary and secondary amines on the iminium group. The product contains cyclic oligomers and polymer molecules with large size rings.

The termination mechanism is still not fully explained. It is believed that it may take place by proton abstractions from the iminium ions by the counterions, or by any nitrogen in the polymer chains, or by the nitrogens of the monomer units. It was also suggested [185, 186] that backbiting and ring expansion terminate the reactions. Such ring expansions result in formations of relatively unreactive piperazine end groups:



Substitution on the ethylene imine ring hinders polymerization [185]. The 2,3 and 1,2 substituted aziridines fail to polymerize. Only low molecular weight linear and cyclic oligomers form from 1 and 2 substituted ethylene imines.

In polymerization of secondary cyclic amines, formation of the nonstrained ammonium salt is actually a termination reaction. If the rate, therefore, of propagation, is not considerably higher than the rate of termination, the formation of high molecular weight material will not be possible. Thus ratio of k_p/k_t should, therefore be high. The rate of polymerization can be written as:

$$R_p = -\mathrm{d}m/\mathrm{d}t = k_p m[P_n^+]$$

where, m is the concentration of the monomer and $[P_n^+]$ is the concentration of the growing chains. Assuming that the termination is a first-order reaction, then, the rate of termination can be expressed as:

$$R_t = -\mathrm{d}[P_n^+]/\mathrm{d}t = k_t[P_n^+]$$

If, on the other hand, termination is a result of reactions of the growing chains with any of the amino functions of the polymer and is a second-order reaction then:

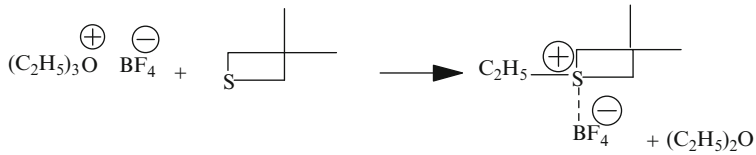
$$R_t = -d[P_n^+]/dt = k_t[P_n^+](m_0 - m)$$

where m_0 is the original monomer concentration

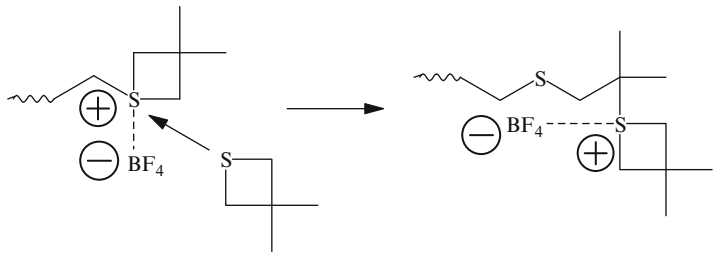
5.13 Ring-Opening Polymerizations of Cyclic Sulfides

Ring-opening polymerizations of cyclic sulfides can be carried out by anionic, cationic, and coordinated mechanisms [187–189]. These polymerizations are easier to carry out then those of the oxygen analogs, because the sulfur–carbon bond is more polarizable. On the other hand, due to the larger size of the sulfur atoms the rings are less strained than in the oxygen compounds. As a result, the sulfur analog of tetrahydrofuran fails to polymerize. In cationic polymerizations, the propagating species are sulfonium ions [189, 190] and in anionic ones the sulfide anions. Goethals and Drigvers proposed the following cationic mechanism for the polymerization of dimethyl thiethane [189]:

1. The initiation mechanism with triethyl fluoroborate consists of alkylation of the monomer molecule and formations of cyclic sulfonium ions. The reaction occurs instantaneously and quantitatively:



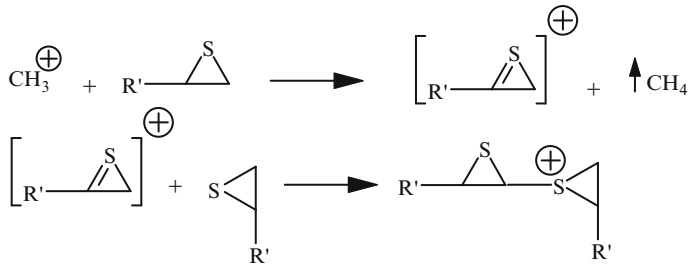
2. The propagation reaction probably involves nucleophilic attacks at the α-carbon atom of the cyclic sulfonium ions by the sulfur atoms from other monomer molecules:



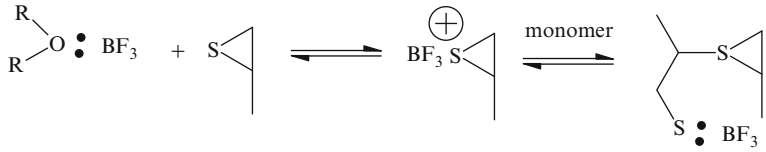
The existence of the sulfonium ions among the propagating species was confirmed with NMR studies [191].

