Ionic polymerization, similar to radical polymerization, involves a chain mechanism in which either cations (cationic polymerization) or anions (anionic polymerization) are the active centers. Because the solution is electroneutral, the number of active centers and their counterions is identical. Whether a monomer with a carbon-carbon double bond can be polymerized anionically or cationically depends on the electron density of the double bond, which in turn depends on the substituents. If the substituents induce a donor effect (OR, NR_2, C_6H_4–CH_3), then the monomer favors a cationic polymerization. By contrast, monomers with acceptor-substituents (CN, COOR, $CONR_2$) can be anionically polymerized. Because the growing chains are identically charged they cannot terminate the reaction by, for example, combining with one another which means they remain active. A complete lack of termination reactions is known as a *living polymerization*. The chains can be extended by the addition of more monomers. Block copolymers can be synthesized by adding other monomers capable of polymerization. Additionally, the molar masses can be controlled using the ratio $[M]:[I]$.

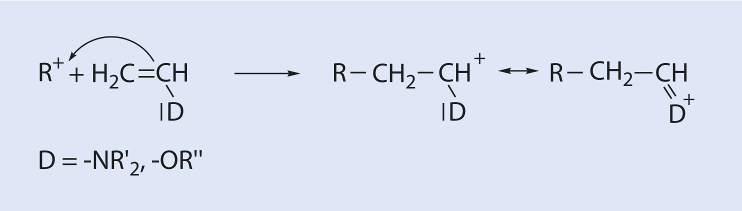
10.1 Cationic Polymerization

Although some of the first polymerizations observed by chemists were probably cationic polymerizations, it was not until it was discovered that isobutene, trioxane, cyclic ethers such as oxirane and tetrahydrofuran, for example, as well as cyclic siloxanes, could be cationically polymerized that a general interest developed in this type of polymerization.

A special feature of cationic polymerization is its high selectivity toward monomers with donor functions (◘ Fig. 10.1).

As is the case for radical polymerization, cationic polymerization has two distinguishable parts, initiation and propagation. A termination of the reaction caused by two growing chains reacting with one another, a typical feature of radical polymerization, is not possible (◘ Fig. 10.2). There are, however, reactions that result in a termination of chain growth, as discussed in ▶ Sect. 10.1.4.2.

As the active species (mostly carbocations) used in cationic polymerization are very reactive, the solvent needs to be chosen with special care and it should be extremely clean; even traces of water or methanol should be avoided. Preferred solvents are CH_2Cl_2, CH_3Cl, $CHCl_3$, benzene, and toluene. The polymerizations are usually carried out at low temperatures because of the reactivity of the species, which increasingly take part in undesirable



$$R^+ + H_2C{=}CH{-}D \longrightarrow R{-}CH_2{-}CH^+{-}D \longleftrightarrow R{-}CH_2{-}CH{=}D^+$$

$$D = \text{-NR}'_2, \text{-OR}''$$

◘ **Fig. 10.1** Addition of a carbocation onto a nucleophilic monomer. *R*, *R′*, *R′′* e.g., alkyl

$$\begin{array}{llllll}
\text{Initiation} & H^+ & + & M & \longrightarrow & HM^+ \ (\equiv R^+) \\
\text{Propagation} & R^+ & + & n\,M & \longrightarrow & R\text{-}M_n^{\ +} \ (\equiv P^+) \\
\text{Termination} & P^+ & + & P^+ & \not\longrightarrow &
\end{array}$$

◘ **Fig. 10.2** Basic steps in a cationic polymerization side reactions, such as Friedel–Crafts reactions or deprotonation, at higher temperatures. It is also advisable to polymerize in a high-vacuum glass apparatus or in a dry box. As an alternative, Schlenk techniques can be used.

10.1.1 Reaction Mechanism

Cationic polymerization can be described using the equation shown in ◘ Fig. 10.3. Vinyl monomers (e.g., isobutene, vinyl ether), carbonyl compounds (e.g., formaldehyde, acetaldehyde), and heterocyclic compounds (e.g., tetrahydrofuran, trioxane) can be cationically polymerized. The growth mechanisms for each of these types of monomers are discussed in the following paragraphs.

