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Ionic Polymerization

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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

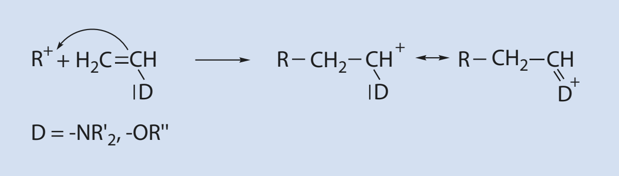
Although some of the first polymerizations observed by chemists were probably cationic polymerizations, it was not until it was discovered that isobutene, trioxane, cyclic ethers such as oxirane and tetrahydrofuran, for example, as well as cyclic siloxanes, could be cationically polymerized that a general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

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



◘ **Fig. 10.2** Basic steps in a cationic polymerization

Initiation $H^+ + M \longrightarrow HM^+ \quad (\equiv R^+)$

Propagation $R^+ + n\,M \longrightarrow R\text{-}M_n^+ \quad (\equiv P^+)$

Termination $P^+ + P^+ \not\longrightarrow$

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 ~ M_n^+, and these coordinate with an additional monomer molecule to yield a chain with an additional monomer and a terminal charge ~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).

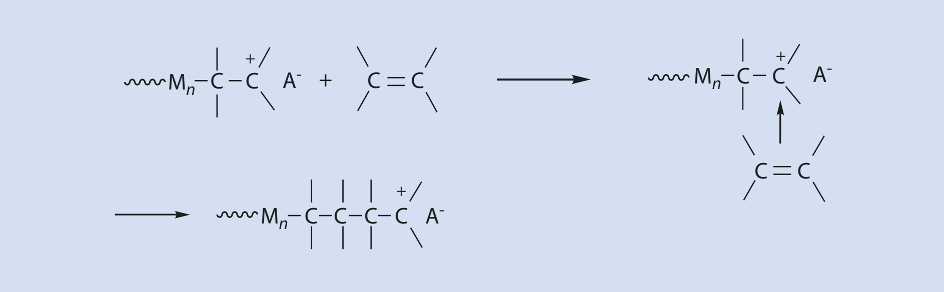
The growth step of the polymerization of carbonyl compounds is shown in ◘ Fig. 10.5. Polymerization takes place because of the nucleophilic attack of the carbonyl function on the charged chain end.

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

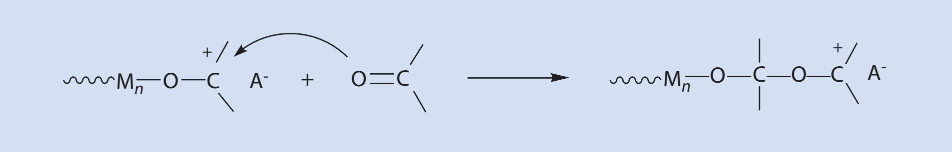
Some cyclic monomers containing oxygen as the hetero atom, which are especially suitable for cationic polymerization, are shown in ◘ Fig. 10.7.

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

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



◘ **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

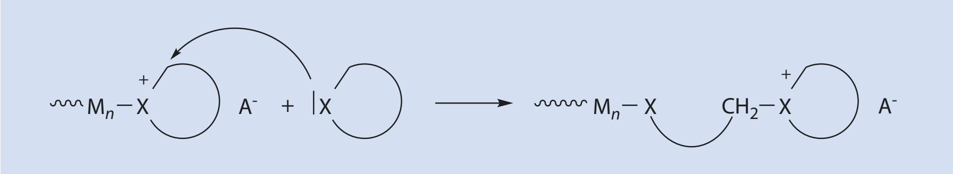
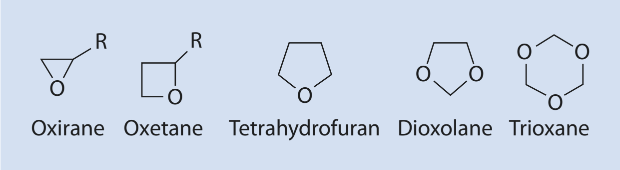


Fig. 10.6 Nucleophilic attack of a heterocyclic monomer on a cationically growing chain

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

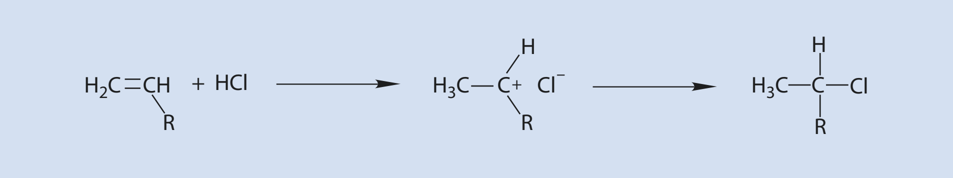


Fig. 10.9 Addition of HCl to an olefin

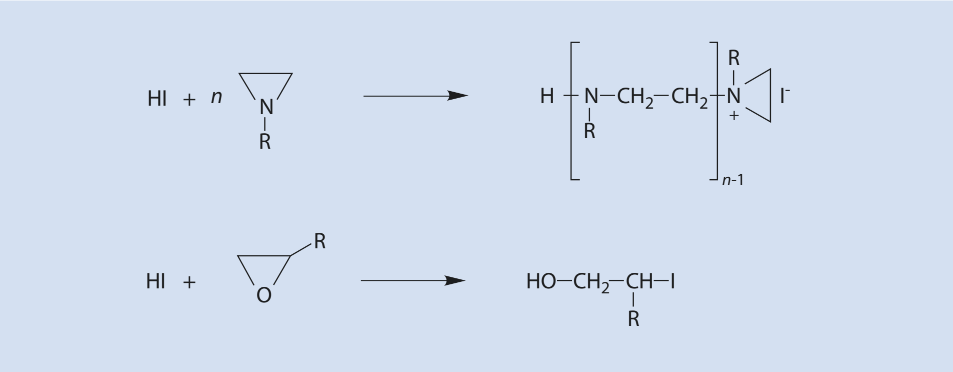


Fig. 10.10 Different reactions of HI with aziridine (polymerization) and oxirane: ring-opening and addition of the counterion

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.

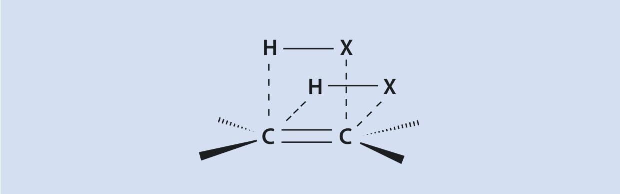
Iodine is also able to initiate cationically the propagation of certain monomers (e.g., vinyl ether) (◘ Fig. 10.14).

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.

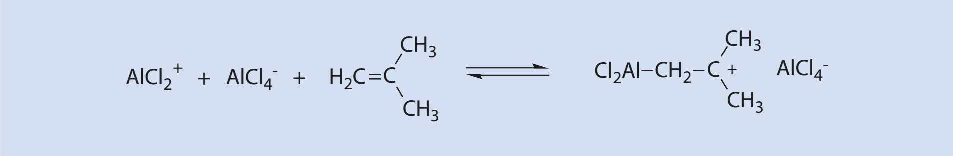
Iodonium and sulfonium salts are interesting initiators which, when irradiated in the presence of donors (DH), form protons which can then initiate a polymerization of vinyl or heterocyclic monomers (◘ Fig. 10.17).

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



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

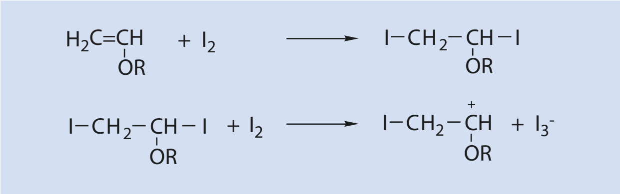
$$2\ AlCl_3 \rightleftharpoons AlCl_2^+ + AlCl_4^-$$



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

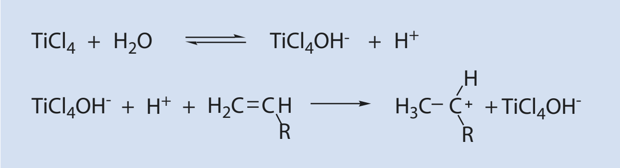
◘ **Fig. 10.13** Initiation of the polymerization of isobutene with $AlCl_3$ via self-dissociation (in the absence of water)

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

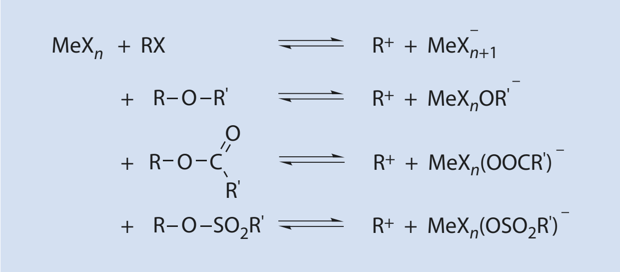


$$H_2C{=}CH(OR) + I_2 \longrightarrow I{-}CH_2{-}CH(OR){-}I$$

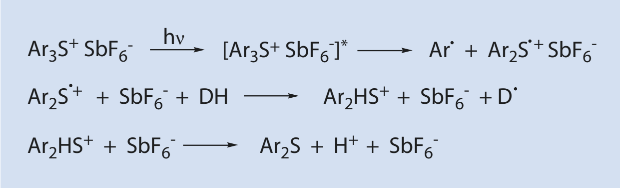
$$I{-}CH_2{-}CH(OR){-}I + I_2 \longrightarrow I{-}CH_2{-}\overset{+}{C}H(OR) + I_3^-$$



▣ **Fig. 10.15** 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).

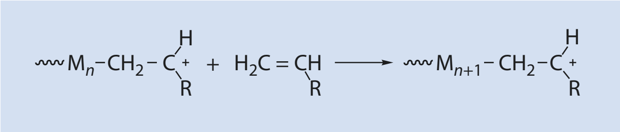
The counterion can exist as an ion pair with the active chain end, as a solvent separated ion pair, or as a free ion (▣ Fig. 10.19).

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



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

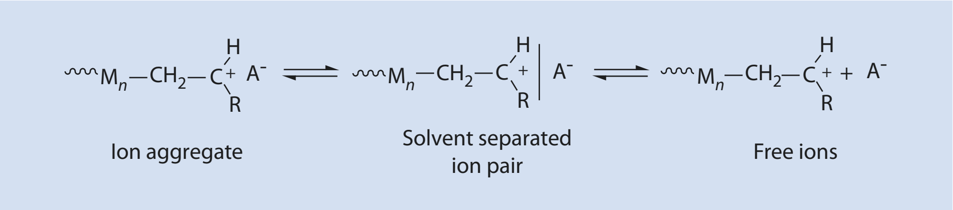


Fig. 10.19 Equilibria between the ion pairs, the solvent separated ion pairs, and the free ions

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

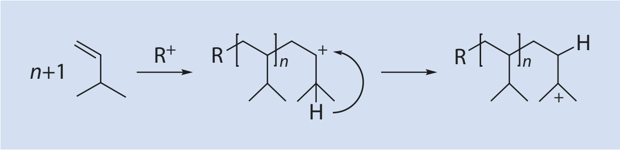
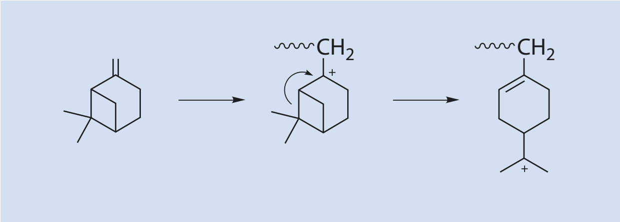


Fig. 10.21 Rearrangement during the cationic polymerization of β-pinene



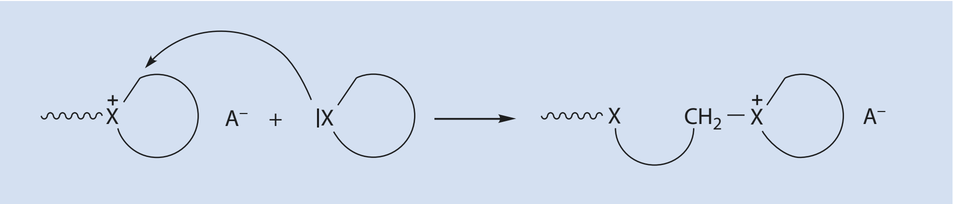


Fig. 10.22 Ring-opening and chain extension via the reaction of an onium ion with a heterocyclic monomer

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.