3. Termination is presumed to occur through formations of unreactive sulfonium ions.

Two mechanisms of formation of sulfonium ions are possible: (1) by approaches to the catalyst's electron accepting sites, (2) by abstraction of hydrides by methyl cations [190]:



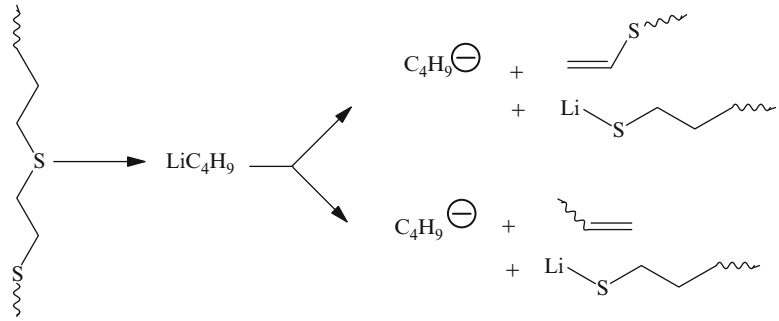
There are indications of a "living" chain-growth mechanism in boron trifluoride diethyl etherate initiated polymerizations of propylene sulfide [192] at conversions of 5–20%. In these early stages of polymerization the molecular weight corresponds to that calculated for typical "living" polymers. This is believed to take place through formations of stable sulfonium ions:



Higher conversions in thiirane polymerizations, however, proceed with chain scission transfer mechanism under the influence of BF_3•$(C_2H_5)_2O$ [192]. This is indicated by a change in the molecular weight distribution, a bimodal character. When the reaction is complete there is a marked decrease in the average molecular weight of the polymer. When thietane polymerizes with triethyl-oxonium tetrafluoroborate initiation in methylene chloride, the reaction terminates after only limited conversion [193]. This results from reactions between the reactive chain ends (cyclic sulfonium salts) and the sulfur atoms on the polymer backbone. In propylene sulfide polymerization, however, terminations are mainly due to formations of 12-membered ring sulfonium salts from intramolecular reactions [193].

When the polymerizations of cyclic sulfides are carried out with anionic initiators, many side reactions can occur. On the other hand, common anionic initiators, like KOH yield optically active polymers from optically active propylene sulfide [194]. An example of a side reaction is formation [192] of propylene and sodium sulfide in sodium naphthalene initiated polymerizations. Such reactions are very rapid even at −78°C. A similar reaction was shown to take place with ethyllithium [195]:

Other side reactions that occur in butyllithium-initiated polymerizations are cleavages of the polysulfides [192]:



High molecular weight polymers can be prepared from ethylene sulfide with a diethylzinc–water catalyst [196]. The polymers form in two steps. Initially insoluble crystalline polymers form at room temperature with a high catalyst to monomer ratio. These product polymers, that contain all of the catalyst act as seeds for further polymerizations. Though the final polymers are insoluble, the molecular weights are estimated to be high. At a conversion of 20% the molecular weights are believed to be about 900,000 [196]. When diethylzinc is prereacted with optically active alcohols, optically active poly(propylene sulfide)s form [197–199]. Cadmium salts are also very effective catalysts for polymerization of thiiranes. The polymers of substituted thiiranes have high stereoregularity.

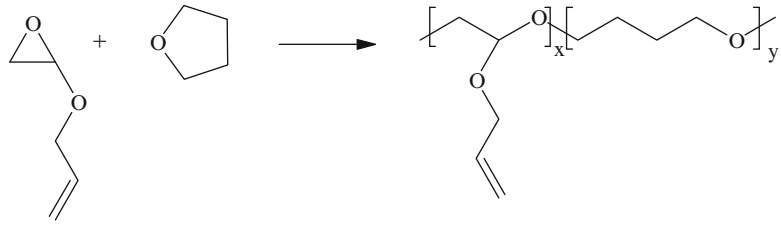
5.14 Copolymerization of Cyclic Monomers

Many copolymers have been prepared from cyclic monomers. These can form through ring-opening copolymerizations of monomers with similar functional groups as well as with different ones. Some cyclic monomers can also copolymerize with some linear monomers. Only a few copolymers of cyclic monomers, however, are currently used industrially.

The composition of the copolymers depends upon the reaction conditions, the counter ions, the solvents, and the reaction temperatures. The initiator system can be very important when cyclic monomers with different functional groups are copolymerized. Also, if different propagating centers are involved in the propagation process, copolymerizations can be very difficult to achieve.

Prominent among copolymers of cyclic ethers are interpolymers of oxiranes with tetrahydrofuran. Thus, ethylene oxide copolymerizes with tetrahydrofuran with the aid of boron trifluoride–ethylene glycol catalytic system [200]. The resultant copolyether diol contains virtually no unsaturation.

Another example is a copolymer of allyl glycidyl ether with tetrahydrofuran formed with antimony pentachloride catalyst [201]:

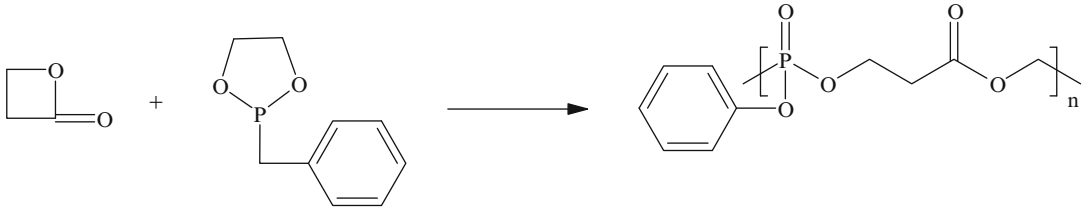


In addition to the above, liquid copolymers form from 1,3-dioxolane with ethylene oxide, when boron trifluoride is used as the catalyst [1]. Also, a rubbery copolymer forms from tetrahydrofuran and 3,3-diethoxycyclobutane with phosphorus pentafluoride catalyst [202]. A 3,3-bis(chloromethyl) oxacyclobutane copolymerizes with tetrahydrofuran with boron fluoride or with ferric chloride catalysis. The product is also a rubbery material [1].