In the growth step of the polymerization of a vinyl monomer the growing chain has a terminal positive charge $\sim M_n^+$, and these coordinate with an additional monomer molecule to yield a chain with an additional monomer and a terminal charge $\sim M_{n+1}^+$. The counterion A^- ensures the electroneutrality of the system. The higher the nucleophilicity of the carbon-carbon double bond, the easier it is for cationic polymerization to take place (◘ Fig. 10.4).

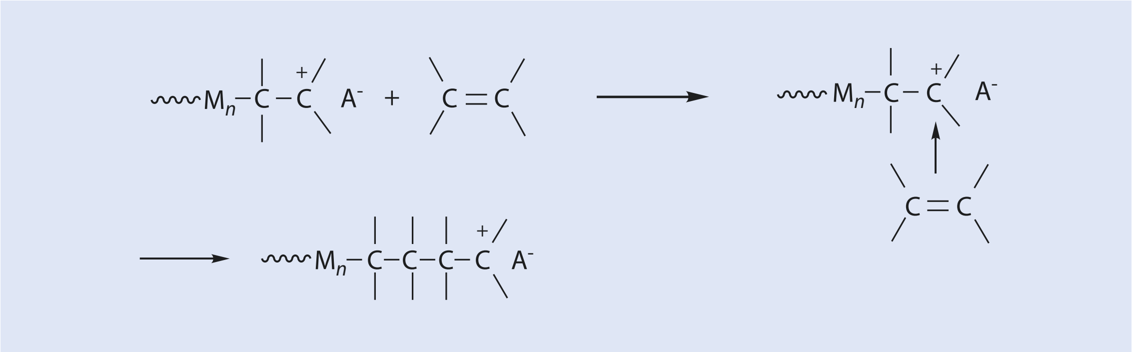
The growth step of the polymerization of carbonyl compounds is shown in ◘ Fig. 10.5. Polymerization takes place because of the nucleophilic attack of the carbonyl function on the charged chain end.

The polymerization of heterocyclic compounds, which occurs via ring-opening polymerization, is shown in ◘ Fig. 10.6.

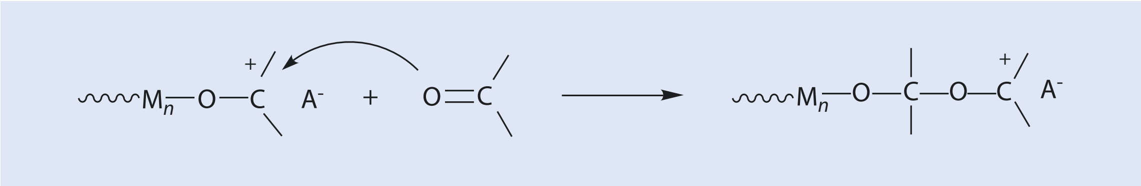
Some cyclic monomers containing oxygen as the hetero atom, which are especially suitable for cationic polymerization, are shown in ◘ Fig. 10.7.

◘ **Fig. 10.3** Propagation in cationic polymerization

$$\sim\!\sim\!\sim M_n^+ \; A^- \; + M \longrightarrow \sim\!\sim\!\sim M_{n+1}^+ \; A^-$$



◘ **Fig. 10.4** Detailed propagation mechanism of the cationic polymerization of a monomer with a C=C double bond



◘ **Fig. 10.5** Propagation mechanism of the cationic polymerization of a monomer with carbonyl group

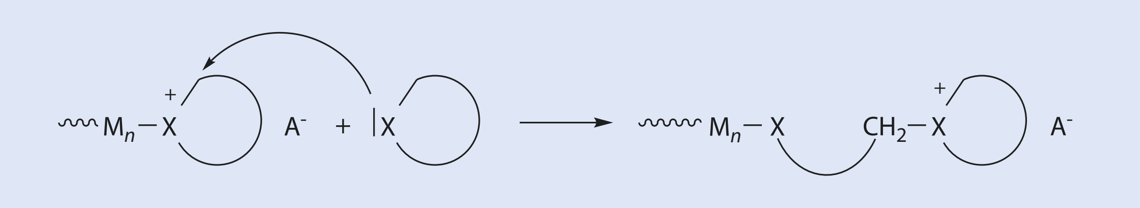
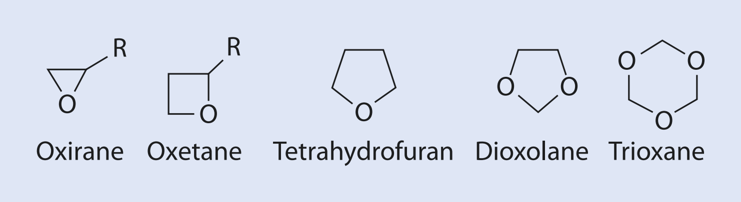