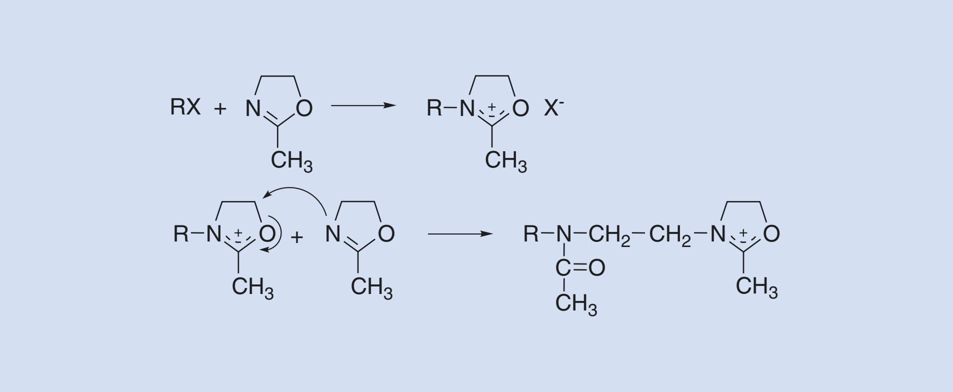


Fig. 10.23 Polymerization of 2-methyl-2-oxazoline initiated by RX (e.g., CH_3Br)

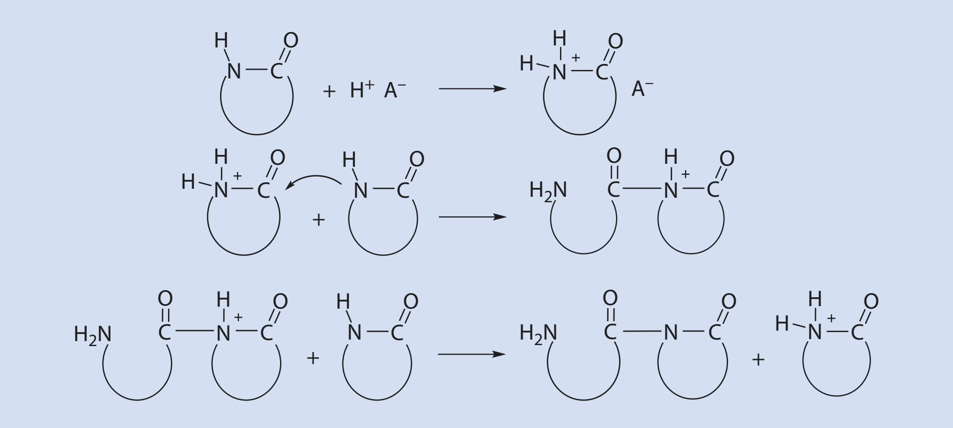


Fig. 10.24 Lactam polymerization involving *activated monomers*

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

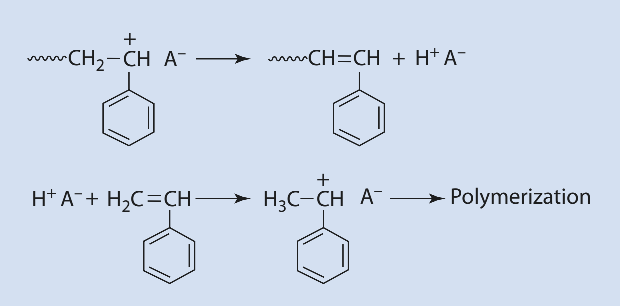
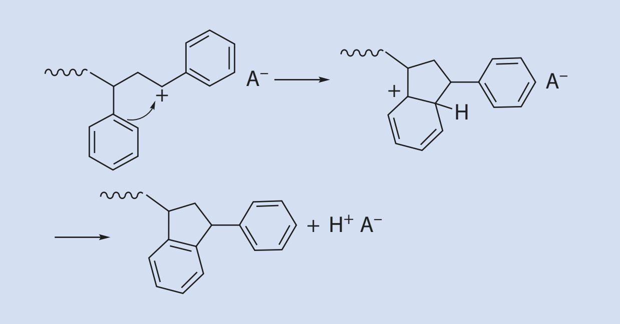


Fig. 10.26 Transfer by Friedel–Crafts alkylation (formation of indane)



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).

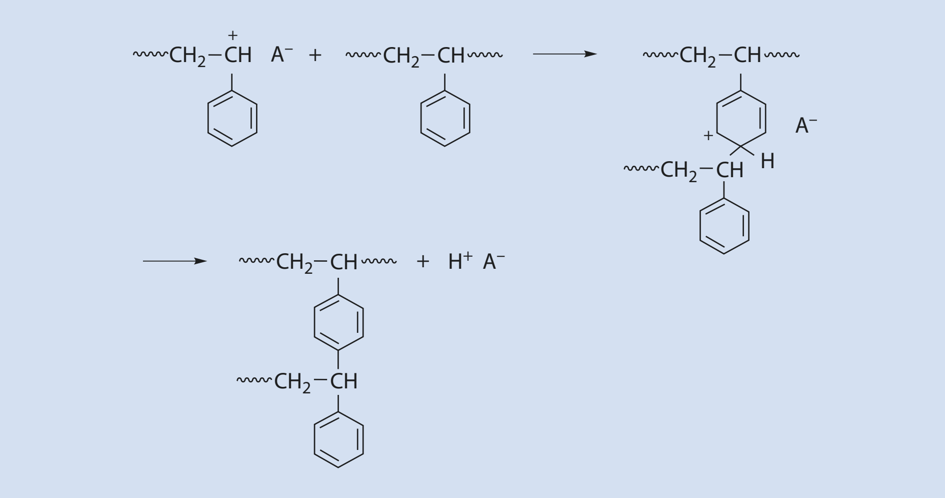


Fig. 10.27 Transfer by intermolecular Friedel–Crafts reactions to form branched polymers

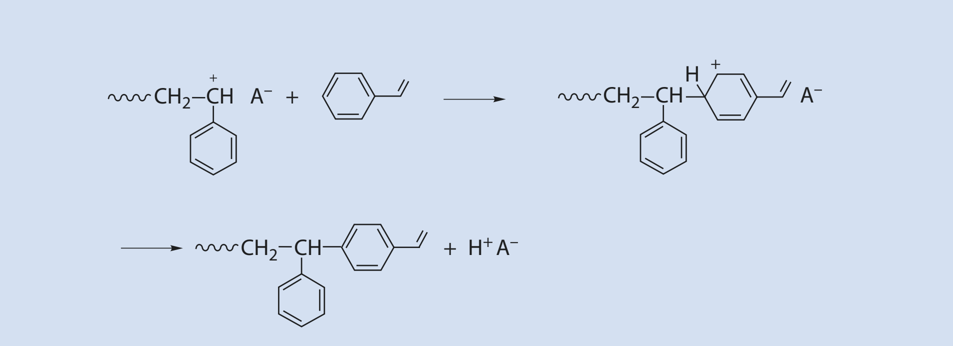


Fig. 10.28 Transfer by an intermolecular Friedel–Crafts reaction to yield a macromonomer

10.1.5 Living and Controlled Cationic Polymerization

Characteristic of living polymerization are the rapid initiation and the absence of transfer and termination. As a result, the molar mass of the polymer should increase in a linear fashion with conversion. Because of the reactivity of the carbenium ions, the above requirements are difficult to meet for the cationic polymerization of vinyl compounds, for example for the technically important polymerization of isobutene. However, it has still proved possible to develop systems which can be called controlled polymerizations.

The best known example of such a system is the INIFER-polymerization of isobutene (Kennedy and Smith 1979, 1980). An *ini*tiator-trans*fer*-reagent such as 1,4-bis (chloroisopropyl)benzene reacts with BCl_3 to become a carbenium ion which is stabilized by neighboring aromatic compounds; however, the equilibrium is shifted far towards the neutral component (Fig. 10.34).

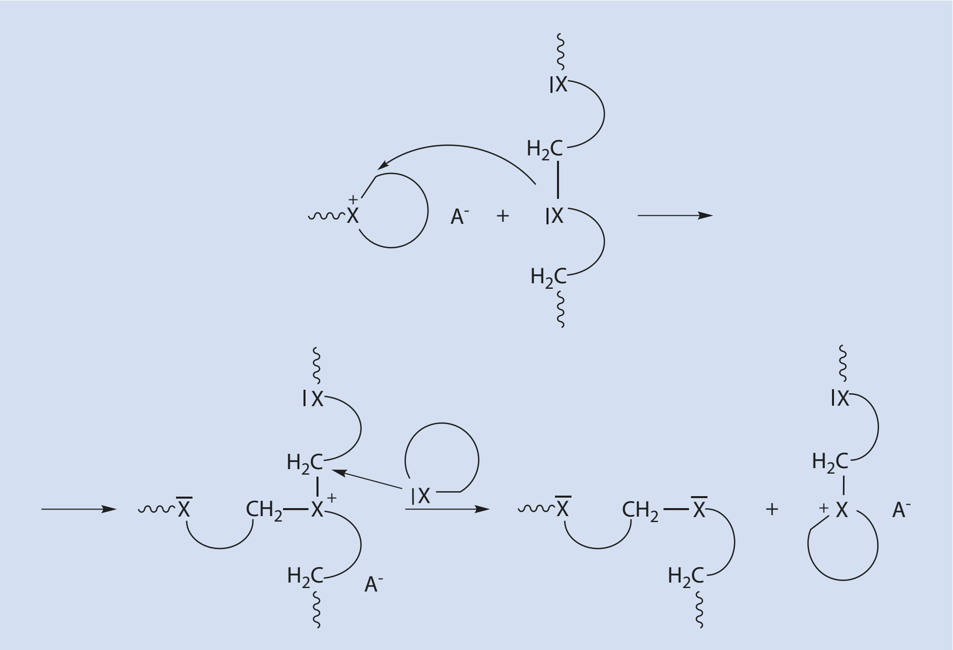


Fig. 10.29 Intermolecular transfer reactions between growing and inactive polymer chains