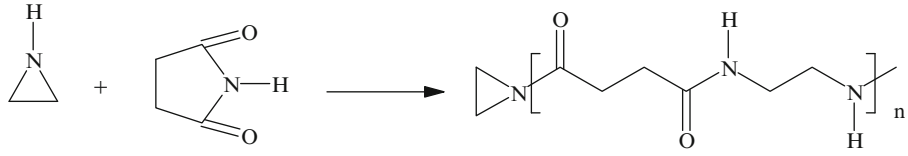
Various copolymers were reported from trioxane with dioxolane or with glycidyl ethers [2, 3]. For instance, a copolymer of trioxane and dioxolane forms with $SnCl_4$, BF_3, or $HClO_4$ catalysts. The products from each reaction differ in molecular weights and in molecular weight distributions. Copolymerizations of trioxane with phenylglycidyl ether yield random copolymers [203].

Different lactones can be made to interpolymerize [204]. The same is true of different lactams [205–207]. The products are copolyesters and copolyamides, respectively.

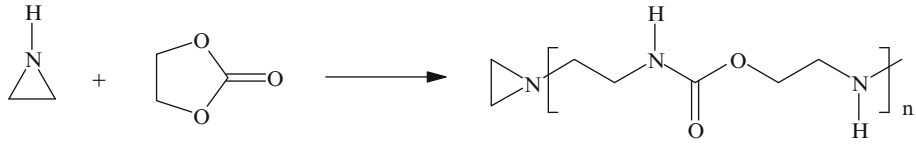
More interesting are copolymers from cyclic monomers of different chemical types. For instance, cyclic phosphite will copolymerize with lactone at 150°C or above in the presence of basic catalysts [208]:



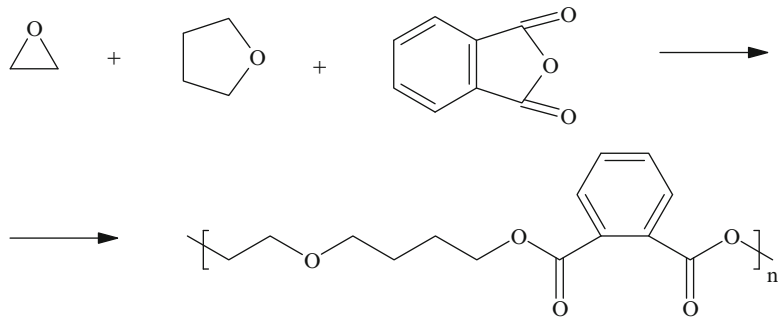
Aziridine copolymerizes with succinimide to form a crystalline polyamide that melts at 300°C [209]:



When in place of succinimide a cyclic carbonate is used, a high molecular weight polyurethane forms [210]:



Terpolymers form from epoxides, anhydrides, and tetrahydrofuran or oxetane with a trialkylaluminum catalyst [211]:

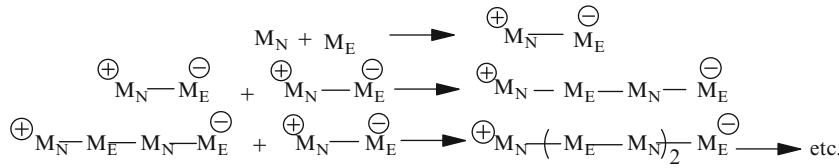


Copolymerizations of caprolactone with caprolactam in various ratios take place with lithium tetraalkylaluminate as the catalyst [212]. The products are mainly random copolymers with some block homopolymers.

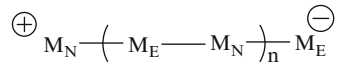
When lactones copolymerize with cyclic ethers, such as β-propiolactone with tetrahydrofuran, in the early steps of the reaction the cyclic ethers polymerize almost exclusively [213]. This is due to the greater basicity of the ethers. When the concentration of the cyclic ethers is depleted to equilibrium value, their consumption decreases markedly. Polymerizations of the lactams commence. The products are block copolymer [213].