Fig. 10.6 Nucleophilic attack of a heterocyclic monomer on a cationically growing chain

Fig. 10.7 Some cyclic monomers containing oxygen as the hetero atom, suitable for cationic polymerization



As well as those cyclic monomers shown in Fig. 10.7, aziridines, thiiranes, phosphazenes, siloxanes, and oxazolines can all also be cationically polymerized via ring-opening polymerization (▶ Sect. 12.3).

10.1.2 Initiators

Numerous Brønsted and Lewis acids are available for the initiation of cationic polymerization. The choice of initiator depends to a large extent on the monomer to be polymerized.

10.1.2.1 Brønsted Acids

Brønsted acids with a suitable acidity can be used as initiators for cationic polymerization (Fig. 10.8). They can be classified either in acetic acid or acetonitrile as the solvent according to their pK_a values (Table 10.1).

Certain proton acids can easily be added onto carbon-carbon double bonds but, if the anion is more nucleophilic than the monomer, a covalent bond forms between the anion and cation, for example, if HCl is used (Fig. 10.9).

Another example is HI; it can initiate the polymerization of aziridine but not of oxirane. The nucleophilicity of the monomer with respect to the initiator counterion determines whether a polymerization takes place (Fig. 10.10).

Perchloric acid $HClO_4$ is a very interesting initiator as it is made up of a very small cation and a non-nucleophilic anion. However, a water-free handling of this acid is very difficult (and important) as even the smallest contamination of the substance can result in an explosion. For this reason it is often only used diluted with CH_2Cl_2 as a solvent. However, care must be taken, even with the diluted acid.

Although the polymerization rate is first order in monomer (as might be predicted from Fig. 10.11), the rate of initiation is often observed to be second order in monomer and not first order as would be expected. A possible explanation for this is the existence of a transition state, in which two initiator molecules are involved (Fig. 10.11).

The reactivity of monomers increases with their nucleophilicity: styrene < α-methyl styrene < 4-methoxy styrene.

Fig. 10.8 Dissociation of a Brønsted acid

$$HA \rightleftharpoons A^- + H^+$$

Table 10.1 pK_a-values for a selection of Brønsted acids suitable as initiators for cationic polymerization

Brønsted acid		**pK_a-Wert**	
Name	**Formula**	**In CH_3COOH**	**In CH_3CN**
Trifluoromethane sulfonic acid	HO_3SCF_3	4.7	2.6
Perchloric acid	$HClO_4$	4.9	1.6
Hydrobromic acid	HBr	5.6	5.5
Sulfuric acid	H_2SO_4	7.0	7.3
Hydrochloric acid	HCl	8.4	8.9
Methane sulfonic acid	HO_3SCH_3	8.6	8.4
Trifluoro acetic acid	$HOOCCF_3$	11.4	10.6