Fig. 10.30 *Back-biting*: Intramolecular transfer

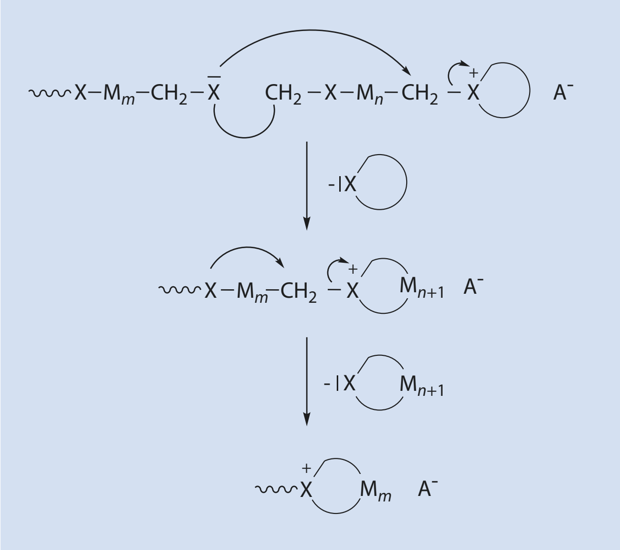
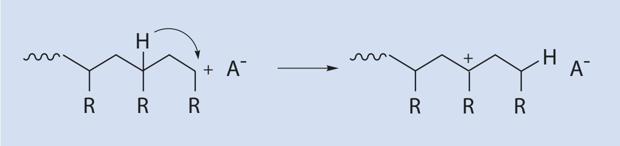


Fig. 10.31 Termination by hydride shift



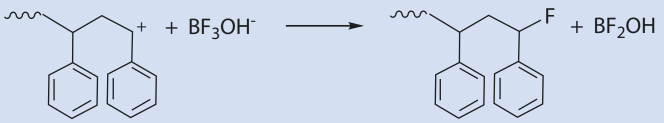
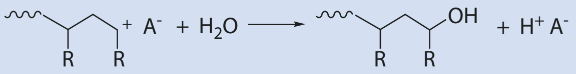


Fig. 10.32 Termination via *anion splitting*

Fig. 10.33 Termination by impurities or added terminating agents, e.g., H_2O



The cation (II, Fig. 10.34) formed during initiation using BCl_3 is able to add isobutene (Fig. 10.35).

The growing chain can then be terminated either by *anion splitting* or by a transfer reaction (reaction between III and I) (Fig. 10.36).

A Cl-terminated polyisobutene (IV) is produced by the reaction of III with BCl_4^-. This reaction is reversible but IV usually reacts from the second isopropyl chloride group adjacent to the aromatic ring with BCl_3—the second arm is initiated (Fig. 10.37).

The species VI can be produced from V by the addition of isobutene (Fig. 10.38).

Finally, VI can terminate by *anion splitting* or by reacting with I to become Cl-terminated (Fig. 10.39).

The latter reaction continues until all I and similar functionalities (IV) have been consumed; polymerization continues until all the monomer has been used up. According to this scheme, macromolecules of controllable molar mass and interesting functional end groups (in this case Cl), so-called *telechelic macromolecules*, can be synthesized.

Using the INIFER mechanism as an example, it was possible to demonstrate that it is unnecessary for the charged chain ends to retain their activity or identity. The desired goal (telechelic macromolecules, block copolymers) can also be achieved by making use of the reversibility of the termination step. The same concept of reversible termination step is also crucial for controlled radical polymerization (▶ Sect. 9.5).

Vinyl ethers can be polymerized in a controlled manner by HI/I_2 or HI/NR_4ClO_4 as the initiator (Fig. 10.40); polymers with adjustable molar mass ($P_n = [M]/[I]$), narrow molar mass distribution ($M_w/M_n \leq 1{,}2$), and with controlled functional end groups can be synthesized in this way.

Block copolymers can be synthesized simply by the sequential addition of different vinyl ethers. If the same polymerization is initiated by Brønsted acids, such block copolymer syntheses are not successful.

By using the bi-functional adduct of the addition of hydrogen iodide to a divinyl ether as an initiator, telechelic macromolecules can be obtained (Fig. 10.41).

Heterocyclic monomers such as tetrahydrofuran can also undergo controlled cationic polymerization (Fig. 10.42).

Particularly worth noting in terms of controlled cationic polymerization are the oxazoline monomers (Fig. 10.23). An amphiphilic block copolymer can be obtained simply by adding a different monomer (e.g., $R' = n\text{-}C_9H_{19}$) after conversion of the first monomer (e.g., $R' = CH_3$) is complete (Fig. 10.43).

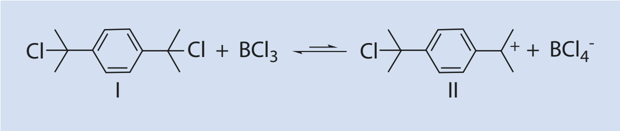


Fig. 10.34 INIFER-mechanism: formation of the initiating cation

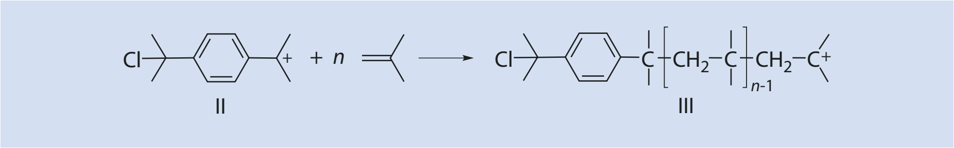


Fig. 10.35 INIFER-mechanism: polymerization of isobutene

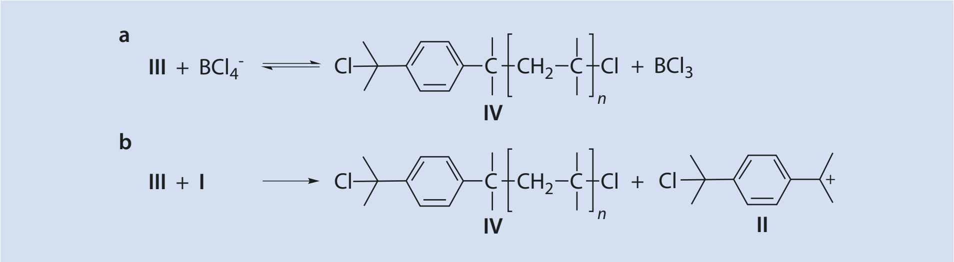


Fig. 10.36 INIFER-mechanism: termination of propagation by: (**a**) anion splitting or (**b**) the initiator

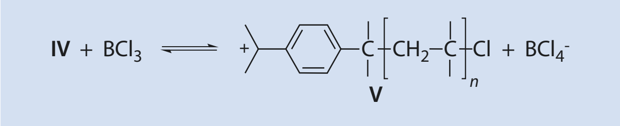


Fig. 10.37 INIFER-mechanism: activation initiating of the second arm of a chloro-terminated polymer

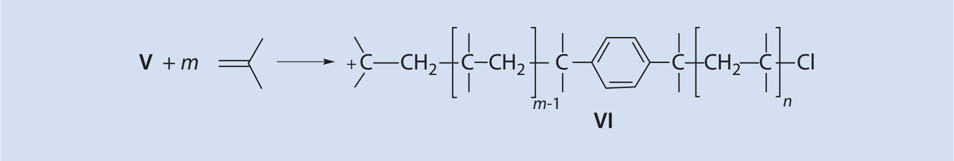


Fig. 10.38 INIFER-mechanism: growth of the second polymer arm

The suitable choice of initiator RX and termination reagent opens further possibilities for variation. As a result of this, molecules such as fluorophilic surfactants with hydrophobic end groups can be synthesized (Fig. 10.44).

For the example in Fig. 10.44, $C_8F_{17}CH_2CH_2–SO_3CF_3$ was used as an initiator and an alkyl-substituted piperazine as a terminating agent.

The controlled polymerizations described in this section result in macromolecules with well defined molar mass, narrow molar mass distributions, and well defined functional end groups; this is an elegant versatile method for synthesizing telechelic macromolecules and block copolymers.

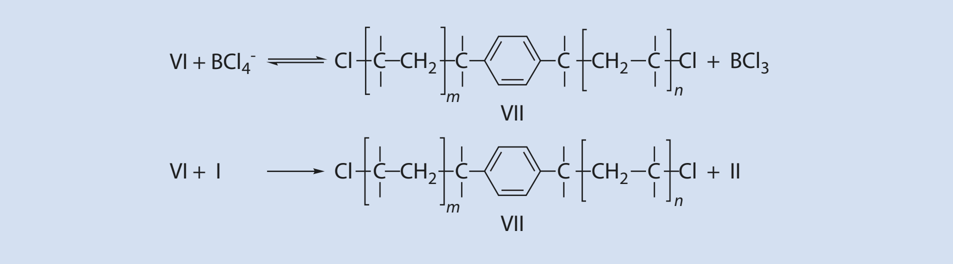


Fig. 10.39 INIFER-mechanism: reactions which lead to α,ω-dichloro polyisobutene

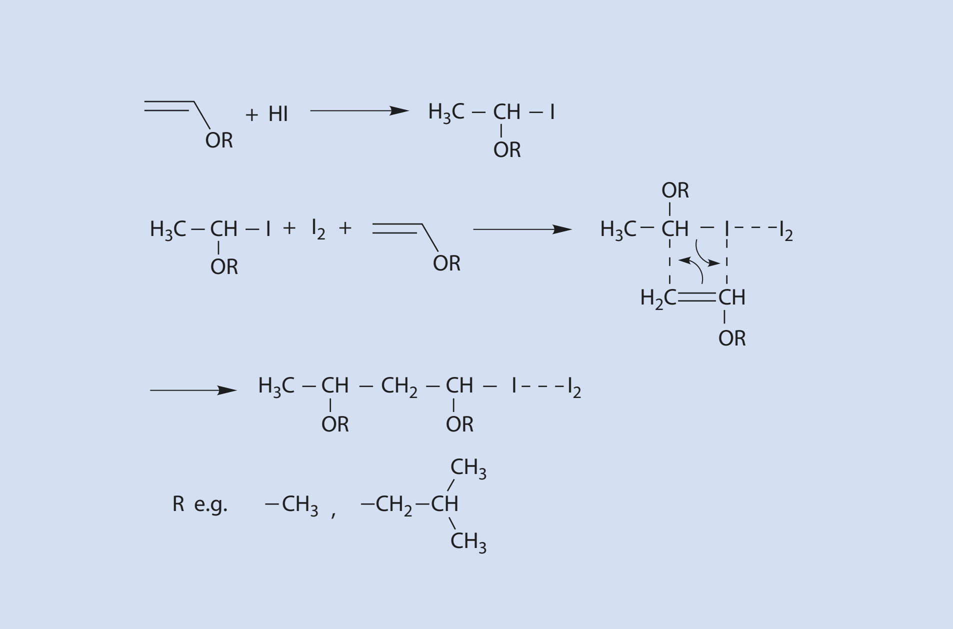


Fig. 10.40 Controlled polymerization of vinyl ethers with HI/I_2

10.1.6 Kinetics of Cationic Polymerization

In contrast to radical or anionic polymerization, there are no coherent, generalized rules for cationic polymerization. This is, apart from other things, because of the many different types of active centers—e.g., free ions, solvated ions, ion pairs, and ion aggregates. Often the influence of transfer reactions is disregarded, the effect of the solvent is underestimated, and unwarranted assumptions of quasi-stationarity are made. Additionally, the extreme reactivity of the active centers, their low concentrations, and their sensitivity to ubiquitous impurities often lead to the real mechanism often not being properly understood.