5.15 Spontaneous Alternating Zwitterion Copolymerizations

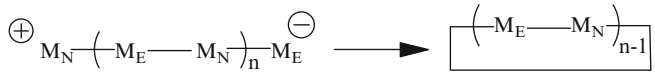
This type of copolymerization results from spontaneous interactions of nucleophilic and electrophilic monomers (M_N and M_E, respectively) without any additions of catalysts. Zwitterions form in the process that subsequently leads to formation of polymers [214–226]. The mechanism is a step-growth polymerization. It can be illustrated as follows:



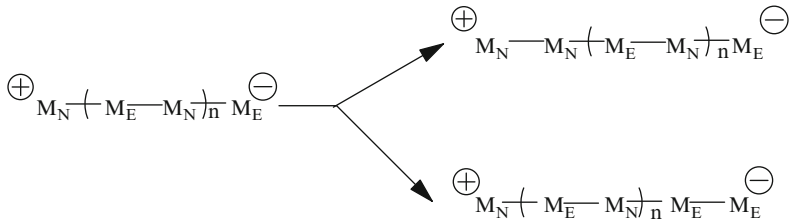
Repeated additions of the charged species and the resulting zwitterionic products lead to high polymers:



The initial zwitterion that forms upon combination of a nucleophilic with an electrophilic monomer is called a *genetic zwitterion* [214]. Intramolecular reactions can produce "macrocycles":

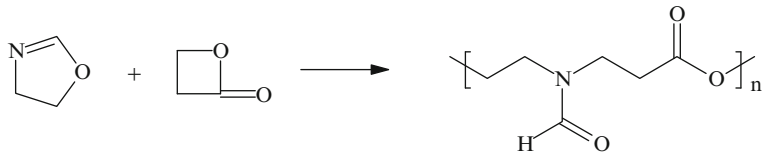


The contribution of the cyclization reaction, however, is, apparently, small [214]. A reaction can also take place between a free monomer and any zwitterion at one of the ionic sites:

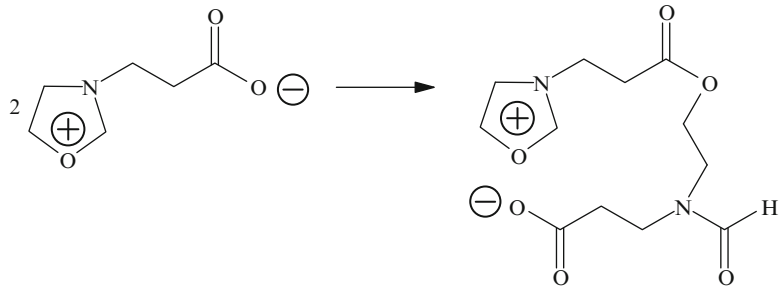


Such reactions disturb the alternating arrangements of the units $-M_N-M_E-$ in the products. The reactivity of the monomers determines whether homopropagations occur as well. Alternating propagation depends upon dipole–dipole interactions between M_N and M_E monomers in preference to ion–dipole reactions between ion centers of zwitterions and monomers in homopropagations [214].

An example of an alternating copolymerization via zwitterion intermediates is a copolymerization of 2-oxazoline with β-propiolactone. It takes place in a solution in a polar solvent like dimethylformamide at room temperature over a period of a day to yield quantitative conversions [215]:



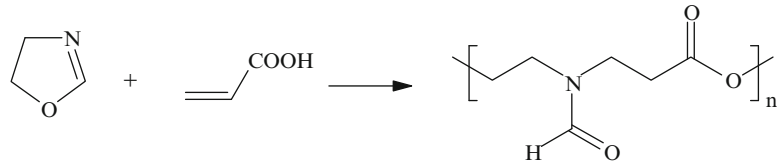
A zwitterion that forms first is the key intermediate for the polymerization. The onium ring from 2-oxazoline is opened by a nucleophilic attack of the carboxylate anion at carbon [214]:



In this reaction the number of copolymer molecules increases at first, then reaches a maximum and finally decreases as the conversion becomes high [214–226]. When the concentration of both

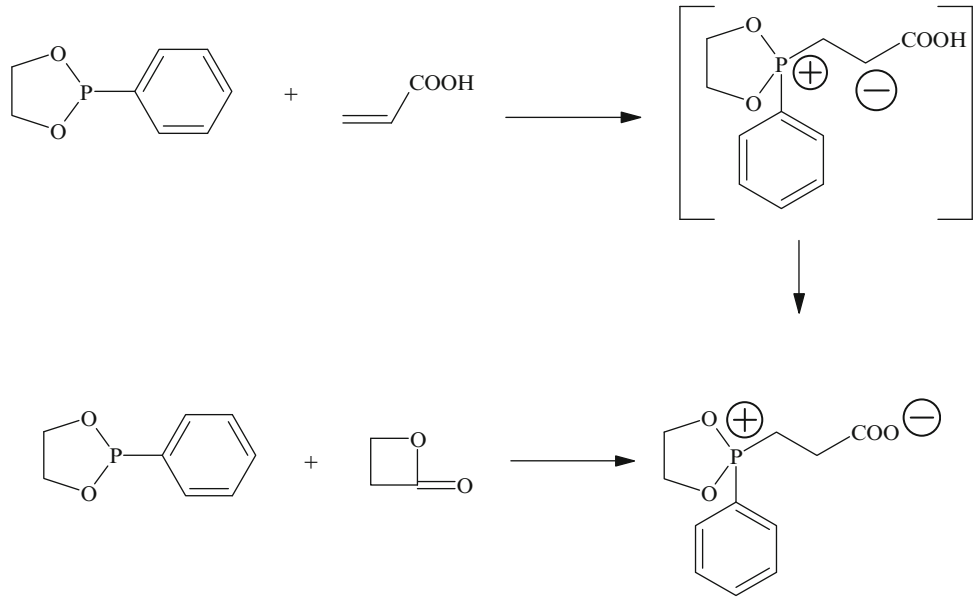
monomers is high then the formation of "genetic" zwitterions is favored. As the concentration of macro-zwitterions becomes high and the monomer concentration decreases, the macro zwitterions react preferentially with each other. When stoichiometry is not observed and β-propiolactone molecules predominate in the reactions mixture, the carboxylate end groups can react in various ways. They can react not only with the cyclic onium sites of the zwitterions, but also with free β-propiolactones and incorporate more than 50% of the propiolactone units [214].