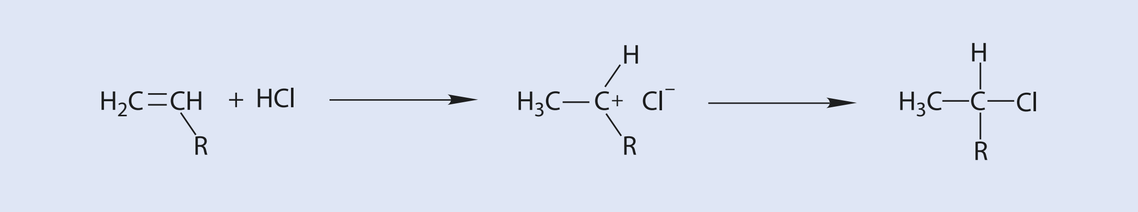


Fig. 10.9 Addition of HCl to an olefin

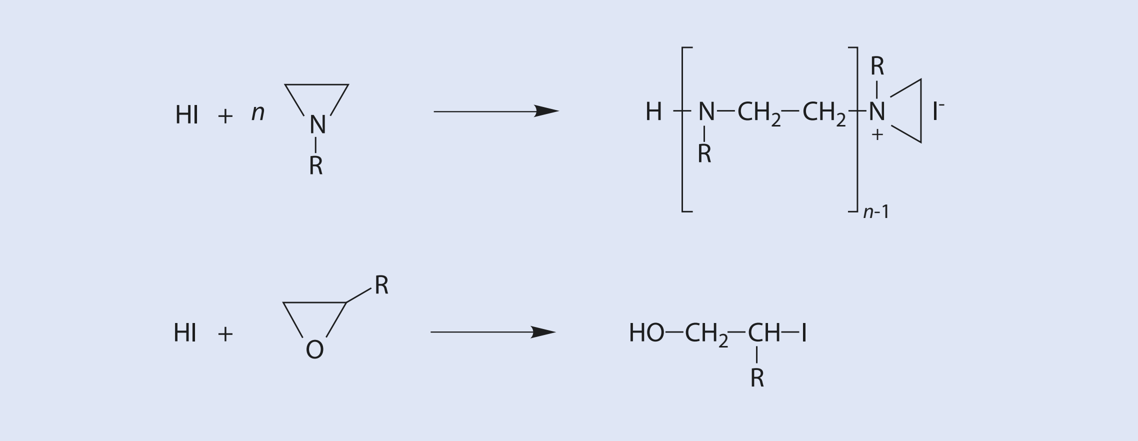


Fig. 10.10 Different reactions of HI with aziridine (polymerization) and oxirane: ring-opening and addition of the counterion

10.1.2.2 Lewis Acids

Typical Lewis acids that can be used for initiating a cationic polymerization are, e.g., $AlCl_3$, BF_3, $TiCl_4$, $SnCl_4$, and $SbCl_5$. The self-dissociation of some of them has been examined (◘ Fig. 10.12).

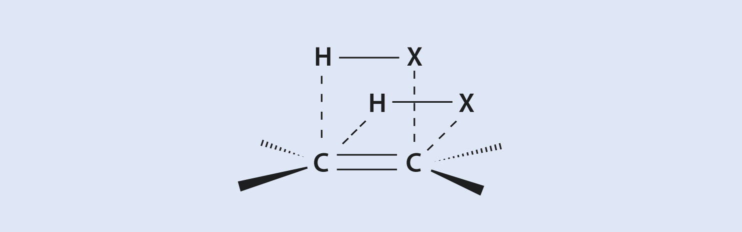
The initiation of a polymerization proceeds occurs according to ◘ Fig. 10.13.

Iodine is also able to initiate cationically the propagation of certain monomers (e.g., vinyl ether) (◘ Fig. 10.14).

The most common and also the most economically significant cationic initiation makes use of the concept of coinitiators, e.g., $TiCl_4/H_2O$ (◘ Fig. 10.15).

Alternative methods for obtaining initiators for cationic polymerization are listed in ◘ Fig. 10.16.

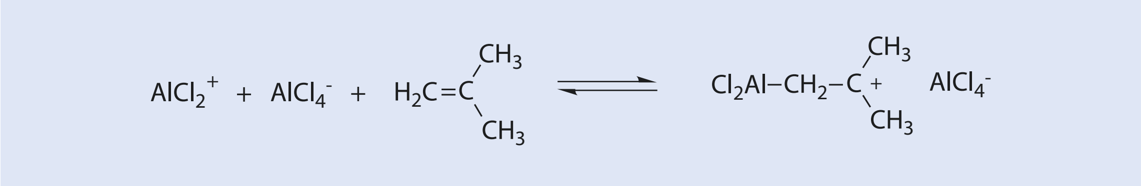
Iodonium and sulfonium salts are interesting initiators which, when irradiated in the presence of donors (DH), form protons which can then initiate a polymerization of vinyl or heterocyclic monomers (◘ Fig. 10.17).