In contrast, the polymerization of isobutyl vinyl ether (IBVE) initiated with 1-(2-methyl propoxy)-1-iodoethane and tetrabutyl ammonium perchlorate (TBAP) as a co-initiator ($(R'I)/(n\text{-}Bu)_4NClO_4$) is relatively well defined.

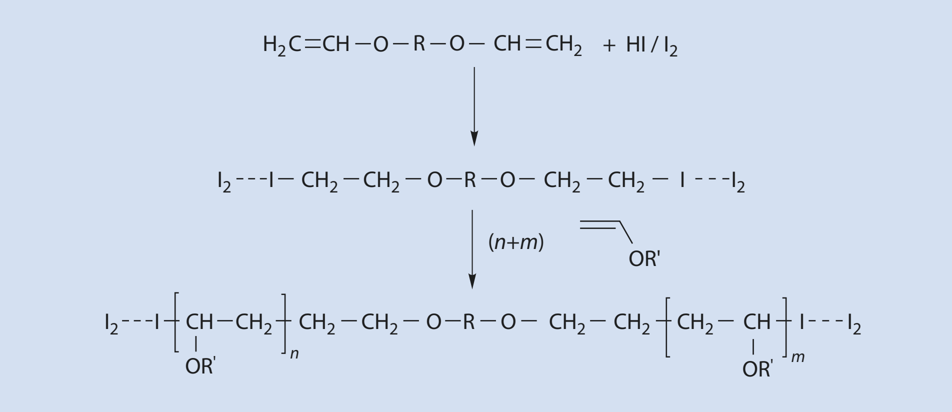
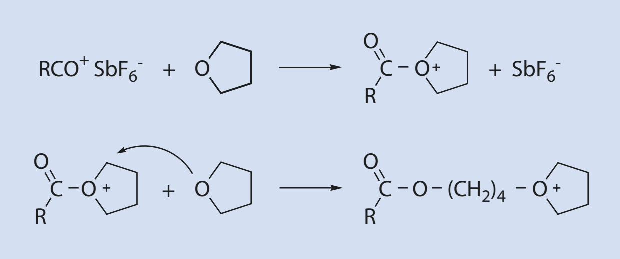


Fig. 10.41 Synthesis of telechelic vinyl ethers

Fig. 10.42 Controlled polymerization of tetrahydrofuran



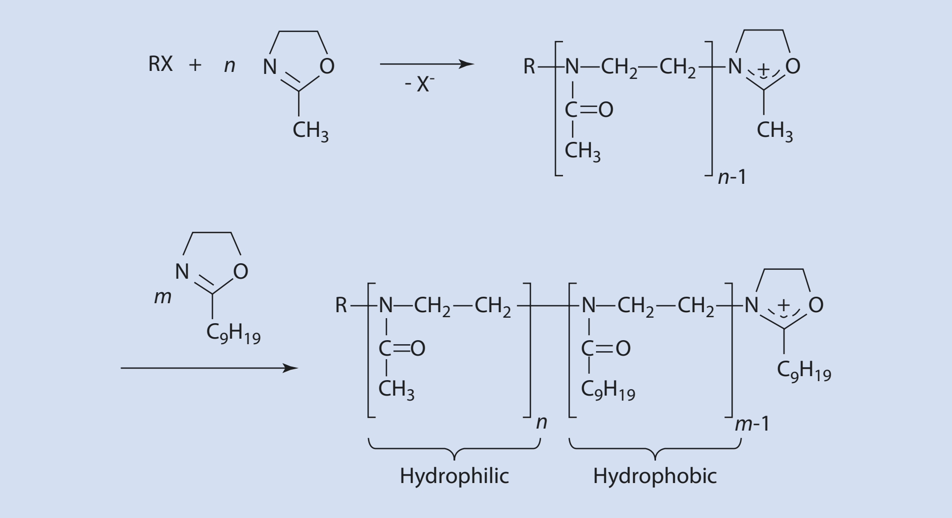


Fig. 10.43 Synthesis of an amphiphilic block copolymer. *Hydrophilic* $COCH_3$ side chain, *hydrophobic* COC_9H_{19} side chain

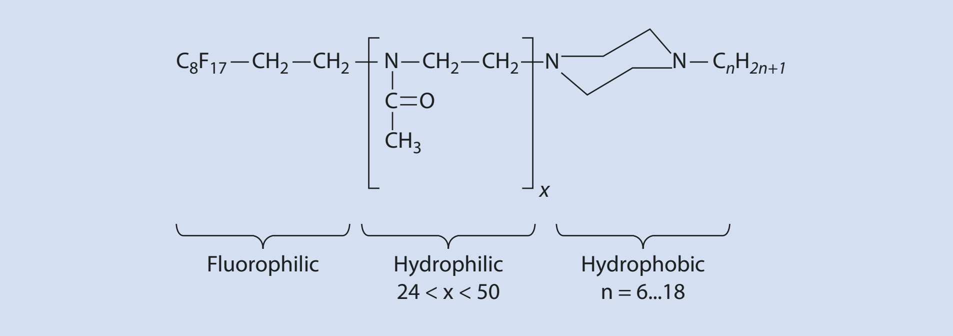


Fig. 10.44 Polymeric fluorophilic tenside with lipophilic terminal groups

As can be seen in Fig. 10.45, the substitution of I^- by ClO_4^- results in an active species, $R'^+ClO_4^-$. The addition of monomer (M) to this leads to the active species, $P^+ClO_4^-$, which is in equilibrium with the PI (see ▶ Sect. 9.5 to appreciate the similarity to controlled radical polymerization). Kinetic measurements such as those described in the following paragraphs (▶ Sects. 10.1.6.1 and 10.1.6.2) corroborate this mechanism.

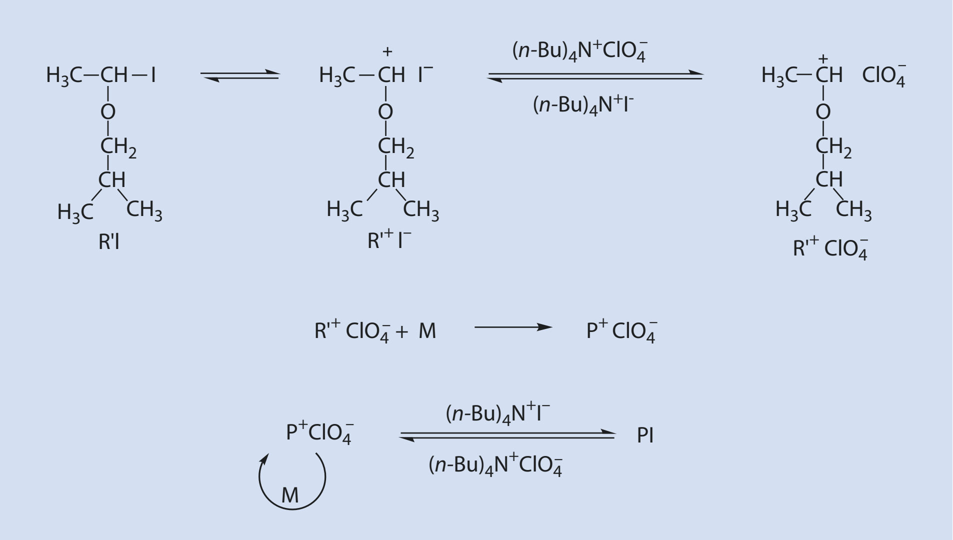


Fig. 10.45 Mechanism of the polymerization of isobutyl vinyl ether (M), initiated with 1-(2-methyl propoxy)-1-iodoethane (R′I)/TBAP

10.1.6.1 Rate of Monomer Conversion During IBVE Polymerization

Monomer conversion is given by the first order equation

$$-\frac{d[M]}{dt} = k_p^{\prime} \cdot [M] \tag{10.1}$$

$k_p^{\prime}$ Measured rate constant of propagation

Studies of the kinetics of the reaction have shown that the rate of conversion of the monomer is not simply dependent on $[M]$, but also on $[R'I]$ and $[TBAP]$ according to

$$k'_p = k_p \cdot [R'I]^{\alpha} \cdot [TBAP] \tag{10.2}$$

k_p "True" rate constant of propagation

α is called the coefficient of interaction and experimentally $\alpha = 1$ $(0.9 < \alpha < 1.1)$.

Taking the expression for the conversion of monomer to polymer p:

$$p = \frac{[M]_0 - [M]}{[M]_0} \tag{10.3}$$

or

$$1 - p = \frac{[M]}{[M]_0} \tag{10.3a}$$

(10.1) gives, after integration:

$$\ln\frac{[M]}{[M]_0} = \ln(1-p) = -k'_p \cdot t \tag{10.4}$$

Plots of $\ln(1-p)$ as a function of the temperature at different temperatures allows values for $k_p^{\prime}$ to be determined from the gradients of the straight lines.

From ◘ Table 10.2 it can be seen that the molar mass of the products is given by the ratio $[M]_0 : [R'I]_0$ $(p = 100\%)$ and that the rate constants $k_p^{\prime}$ are approximately linearly proportional to $[TBAP]_0$.

10.1.6.2 Influence of the Solvent and the Structure of the Co-initiator on the Rate of Polymerization of IBVE

The rate of polymerization of IBVE increases significantly with the polarity of the solvent. At −40 °C the polymerization of IBVE is 300 times faster in methylene dichloride than in toluene.

Both the co-initiator cation (◘ Table 10.3) and its anion (◘ Table 10.4) affect the rate of polymerization.

The rate of polymerization of IBVE is reduced by a factor of 17 by changing $R = C_2H_5$ to $R = n\text{-}C_8H_{17}$ or $n\text{-}C_{12}H_{25}$ in R_4NClO_4.

Although the rate of polymerization of IBVE is similar with the anions PF_6^- and ClO_4^-, it is noticeably slower with BPh_4^-.

Table 10.2 Polymerization of IBVE, initiated with R′I/TBAP—influence of $[M]_0$, $[R'I]_0$, $[TBAP]_0$ and temperature on the rate constants $k_w{}'$ and on M_n

T (°C)	$[M]_0$ (mol/L)	$[R'I]_0$ (10^{-2}) mol/L	$[TBAP]_0$: $[R'I]_0$	k'_p (10^{-3} s^{-1})	M_n (g/mol)	M_w/M_n
−15	1.0	0.61	0.49	0.64	16,400	1.12
−15	1.0	0.57	1.75	1.55	17,200	1.10
−15	1.0	0.57	2.63	2.48	17,600	1.12
−30	0.5	2.50	0.10	0.14	2,100	1.10
−30	0.5	2.50	0.50	0.83	2,000	1.08
−30	0.5	2.50	1.00	1.42	2,100	1.10
−30	0.5	2.50	2.00	4.39	1,900	1.12

Table 10.3 Polymerization of IBVE at −15 °C in methylene dichloride, initiated with R′I/R_4NClO_4—influence of the coinitiator R on the rate of polymerization ($[M]_0 = 1.0$ mol/L, $[R'I]_0 = 0.57 \cdot 10^{-2}$ mol/L, $[R_4NClO_4]_0 = 0.3 \cdot 10^{-2}$ mol/L)

R	CH_3	C_2H_5	n-C_4H_9	n-C_6H_{13}	n-C_8H_{17}	n-$C_{12}H_{25}$
$k_p{}'$ [10^{-4} s^{-1}]	Poorly soluble	5.89	6.37	2.10	0.28	0.28

Table 10.4 Polymerization of IBVE at −15 °C in methylene dichloride, initiated with R′I/R_4NClO_4—influence of the coinitiator A^- on the rate of polymerization ($[M]_0 = 1.0$ mol/L, $[R'I]_0 = 0.57 \cdot 10^{-2}$ mol/L, $[R_4NClO_4]_0 = 0.3 \cdot 10^{-2}$ mol/L)

A^-	$BPh_4{}^-$	$BF_4{}^-$	$PF_6{}^-$	$ClO_4{}^-$
$k_p{}'$ [10^{-4} s^{-1}]	0.05	1.30	4.97	6.37

This trend is in accordance with the *special salt effect* described for nucleophilic substitution reactions in the presence of tetraalkyl ammonium salts (Winstein et al. 1961).