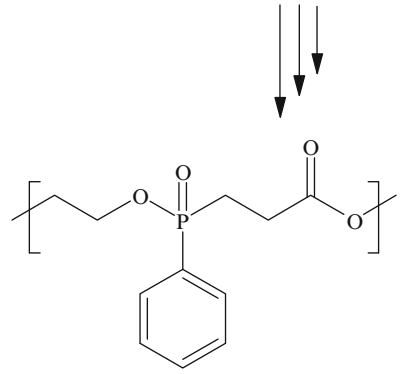
Another example of such copolymerization is that of 2-oxazoline with acrylic acid. The reaction can be carried out by combining the two in equimolar quantities and then heating the reaction mixture to 60°C in the presence of a free radical inhibitor. Such an inhibitor can be *p*-methoxy phenol. The reaction mixture becomes viscous as an alternating copolymer forms [218]:



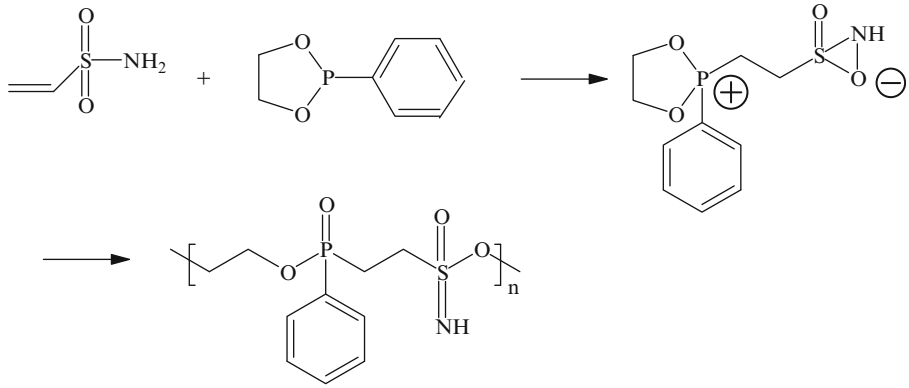
This copolymer is identical to the one obtained from reacting 2-oxazolone with β-propiolactone. The acrylic acid is converted into the same repate unit as the one that forms from ring-opening of β-propiolactone shown in the previous example. The suggested reaction mechanism involves a nucleophilic attack by oxazolone on acrylic acid and is followed by proton migration [214]:

A similar proton migration takes place in copolymerizations of acrylamide with cyclic imino ethers. The proton migration is part of the propagation process [219]. Other examples are copolymerizations of a nucleophilic monomer, 2-phenyl-1,2,3-dioxaphospholane with electrophilic monomers [224, 225]. Here too the electrophilic monomers can be either acrylic acid or propiolactone. Identical products are obtained from both reactions [223]:

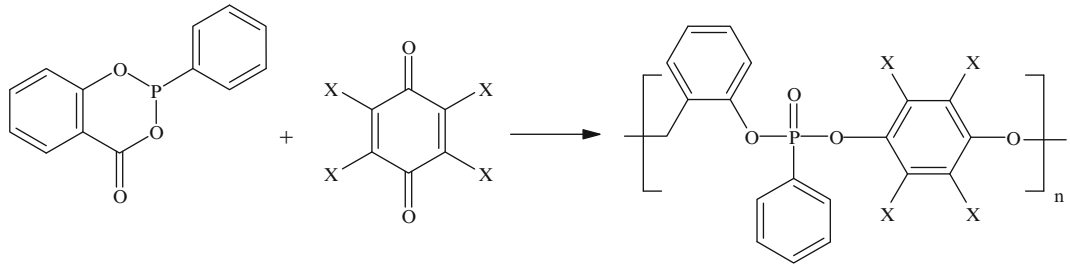




The opening of the phosphonium ring requires higher temperatures (above 120°C) and follows the pattern of the Arbusov reaction [224, 226]. Examples of some other monomers that can also act as nucleophiles in the above reaction are *p*-formyl benzoic acid [214], acrylamide [224], and ethylene sulfonamide. All three react in the same manner [224]:

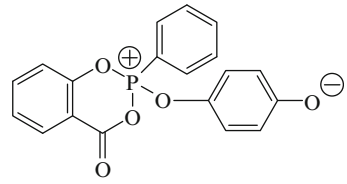


It is reasonable to expect that some compounds can act at one time as M_N monomers and at other times as M_E, depending upon the comonomer. This is the case with salicylyl phenyl phosphonite [224]. In the presence of bezoquinone it behaves as an M_N monomer and produces a 1:1 alternating copolymer at room temperature [224]:



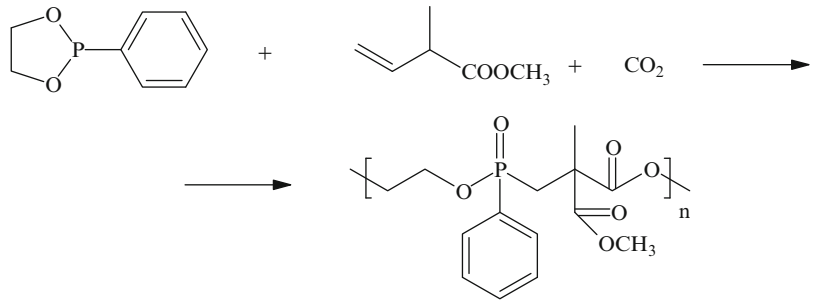
where, X = Y = H; X = Y = Cl; X = Y = CH_3; X = Cl; and Y = CN.