◘ **Fig. 10.11** Transition state for the reaction of HX with an olefin. *X* halogen

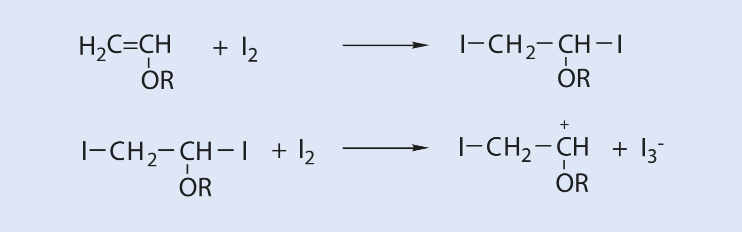
◘ **Fig. 10.12** Self-dissociation of the Lewis acid $AlCl_3$

$$2\ AlCl_3 \rightleftharpoons AlCl_2^+ + AlCl_4^-$$



$$AlCl_2^+ + AlCl_4^- + H_2C{=}C(CH_3)_2 \rightleftharpoons Cl_2Al{-}CH_2{-}C^+(CH_3)_2\ \ AlCl_4^-$$

◘ **Fig. 10.13** Initiation of the polymerization of isobutene with $AlCl_3$ via self-dissociation (in the absence of water)

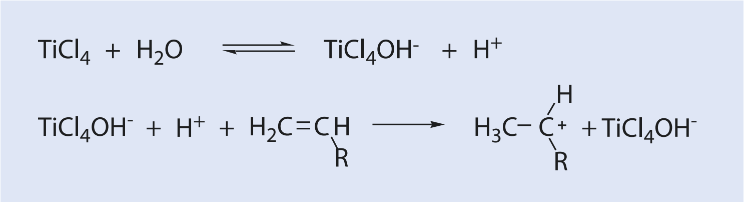


$$H_2C{=}CH(OR) + I_2 \longrightarrow I{-}CH_2{-}CH(OR){-}I$$

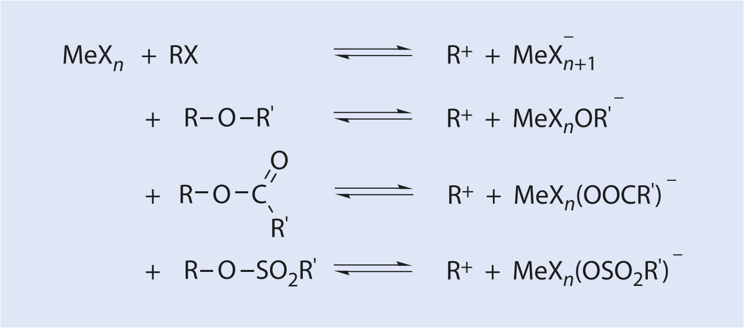
$$I{-}CH_2{-}CH(OR){-}I + I_2 \longrightarrow I{-}CH_2{-}\overset{+}{C}H(OR) + I_3^-$$

◘ **Fig. 10.14** Mechanism of the iodine initiated polymerization of vinyl ethers

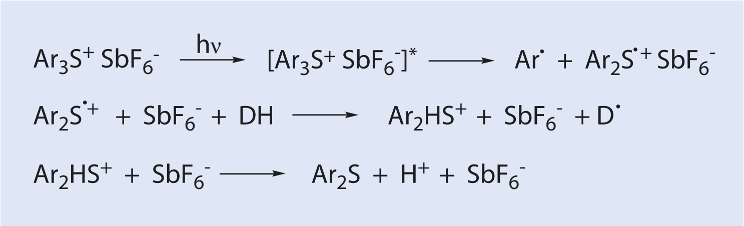
▣ **Fig. 10.15** Initiation with a Lewis acid and coinitiator taking $TiCl_4/H_2O$ as an example



▣ **Fig. 10.16** Possibilities for synthesizing R^+. *Me* metal, *X* halogen, *R*, *R′* e.g., CH_3



▣ **Fig. 10.17** Mechanism of the formation of protons from sulfonium salts in the presence of a proton donor (DH). *Ar* aromatic ring



These types of initiators are easy to synthesize, structurally flexible, and thus can be adapted to a range of light wavelengths. They have been successfully used in printing inks, various types of coating materials, and for the production of multi-layered OLEDs.