In summary it can be stated that:

- IBVE polymerization, initiated with R′I and TBAP, is a living polymerization with a reversible termination step
- The rate of polymerization increases linearly with $[M]$, $[R'I]$ and $[TBAP]$
- The rate of polymerization increases linearly with the polarity of the solvent

Even from this simple and comparatively well-defined example it is clear that the kinetics of cationic polymerization are rather complex. Thus, it becomes clear why there are, as yet, no generalized kinetic schemes for cationic polymerization and also that the results obtained with one monomer cannot simply be used to describe another system.

10.2 Anionic Polymerization

Already in the early part of the twentieth century butadiene was being polymerized anionically in hydrocarbons with a dispersion of sodium in hydrocarbon solvents (*BUNA*). This process could, however, not compete technologically against the radical polymerization of butadiene and was soon abandoned. The seminal work of M. Szwarc on anionic living polymerization paved the way for telechelic macromolecules, block copolymers, and polymers with diverse architectures (Szwarc 1956).

Similar to cationic polymerization, a high selectivity towards monomers is characteristic of anionic polymerization. In contrast to cationic polymerization, anionic polymerization works best with monomers having acceptor groups adjacent to their double bond (Fig. 10.46).

The sensitivity of the active species demands great care when choosing and purifying the solvents to be employed. Solvents often chosen are tetrahydrofuran and aliphatic and aromatic hydrocarbons. Traces of water and alcohols should be avoided as these deactivate the growing chains. Solvents such as CH_2Cl_2 and $CHCl_3$ also lead to chain termination (Fig. 10.47).

The polymerizations are generally carried out at temperatures below room temperature to facilitate control of the otherwise rapid reactions and to suppress side reactions.

The absence of termination and transfer steps allows living polymerization and enables polymers with narrow molar mass distributions ($M_w/M_n < 1{,}1$), well-defined functional end groups (telechelic structures), and block copolymers to be synthesized. Telechelic polymers can be obtained by deliberately stopping the polymerization with specific termination reagents (Fig. 10.48).

10.2.1 Reaction Mechanism

Anionic polymerization takes place according to the scheme given in Fig. 10.49.

The active, negatively charged chain reacts with an additional monomer and is thus extended by one monomer unit. K^+ represents the positively charged counterion, gener-

Fig. 10.46 Addition of a nucleophile to an electrophilic monomer

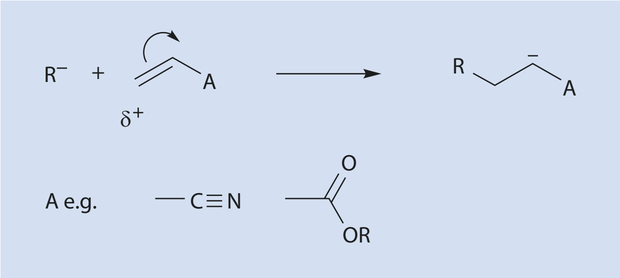


Fig. 10.47 Chain termination via nucleophilic substitution of the halogen in RCl by a polymeric anion

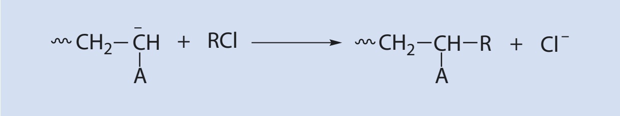

$$\sim CH_2-\underset{A}{\overset{-}{CH}} + RCl \longrightarrow \sim CH_2-\underset{A}{CH}-R + Cl^-$$

Fig. 10.48 Reactions of anionic species with monomer and terminating reagents, here: CO_2. *M*, *M₁*, *M₂* monomers

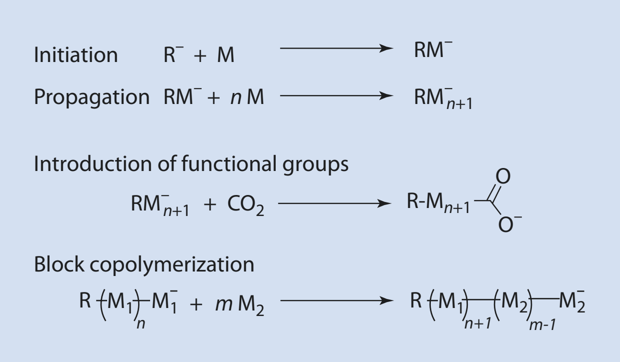
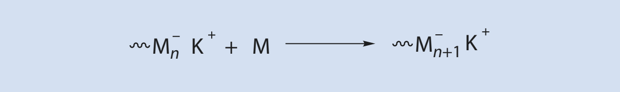


Fig. 10.49 Propagation during anionic polymerization. *K*⁺ counterion, cation



ally a metal cation such as Li^+. The similarity of propagation in the anionic polymerization of vinyl compounds with the same steps in cationic or radical polymerizations makes detailed discussion here unnecessary.

In addition to vinyl compounds with acceptor groups, such as acrylic esters, acrylonitriles, and vinyl ketones mentioned above, butadiene, styrene, and vinyl pyridine can also be anionically polymerized. It is also possible to polymerize heterocyclic compounds such as oxirane, thiirane, and lactam anionically (▶ Sect. 12.4).

10.2.2 Initiation

The initiation of anionic polymerization takes place either by the direct addition of a nucleophile to the carbon-carbon double bond of a monomer or by an electron transfer reaction. Both mechanisms are dealt with in the following paragraphs (▶ Sects. 10.2.2.1 and 10.2.2.2). Individual paragraphs deal with the so-called *group-transfer* polymerization (▶ Sect. 10.2.2.3) and the polymerization of lactams, of Leuchs' anhydride, and of acrylamides (▶ Sect. 10.2.2.4), and a further paragraph deals with multifunctional initiators (▶ Sect. 10.2.2.5).

10.2.2.1 Nucleophilic Initiators

Covalent or ionic metal amides such as $NaNH_2$ and $LiN(C_2H_5)_2$, alkoxides, hydroxides, cyanides, phosphines, and amines can all be employed as initiators. Organic metal compounds such as n-C_4H_9Li (Fig. 10.50) and Grignard compounds such as PhMgBr are especially popular.

Lithium alkyl and aryl compounds are often used as these are easily soluble in hydrocarbons.

Neutral nucleophiles, which generate zwitterionic growing chain ends, are not so frequently used as initiators for anionic polymerization (Fig. 10.51).

The choice of initiator depends on the monomer to be polymerized. Monomers such as styrene and 1,3-butadiene require more nucleophilic initiators such as amide or alkyl

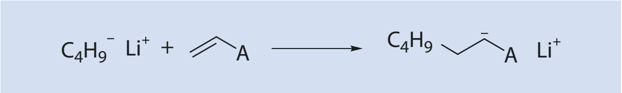


Fig. 10.50 Initiation of anionic polymerization with *n*-BuLi

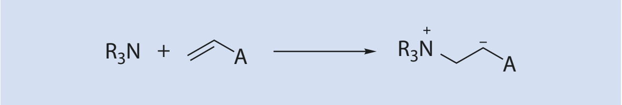


Fig. 10.51 Initiation by a neutral nucleophile. *A*, e.g., COOR or CN

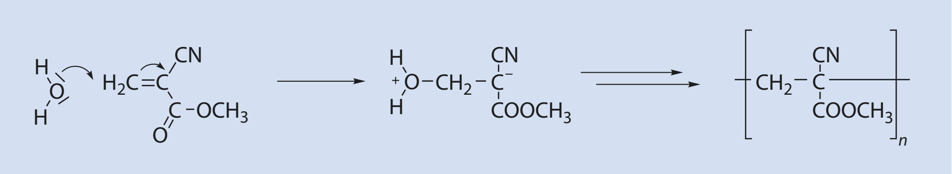


Fig. 10.52 Water as initiator for the anionic polymerization of 2-cyano-acrylic acid methyl ester

carbonate ions. Less nucleophilic initiators such as alkoxides can be used for the polymerization of acrylonitrile, methyl vinyl ketone, and methyl methacrylate. The polymerization of a monomer with two electron-withdrawing substituents, e.g., methyl cyanoacrylate, can be initiated by very weak nucleophiles such as Br^-, CN^-, amines, phosphines, and even water ("Superglue") (Fig. 10.52).

10.2.2.2 Electron Transfer

The reaction of sodium with naphthalene results in a radical ion (Fig. 10.53) which can be used as an initiator for the polymerization of styrene and other anionically polymerizable monomers.

The color changes spontaneously when the polymerization of styrene is initiated by a solution of naphthalene radical ions in tetrahydrofuran; the dark green solution turns a deep cherry red (Fig. 10.54).

The styrene radical ion dimerizes to a dianion (Fig. 10.55).

Because of resonance stabilization I (Fig. 10.55) is formed. The alternative conceivable products of a radical combination, II and III, are either not stabilized at all (II) or significantly less stabilized (III) and therefore do not form.

The dianion I grows by adding additional monomer and becomes a macromolecule with a negative charge at both ends. These dianions can be converted into molecules with interesting functional groups at both ends, telechelics, by reaction with specially chosen termination reagents (Fig. 10.56).

If stored with suitable precautions (protection against moisture), living polystyrene anions, for example, can be kept for longer periods. The polymerization can then be resumed either by further addition of monomer or, if a different monomer is introduced, a block copolymer can be produced (Fig. 10.57).