The above reaction is called a ***redox copolymerization*** reaction [224]. The trivalent phosphorus in the monomer is oxidized to the pentavalent state in the process of polymerization and the quinone structure is reduced to hydroquinone. The phosphonium-phenolate zwitterion is the key intermediate:

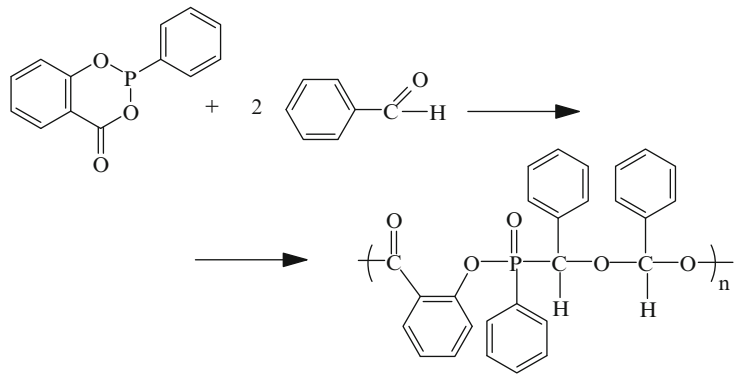


Nucleophilic attack of the phenoxide anion opens the phosphonium ring due to enhanced electrophilic reactivity of the mixed anhydride and acid structures [224]. Salicylyl phenylphosphonite, however, in combination with 2-methyl-2-oxazoline behaves as an M_E monomer [224].

Terpolymerizations by this mechanism of sequence ordered 1:1:1 components can also take place. The following is an example [224]:

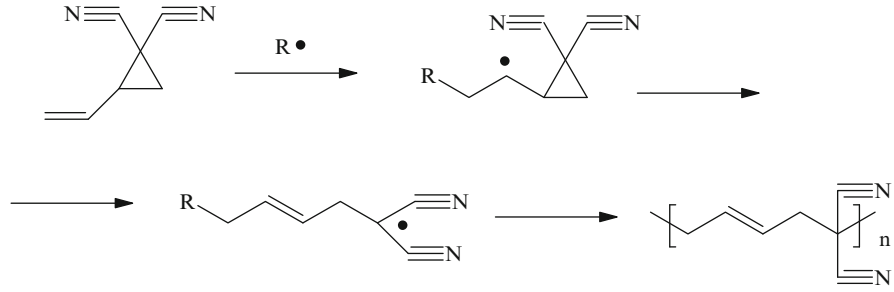


In addition 2:1 binary copolymerizations were also observed. Following is an example of a binary copolymerization [226]:



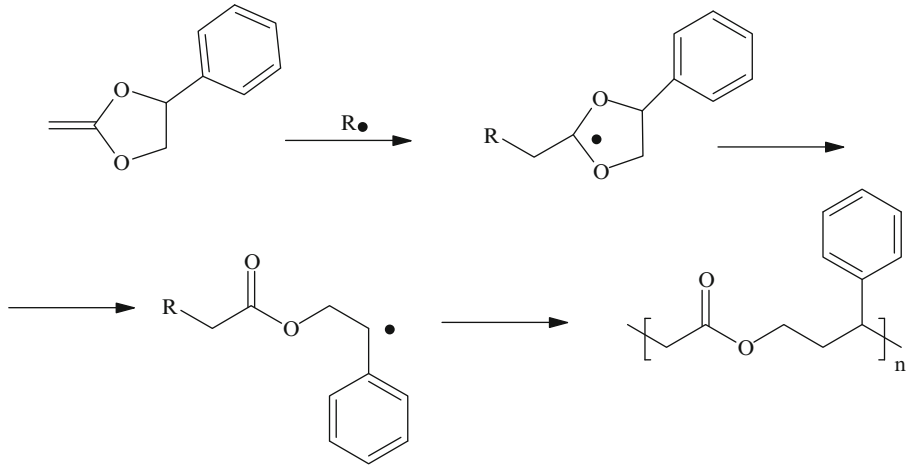
5.16 Ring-Opening Polymerizations by a Free Radical Mechanism

There are some reports in the literature of ring-opening polymerizations by free radical mechanism. One is a polymerization of substituted vinyl cyclopropanes [227]. The substituents are radical stabilizing structures that help free radical ring-opening polymerizations of the cyclopropane rings. This can be illustrated as follows:

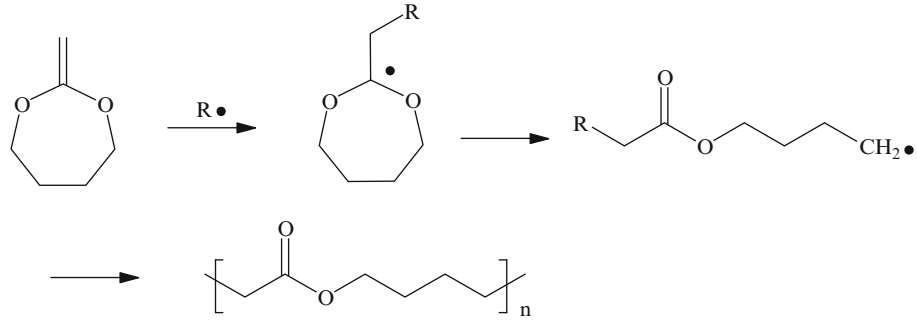


A high molecular weight polymer forms. In place of nitrile groups ester groups can be utilized as well. The polymerizations of vinyl cylopropanes proceed by cationic and coordination mechanisms exclusively through the double bonds. Free radical polymerizations of these substituted vinyl cyclopropanes, however, take place only through ring-opening polymerizations of the propane rings.

In a similar manner, ring-opening polymerizations of five-membered acetals are helped by free-radical stabilizing substituents [228]. Complete ring-opening polymerizations take place with phenyl substituted compounds:

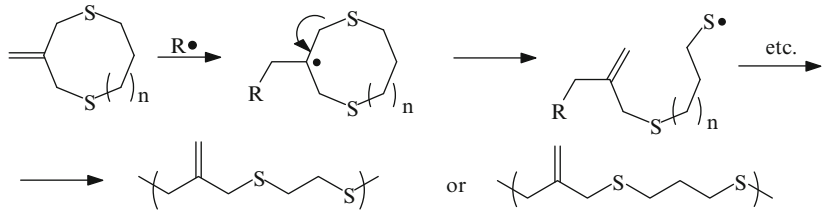


Some other heterocyclic monomers, like acetals, also polymerize by free-radical mechanism [229]. Particularly interesting is an almost quantitative ring-opening polymerization of a seven-membered acetal, 2-methylene-1,3-dioxepane [230]:



The product is an almost pure poly(ε-caprolactone).

Cyclic allylic sulfides were shown to polymerize by a free-radical ring-opening mechanism [231]. The key structural unit that appears to be responsible for the facile ring-opening is the allylic sulfide fragment. In it the carbon–sulfur bond is cleaved [231]:



It was also reported recently that a controlled free-radical ring-opening polymerization and chain extension of the "living" polymer was achieved in a polymerization of 2-methylene-1,3-dioxepane in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) [232] The reaction was initiated with di-*tert*-butyl peroxide at 125°C

At high concentrations of the piperidinyloxy radical, the polydispersity of the product was 1.2 [232]

5.17 Thermodynamics of Ring-Opening Polymerization

The stability of the ring structure as well as the stability of the resultant linear polymer determines the polymerizability of cyclic monomers. Thermodynamic factors, therefore, are of paramount importance in ring-opening polymerizations [233]. Actually, the polymerization of many bond-strained ring monomers is favored thermodynamically. Thus, for instance, ΔH, for three-membered cycloalkanes is −113.0 kJ/mole and ΔS is −69.1 J/mole °C. It was shown (Sawada) that in three- and four-membered ring structures, the change in enthalpy is a major factor in determining ΔF, the change in free energy. For three-membered cycloalkanes ΔF is −92.0 kJ/mole, while for four-membered ones it is −90.0 kJ/mole. The entropy change, ΔS is a major factor in polymerization of five-membered cyclic monomers. The six-membered ring monomers that are relatively strain free are very hard to polymerize. An exception is trioxane, whose ΔH is close to zero. On the other hand, the enthalpy and entropy factors contribute about equally to the free energy change of larger rings. This means that with increases in temperature ΔF becomes less and less negative and above certain temperatures some large cyclic monomers will not polymerize. The transanular strain in seven- and eight-membered rings contributes to their polymerizability. Presence of substituents in cyclic monomers has a negative effect on the thermodynamic feasibility to polymerize. On the other hand, thermodynamic feasibility alone does not determine whether a cyclic monomer will polymerize.

The entropy changes do not show much dependence of on angle strain. They are susceptible, however, to configurational influences. Sawaada [233] writes the entropy change of polymerization as a function of the probability of ring closure:

$$\Delta S_{\mathrm{p}} = -b \ln P - a$$

where P is the probability of ring closure and a and b are constants. The probability of ring closure for a chain with n repeating units can be taken as a function of the probability that the chain ends will come together. This probability is usually expressed as a radius of gyrations, (r^2), the root square

distance of end to end. The entropy change for three-membered rings would have a large negative value. For larger rings the negative value would be less, because the end to ends would be further apart. Statistical mechanics treatment has shown that the entropy change of ring closure is [223]:

$$\Delta S_{\mathrm{r}} = R \ln\{PV/2xV_{\mathrm{s}}N\}$$

where P is the probability of ring closure or the fraction of chain ends that will come together and close to form ring structures, V is the total volume of the system, V_{s} is the volume of a constrained skeletal atom prior to bond breaking, x is the number of monomer units in the ring, and N is the Avogadro's number.