Initiators such as HI/I_2, $HI/Bu_4N^+ClO_4^-$, or $RCO^+SbF_6^-$ are especially suitable for controlling the cationic polymerization of specific monomers (▶ Sect. 10.1.5).

10.1.3 Chain Growth During Cationic Polymerization

The chain carriers are often carbon cations which propagate via an electrophilic addition to the monomer (▣ Fig. 10.18).

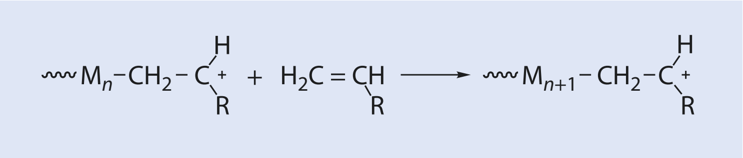
The counterion can exist as an ion pair with the active chain end, as a solvent separated ion pair, or as a free ion (▣ Fig. 10.19).

The considerable reactivity of the carbocations can lead to alternative, irregular structures along the polymer chain because of, for example, rearrangements (▣ Figs. 10.20 and 10.21).

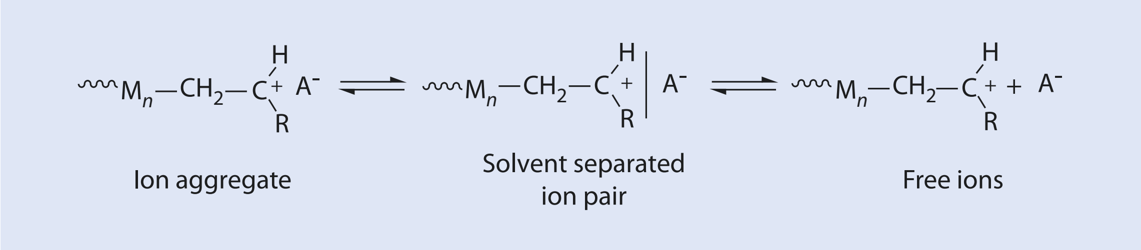
In the cationic polymerization of heterocycles, propagation is via onium ions and ring-opening (▣ Fig. 10.22 and ▶ Chap. 12. The different types of ring-opening polymerizations are dealt with in more detail in ▶ Chap. 12. Only the mechanistic details essential for a general understanding of cationic polymerization are discussed here.)

An example of this type of reaction is the polymerization of 2-methyl-2-oxazoline (▣ Fig. 10.23).

Fig. 10.18 Electrophilic addition of the growing chain to a monomer



$$\sim\sim M_n-CH_2-\overset{H}{\underset{R}{C}}{}^{+} + H_2C=\underset{R}{CH} \longrightarrow \sim\sim M_{n+1}-CH_2-\overset{H}{\underset{R}{C}}{}^{+}$$



$$\sim\sim M_n-CH_2-\overset{H}{\underset{R}{C}}{}^{+}\,A^- \rightleftharpoons \sim\sim M_n-CH_2-\overset{H}{\underset{R}{C}}{}^{+}\,|\,A^- \rightleftharpoons \sim\sim M_n-CH_2-\overset{H}{\underset{R}{C}}{}^{+} + A^-$$

Fig. 10.19 Equilibria between the ion pairs, the solvent separated ion pairs, and the free ions

Fig. 10.20 Irregular structures resulting from hydride transfer during the polymerization of 3-methylbut-1-ene

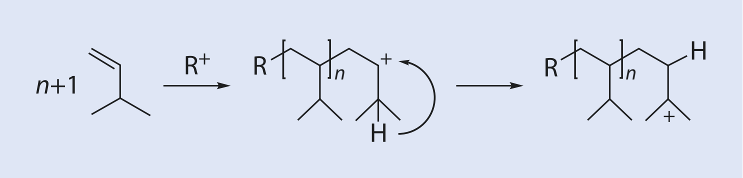
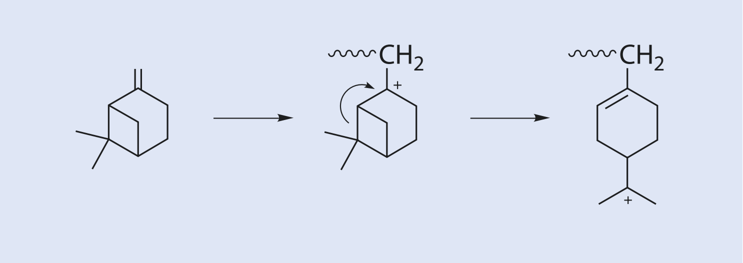