The synthesis of ABA block copolymers with A = polystyrene and B = 1,4 polybutadiene is commercially very important. The polymerization of styrene is started using BuLi. Then butadiene is added to yield a simple A-B block copolymer. After the addition of SiR_2Cl_2, two growing anions are linked via an SiR_2 bridge produced by the

Fig. 10.53 Formation of a radical anion from the reaction of sodium with naphthalene

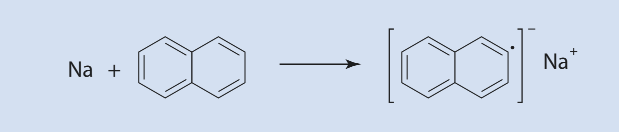
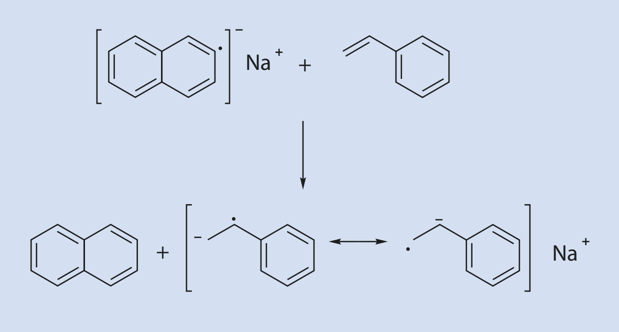


Fig. 10.54 Sodium naphthalene as an initiator for the polymerization of styrene



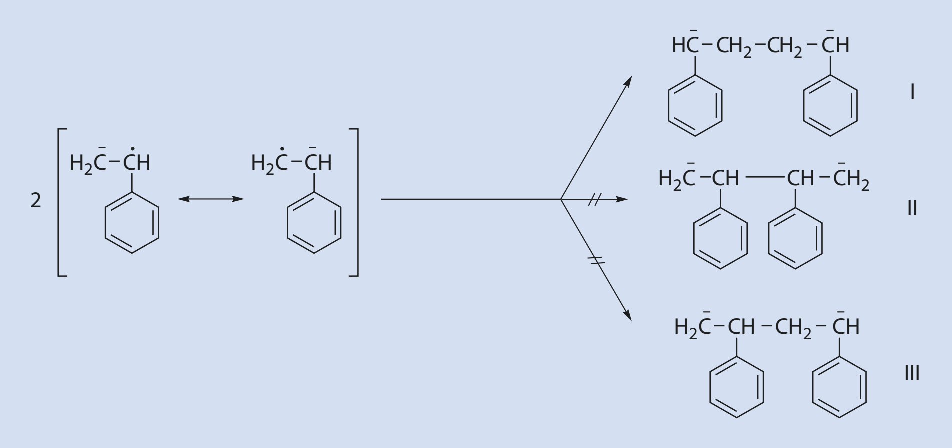


Fig. 10.55 Dimerization of a styryl-radical anion to the corresponding dianion

nucleophilic substitution of the halogens to yield an A-B-A block copolymer (Fig. 10.58).

Theoretically it would be possible to synthesize the A-B-A block copolymer simply by adding styrene monomer to the living A-B block copolymer but the lack of reactivity of the butadienyl anion (allyl anion) with respect to styrene prohibits this route.

10.2.2.3 Group Transfer Polymerization

Group transfer polymerization (GTP) is shown schematically using the example of methyl methacrylate in Fig. 10.59. A silylated acetal of dimethyl ketene (1-methoxy-2-methyl-1-trimethylsilyl oxypropene) capable of initiating the controlled anionic polymerization

Fig. 10.56 Synthesis of telechelic polystyrene by reacting the growing polymeric dianion with CO_2 or oxirane

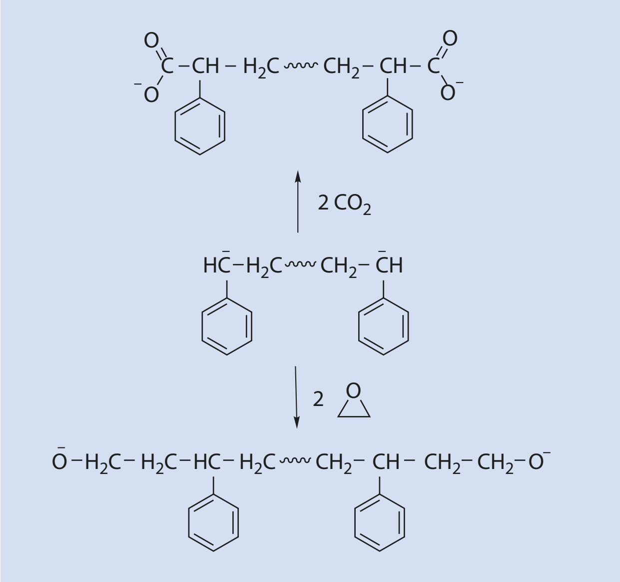
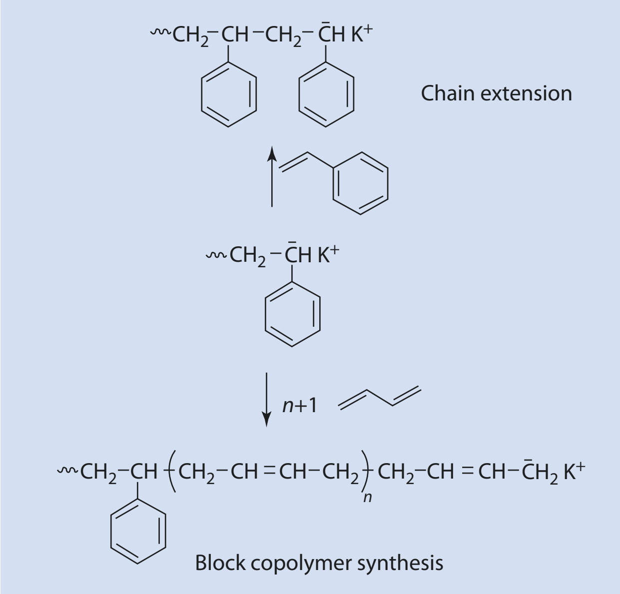


Fig. 10.57 Chain extension and block copolymer synthesis via living polymerization



of methyl methacrylate in the presence of fluoride anions (as NR_4F), $ZnCl_2$, or AlR_2Cl is used as an initiator (Fig. 10.59).

In contrast to the conventional anionic polymerization of MMA, e.g., initiated by BuLi, GTP is especially suited for the synthesis of PMMA with a narrow molar mass distribution.

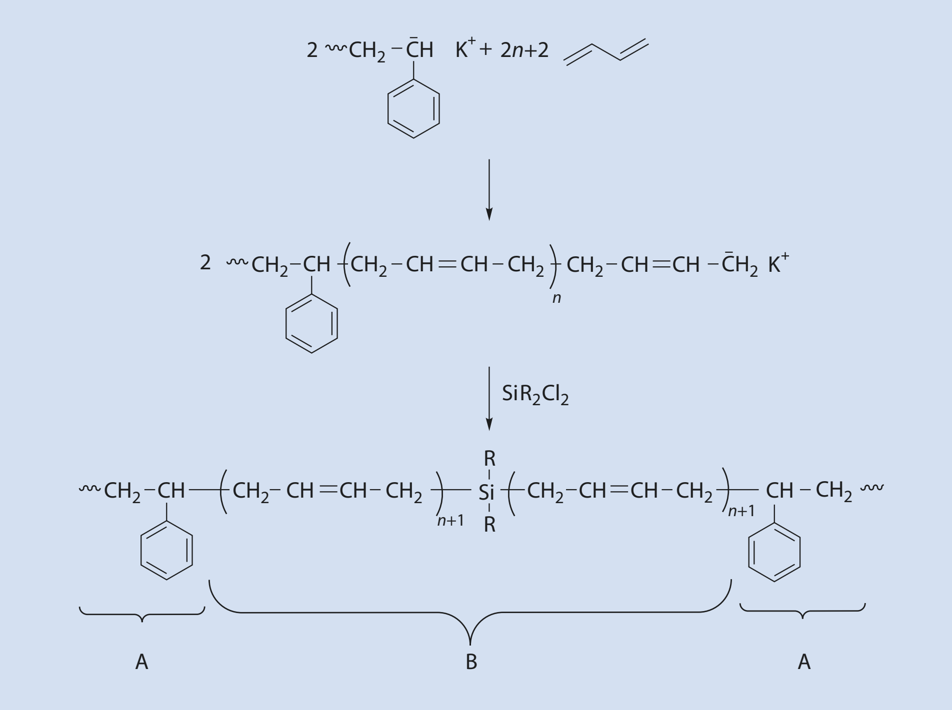


Fig. 10.58 Synthesis of an ABA-block copolymer from a living anionic polymerization by a controlled termination with the bifunctional termination reagent (SiR_2Cl_2). *R*, e.g., CH_3

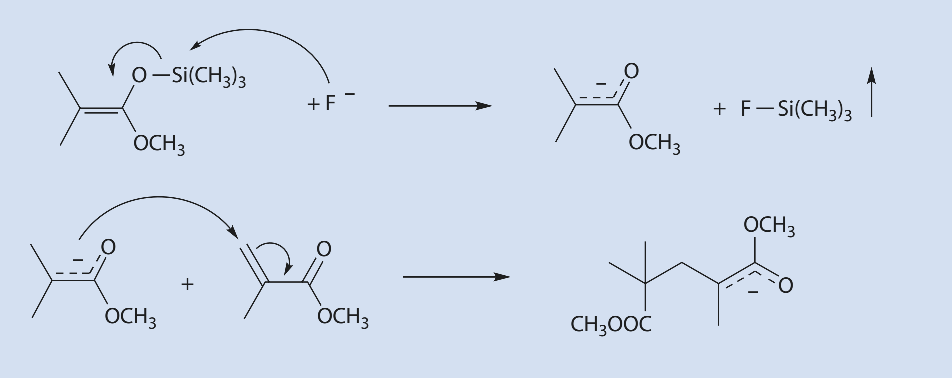


Fig. 10.59 Initiation of the group-transfer-polymerization of methyl methacrylate

10.2.2.4 Polyamides from Lactams, Leuchs' Anhydride, or Acrylamide

Lactams and Leuchs' anhydride polymerize via an *activated monomer* mechanism (▶ Sect. 12.4.3 and Figs. 10.60 and 10.61).

Polyamide-2 is produced during this process (▶ see Sect. 8.3.2 for the polyamide nomenclature) and CO_2 is eliminated with each propagation step (▶ Sect. 12.4.3).