Review Questions

Section 5.1

1. Are the mechanisms of ring-opening polymerizations of cyclic monomers chain-growth of step-growth reactions? Explain

Section 5.2

1. Write the rate expression for propagation in ring-opening polymerizations where there is an equilibrium between propagation and depropagation.
2. Write the kinetic expression for the total concentration of monomer segments that are incorporated into the polymer.

Section 5.3

1. Oxiranes can be polymerized by three different mechanisms. What are they? Explain.
2. Write the chemical reactions for the mechanism of polymerization of ethylene oxide with the aid of stannic chloride. Does a high molecular weight polymer form? If not, explain why.
3. Write the chemical reactions for the mechanism of polymerization of propylene oxide with boron trifluoride–water.
4. Describe the mechanism and write the chemical reactions of ring-opening polymerizations of oxiranes with potassium hydroxide. In polymerization of propylene oxide with KOH what type of tacticity polymer forms. Explain.
5. Describe the mechanism and write the chemical equations for coordinated anionic polymerizations of propylene oxide by ferric chloride and by diethylzinc–water. Show reaction mechanism.
6. Discuss the general characteristics of steric control in the polymerizations of oxiranes.
7. Explain the mechanism postulated by Tsuruta of steric control in polymerizations of oxiranes with the aid of organozinc compounds, giving the structure of the catalyst and the mode of monomer insertion and the mode or ring opening.

Section 5.4

1. Describe the initiation process in polymerizations of oxetanes, including initiators and reaction mechanism
2. Describe the mechanism of propagation in polymerizations of oxetanes.

Section 5.5

1. Discuss, including chemical equations, the initiation reactions in tetrahydrofuran polymerization, including the mechanism and various initiators
2. Discuss the propagation reaction in polymerization of tetrahydrofuran.
3. When are both ionic and covalent species present during the polymerization of tetrahydrofuran. Explain conditions that cause formation of both species and draw structures of both.
4. Describe the termination reaction in tetrahydrofuran polymerization, including living polymerization.

Section 5.6

1. How do the rates of oxepane polymerization compare with those of oxetane and tetrahydrofuran? What affects these rates.

Section 5.7

1. How and why do the cationic polymerizations of cyclic acetals differ from those of other cyclic ethers?
2. What initiators are effective in polymerizations of trioxane? Discuss polymerizations with different initiators.
3. Describe typical polymerization conditions of trioxane.
4. Explain the proposed reaction mechanisms for polymerization of trioxane including the coordinated mechanism in polymerizations with molybdenum acetylacetonate. Illustrate all with chemical structures.
5. Discuss the polymerization of dioxalane, showing mechanism of initiation, propagation, and terminations with different initiators.
6. How does a polymer and a copolymer form side by side in boron trifluoride initiated polymerizations of dioxepane?
7. What type of structures are obtained from ring-opening polymerizations of trioxocane? Show and explain.

Section 5.8

1. Describe cationic polymerization of lactones, showing the initiation and propagation processes.
2. Repeat question one for anionic polymerization.

3. Describe the coordination polymerization of lactones.
4. What are the instances of "living" polymerizations of cyclic lactones and what type of catalysts yield this type of polymerization? Describe and give examples.

Section 5.9

1. What are the three mechanisms of polymerization of lactams?
2. Describe the catalysts that are useful in cationic polymerizations of lactams and the mechanism of polymerization.
3. Show how amidine salts form in cationic polymerizations of lactams and explain how that influences the reaction.
4. Discuss the anionic polymerization of lactams and compare that with the cationic one.
5. What is meant by lactomolytic propagation? Explain.
6. Describe the proposed mechanism for polymerizations of lactams with dialkoxyaluminum hydrides.
7. Describe hydrolytic polymerization of lactams.
8. Compare cationic, anionic, and hydrolytic polymerizations of lactams by writing out all three modes of polymerization side by side and discuss and show the side reactions that take place in each one of them.

Section 5.10

1. Discuss the polymerization of *N*-carboxy-α-amino acid anhydrides

Section 5.11

1. What is metathesis polymerization? Explain the mechanism and show the reaction on a disubstitued olefin.
2. Describe metathesis polymerization of methyl cyclobutene showing the mechanisms of initiation and propagation.
3. Describe "living" metathesis polymerization. What types of catalysts are useful in such polymerizations?

Section 5.12

1. Describe the polymerization of aziridines, showing the initiation and propagation processes.

Section 5.13

1. Explain the three mechanisms by which cyclic sulfides can be polymerized. Describe each.
2. Describe the initiation and propagation reactions in cationic polymerizations of cyclic sulfides.

3. Describe the termination reaction in cyclic sulfides cationic polymerizations.
4. What type of side reactions can occur in anionic polymerizations of cyclic sulfides?

Section 5.14

1. Discuss copolymerizations of cyclic monomers giving several examples.

Section 5.15

1. How does a spontaneous zwitterion copolymerization occur. Explain.
2. What is meant by a genetic zwitterion?
3. Give several examples of zwitterion copolymerization.

Section 5.16

1. Explain ring-opening polymerizations by free-radical mechanism, giving two examples.

Recommended Reading

K.J. Ivin and J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997

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