Fig. 10.21 Rearrangement during the cationic polymerization of β-pinene



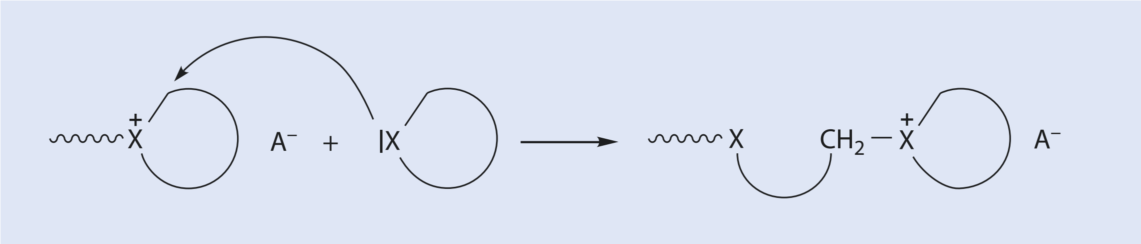


Fig. 10.22 Ring-opening and chain extension via the reaction of an onium ion with a heterocyclic monomer

The polymerization of lactams (most often the seven-atom ring lactam) is interesting and involves a so-called *activated monomer* in the transition stage (Fig. 10.24).

According to this, mechanism propagation is via a monomer protonated at the lactam-nitrogen. However, it has also been suggested that the initial step is the protonation of the carbonyl oxygen.

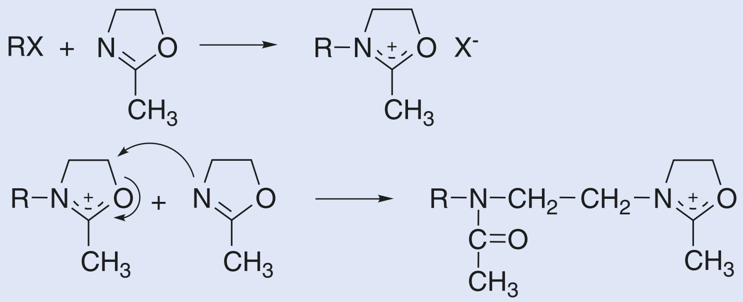


Fig. 10.23 Polymerization of 2-methyl-2-oxazoline initiated by RX (e.g., CH_3Br)

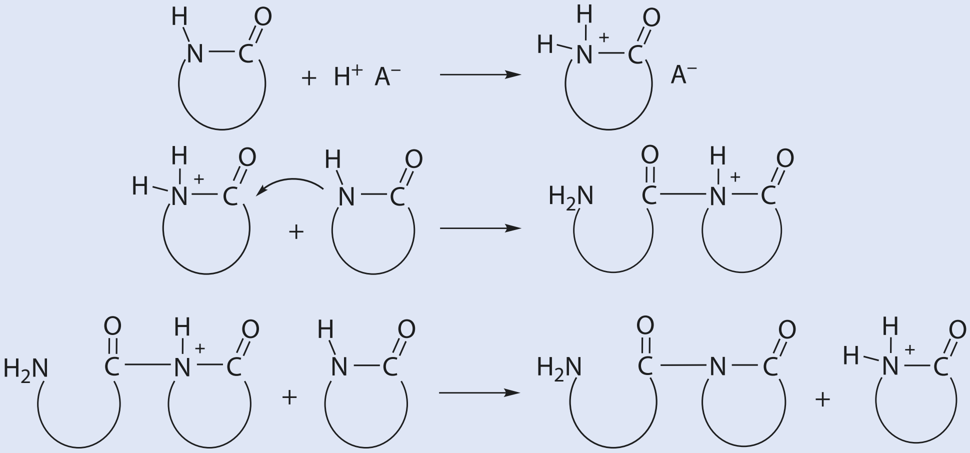


Fig. 10.24 Lactam polymerization involving *activated monomers*

10.1.4 Transfer and Termination

As has already been explained at the beginning of the chapter, the growing chains cannot terminate by combining with one another. Because of the reactivity of cationic chain ends there are a large number of reactions which can lead to chain termination or the transfer of the charge from one chain to another. These reactions are discussed in the following paragraphs (► Sects. 10.1.4.1 and 10.1.4.2).