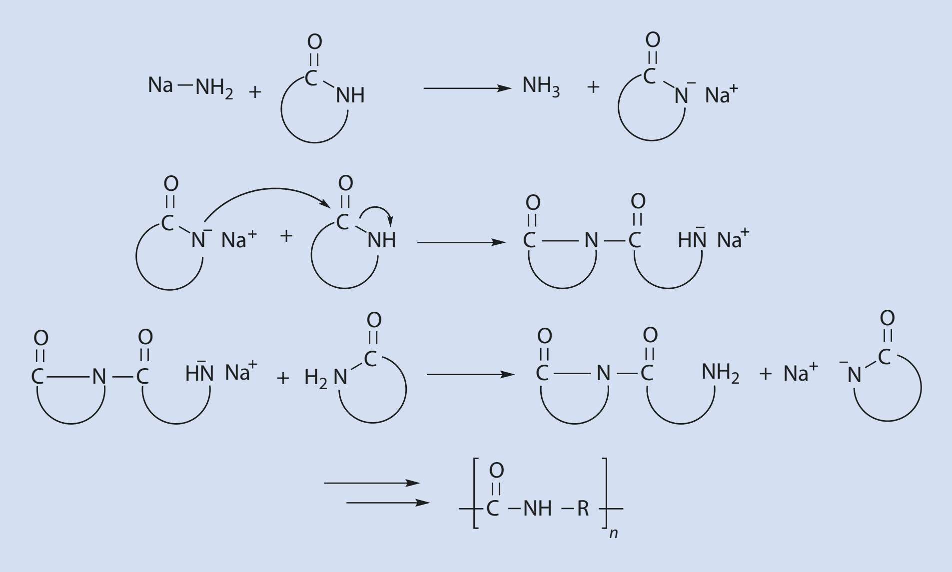


Fig. 10.60 Initiation of the anionic polymerization of lactams

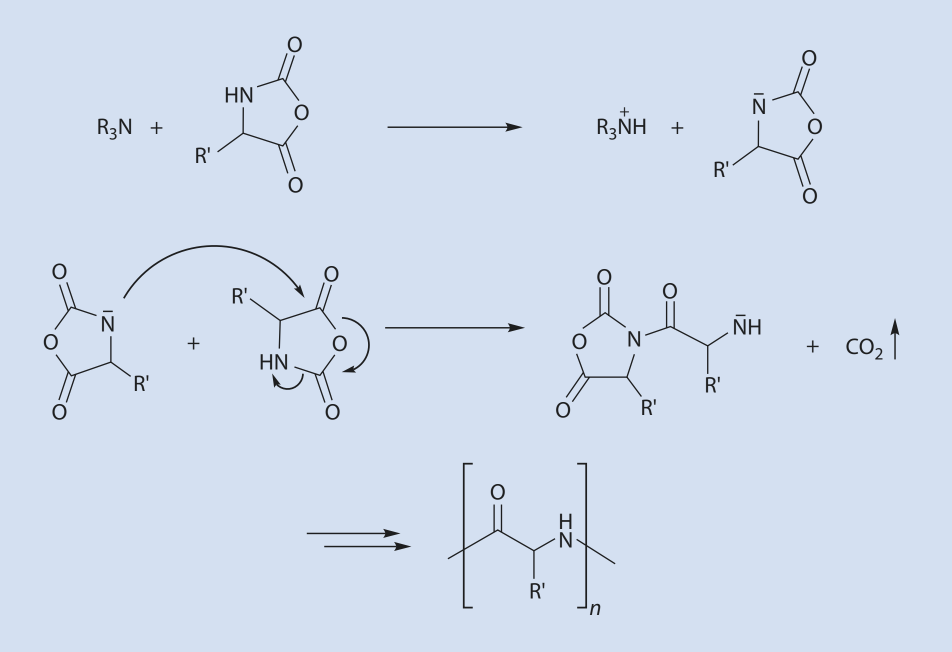
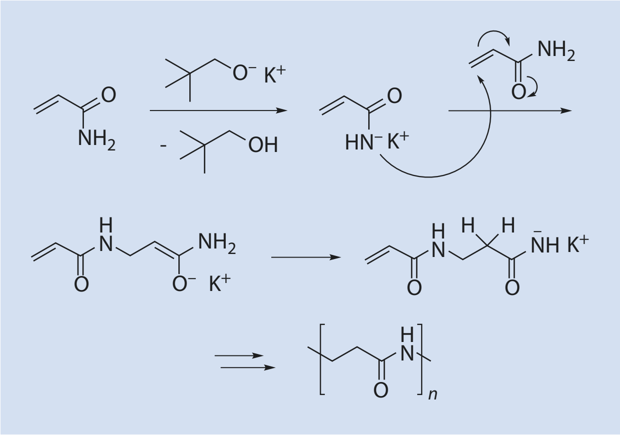
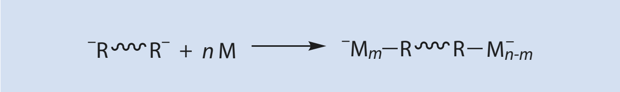


Fig. 10.61 Initiation of the anionic polymerization of Leuchs' anhydride



■ **Fig. 10.62** Synthesis of polyamide-3 from acrylamide



■ **Fig. 10.63** Initiation with a bifunctional initiator

A polyamide-3 instead of the expected polyacrylamide is produced if a strong base is present (■ Fig. 10.62).

10.2.2.5 Bi- and Multifunctional Initiators

Bifunctional initiators that lead to chain growth in two directions are suitable for the synthesis of telechelics, and multifunctional initiators are used to synthesize star polymers (three or more arms) (■ Fig. 10.63).

The synthesis of a bifunctional initiator from styrene was discussed in ► Sect. 10.2.2.2. By analogy, a similar initiator can be synthesized from 1,1-diphenylethylene (■ Fig. 10.64).

A selection of bifunctional initiators which can be synthesized by combining the appropriate olefins with BuLi are shown in ■ Figs. 10.65 and 10.66.

However, the synthesis of multifunctional initiators is not trivial. A more elegant solution is to couple growing chains with a multifunctional termination reagent (■ Fig. 10.67).

10.2.3 Role of Termination Reactions and Reagents in Anionic Polymerization

Reactions that deactivate the growing chain so that no further monomer can be added to it are described in this section.

10.2.3.1 Polymerization Without Termination

Termination reactions, such as the combination which can be observed during radical polymerization, do not occur during living ionic polymerization because identically charged species cannot terminate one another. The anionic polymerization of non-polar

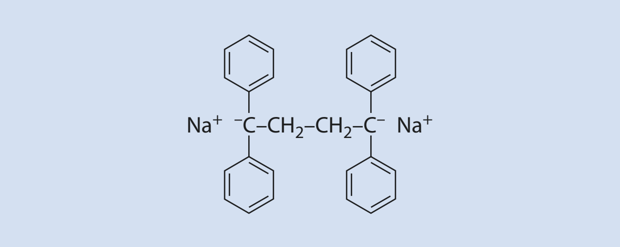


Fig. 10.64 Bifunctional initiator based on 1,1-diphenyl ethylene

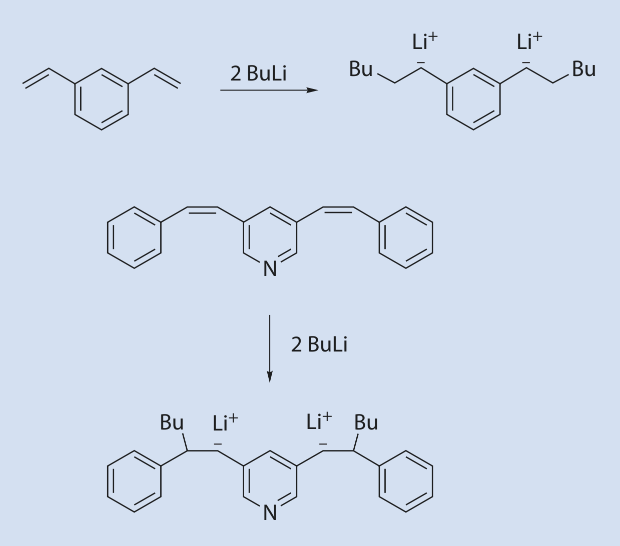


Fig. 10.65 Bifunctional initiators from diolefins and BuLi

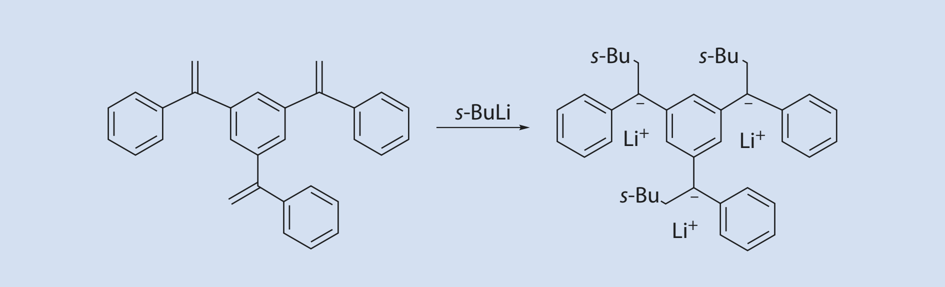


Fig. 10.66 An example of a trifunctional initiator

monomers such as styrene and 1,3-butadiene takes place without termination because the growing chain ends are relatively weak nucleophiles and are thus only rarely terminated by proton abstraction from, for example, the solvent or already formed polymers. A simple collapse of the counterions is also not observed (Fig. 10.68).

Fig. 10.67 Synthesis of a three-arm polymer by controlled termination

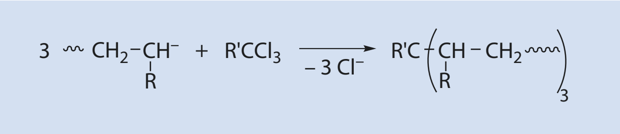


Fig. 10.68 Collapse of the counterion does not occur

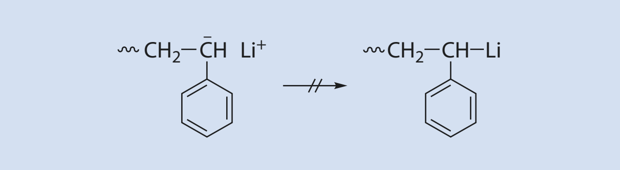
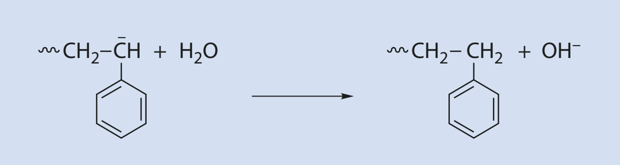


Fig. 10.69 Termination of an anionic polymerization by water



If propagation continues until all the monomer has been consumed, the growing chain remains active provided no transfer takes place. Because of this, this type of polymerization is referred to as living polymerization. These polymeric carbanions are often colored because of conjugation with the substituent R of the last monomer unit; R = Ph, for example, is cherry red. A fading of the color would be an indication for a termination reaction.

10.2.3.2 Termination by Contamination and Deliberately Added Reagents

Elaborate experimental techniques (including, for example, high vacuum or Schlenk techniques and carefully purified and dried solvents) are indispensable for synthesizing good quality products; moisture on the glass surfaces is often sufficient to have a negative effect (◘ Fig. 10.69).

By analogy with the reaction shown in ◘ Fig. 10.56, the active chain ends can be converted into interesting functional groups if solid CO_2, oxiranes, or halogen-containing termination reagents are added rather than water. The addition of oxirane can result in the formation of block copolymers. This can, however, be avoided by adding only a stoichiometric amount of the oxirane and rapidly quenching with water. As well as the introduction of –COOH and –OH end groups, the introduction of amino groups may also be desired. One way of producing $-NH_2$ terminated polystyrene is shown in ◘ Fig. 10.70.

10.2.3.3 Hydride Elimination

Over a longer time period of time (days or weeks), a decrease in the carbanion concentration in a solution of polystyryl anions in THF is often observed despite the absence of termination reagents. This is because of hydride elimination taking place (◘ Fig. 10.71).

The first step is a hydride elimination. The reaction of the resulting CH = CH(Ph) chain ends with another carbanion yields a stable and thus unreactive allyl anion. NaH can, if there is still monomer present, initiate new chain growth.