10.1.4.1 Transfer Reactions

A transfer reaction that often occurs during the cationic polymerization of vinyl monomers is a β-H-elimination (◘ Fig. 10.25).

If aromatic groups are present the intramolecular Friedel–Crafts reaction is another transfer reaction worth considering (◘ Fig. 10.26).

Fig. 10.25 Transfer via β-H-elimination. Cationic polymerization of styrene as an example

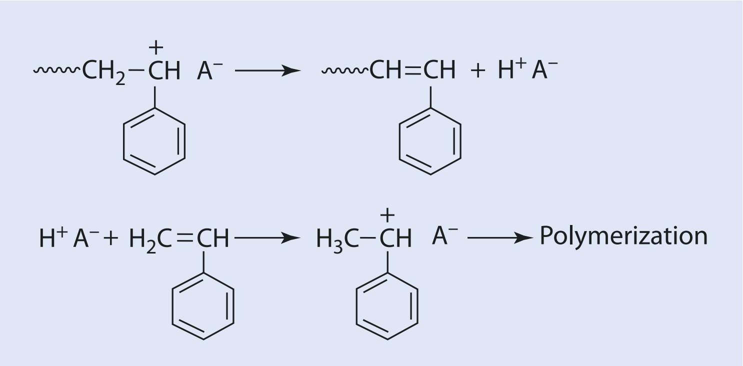
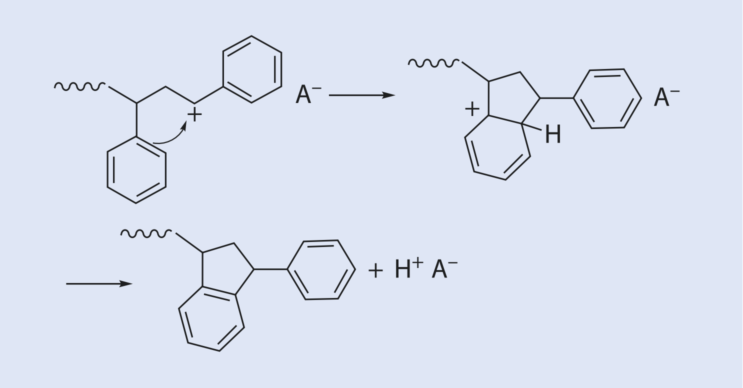


Fig. 10.26 Transfer by Friedel–Crafts alkylation (formation of indane)



Intermolecular Friedel–Crafts reactions are also observed. These are also transfer reactions but in this case also result in different polymer structures, namely branched structures or macromonomers (Figs. 10.27 and 10.28).

Inter- and intramolecular reactions during the cationic polymerization of heterocycles are also *transfer* reactions (Figs. 10.29 and 10.30).

During the first step, the nucleophilic X (X = O, S, NR) from somewhere along the chain reacts with the electrophilic α-C-atom of an active center. If remaining monomer reacts with such a branched cation at the α-C-atom the reaction yields a neutral linear chain and a charged species which continue to grow.

When such reactions are intramolecular so that rings are formed, then this is referred to as *back-biting* (Fig. 10.30).

The result of this reaction is a depolymerization with the formation of rings of varying size.

10.1.4.2 Termination Reactions

Because of the reactivity of the active species, there are many possibilities for termination during cationic polymerization. These reactions do not necessarily destroy the active center. It is often sufficient for the cation to rearrange into an inactive species (Fig. 10.31). For example, a hydride shift can lead to an inactive species caused by steric considerations.

If *anion splitting* occurs, which is also occasionally referred to as the decomposition of the anion, then termination occurs through the reaction of the active cation with part of the counterion (Fig. 10.32).

Termination most frequently occurs, however, because of remaining impurities, such as H_2O (Fig. 10.33).