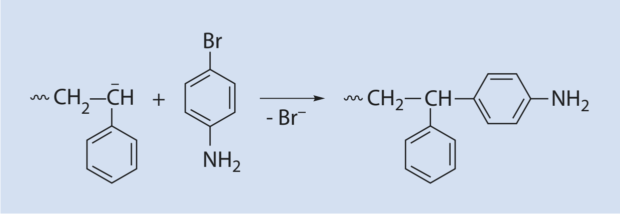


Fig. 10.70 Intentional termination of an anionic polymerization with 4-bromoaniline

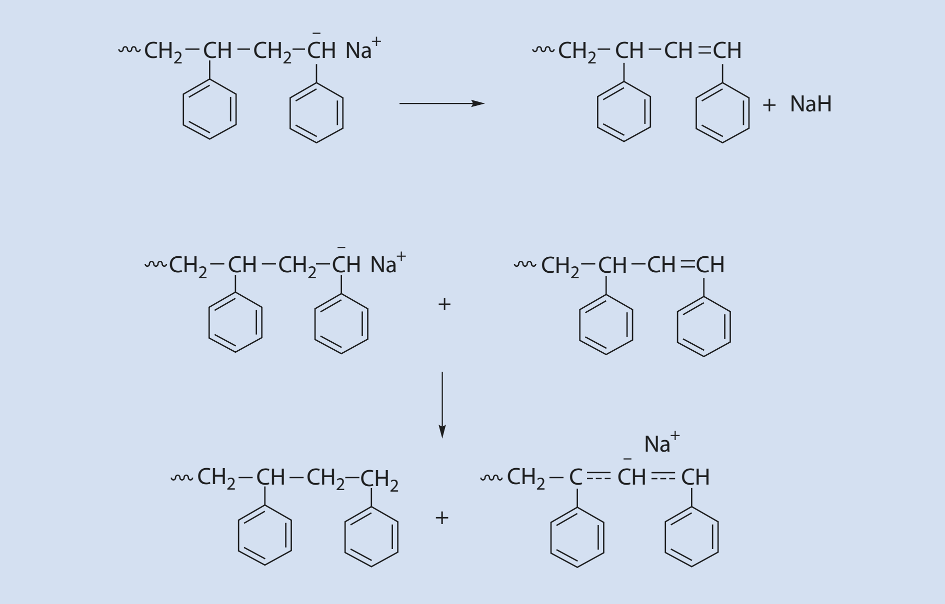


Fig. 10.71 Formation of an unreactive 1,3-diphenyl allyl anion

10.2.3.4 Termination Reactions During the Anionic Polymerization of Methyl Methacrylate

Three different termination reactions can be observed during the anionic polymerization of methyl methacrylate:

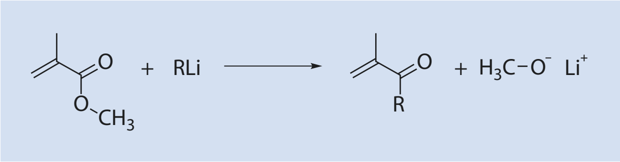
1. A reaction of the initiator with the functional group of the monomer leading to the less reactive alkoxide (Fig. 10.72)
2. A nucleophilic reaction of the polymeric anion with the monomer (Fig. 10.73)
3. An intramolecular back-biting reaction (Fig. 10.74)

These termination reactions can be avoided, for the most part, by using initiators that are less nucleophilic, such as 1,1-diphenyl hexyl lithium (instead of *n*-BuLi), lower temperature (approx. −70 °C), and polar solvents (ether rather than hydrocarbons).

10.2.4 Kinetics of Anionic Polymerization

In contrast to cationic polymerization, the proposed mechanisms and the experimental results from kinetics studies with vinyl monomers can be explained by a single consistent model. In the following paragraphs the kinetics of polymerizations without termination

Fig. 10.72 Nucleophilic substitution of the OCH_3-group of the monomer by R



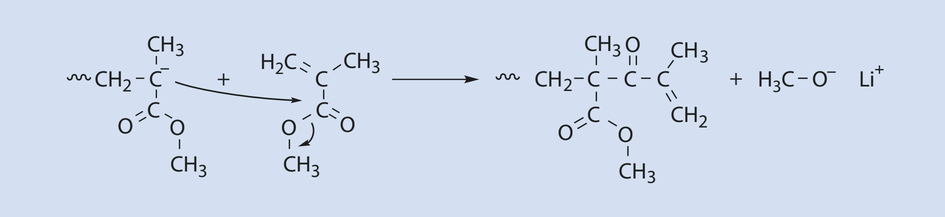


Fig. 10.73 Reaction of the polymeric anion with the monomer

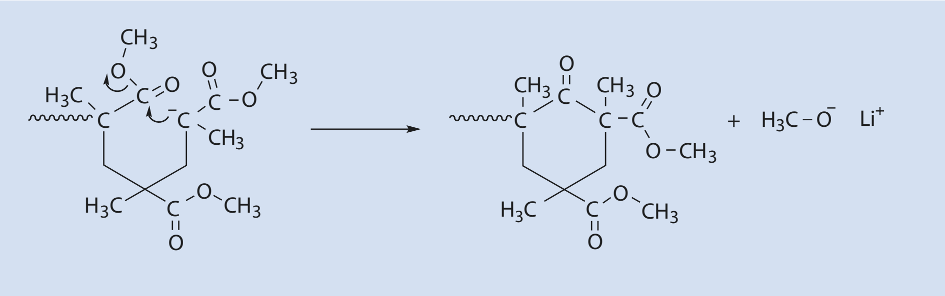


Fig. 10.74 Ring closure as the result of intramolecular back-biting reaction

Fig. 10.75 Polymerization-depolymerization equilibrium. k_p rate constant of propagation, k_{dp} rate constant of depolymerization

$$M_n^- + M \underset{k_{dp}}{\overset{k_w}{\rightleftharpoons}} M_{n+1}^-$$

(▶ Sect. 10.2.4.1), those in which free ions and ion pairs compete with one another (▶ Sect. 10.2.4.1), and, lastly, those which take place in non-polar solvents (▶ Sect. 10.2.4.2) are discussed.

The monomer is consumed by propagation and regenerated by depolymerization (Fig. 10.75).

All active species M^- are present at the beginning of polymerization because of the rapid initiation and very quick start in comparison to growth. The following holds for the change in monomer concentration over time:

$$-\frac{d[M]}{dt} = k_p [M]\left[M_n^-\right] - k_{dp}\left[M_{n+1}^-\right] \tag{10.5}$$

k_p	Rate constant of propagation
k_{dp}	Rate constant of depolymerization

If the rates of polymerization and depolymerization are equal:

$$\frac{d[M]}{dt} = 0 \tag{10.6}$$

and

$$K = \frac{k_p}{k_{dp}} = \frac{\left[M_{n+1}^-\right]}{\left[M_n^-\right][M]} = \frac{1}{[M]_e} \tag{10.7}$$

$[M]_e$ Equilibrium monomer concentration
K Equilibrium constant

With the assumption that

$$\left[M_{n+1}^-\right] = \left[M_n^-\right] \tag{10.8}$$

a simple relationship between the equilibrium constant K and the equilibrium monomer concentration $[M]_e$ can be derived (see (10.7)). Combining (10.5) with (10.7) results in

$$-\frac{d[M]}{dt} = k_p\left[M_n^-\right]\left([M]-[M]_e\right) \tag{10.9}$$

Separation of the variables yields the following:

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M]-[M]_e} = k_p\left[M_n^-\right] \cdot \int_0^t dt \tag{10.10}$$

Integration of (10.10) gives

$$\left[-\ln\left([M]-[M]_e\right)\right]_{[M]_0}^{[M]} = \left[k_p\left[M_n^-\right]t\right]_0^t \tag{10.11}$$

$$\ln\frac{\left([M]_0-[M]_e\right)}{\left([M]-[M]_e\right)} = k_p\left[M_n^-\right]t \tag{10.12}$$

The rate constant k_p can be determined from the gradient of a plot of ▣ Fig. 10.76.

In some cases the experimentally determined values for k_p increase inversely proportional to the initiator concentration (▣ Fig. 10.77). This is an indication of a complication, namely a competition between free ions and ion pairs as the initiating species. If both of these are present at the same time then, with increasing dilution, the equilibrium shifts and the concentration of free ions increases (▶ Sect. 10.2.4.1).

The addition of $NaB(Ph)_4$ (*Kalignost*), which is completely dissociated in tetrahydrofuran, results in the equilibrium between the free ions and ion pairs of the initiator being shifted towards the side of the ion pairs because of an increase in the concentration of sodium ions (▣ Fig. 10.78).

Fig. 10.76 Plot to determine the propagation rate constant k_p

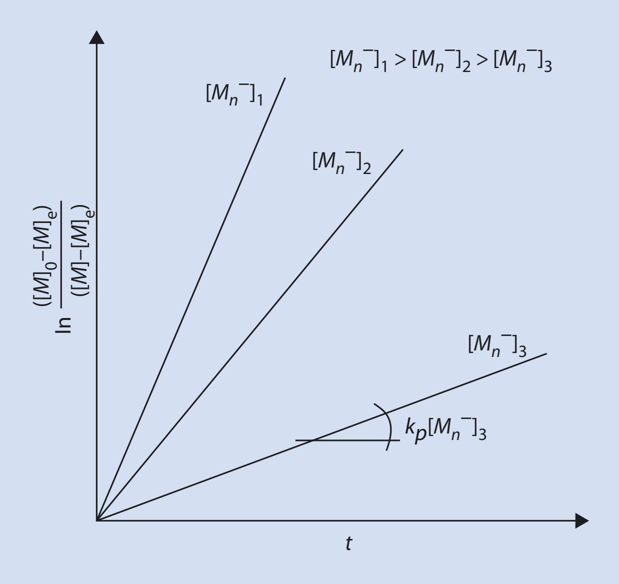
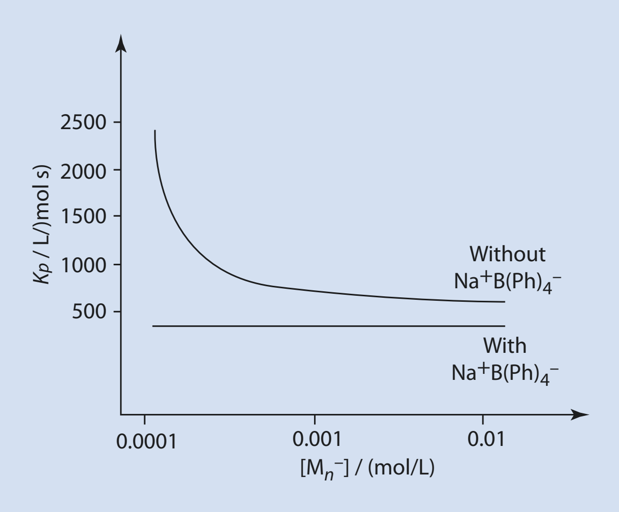


Fig. 10.77 Typical plot of the propagation rate constants experimentally determined for a polymerization involving both free ions and ion pairs (e.g., sodium naphthalene styrene in THF)



10.2.4.1 Competitive Growth of Two Different Species

During ionic polymerization it is to be expected that both the initiator and the growing chains, are part of the equilibria between the ion pairs and the free ions, depending on the polarity of the solvent and the concentration of the active species (Fig. 10.78).

The following demonstrates how the coexistence of two different active polymerization species can be taken into account kinetically.

Considering only the equilibrium between the free ions and ion pairs, for the dissociation constant K_D with $[Na^+] = [M_n^-]$:

$$K_D = \frac{[Na^+][M_n^-]}{[M_n^- Na^+]} = \frac{[M_n^-]^2}{[M_n^- Na^+]} \tag{10.13}$$

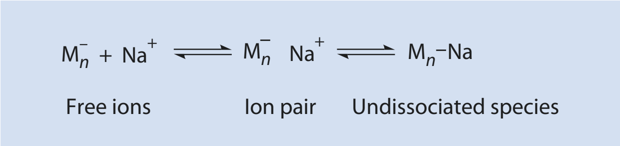


Fig. 10.78 Equilibria between free ions, ion pairs, and the undissociated species

K_D can be obtained from conductivity and spectroscopic measurements.

The monomer is only consumed by the propagation reaction so that

$$-\frac{d[M]}{dt} = k_{\pm}\left[M_n^- Na^+\right][M] + k_-\left[M_n^-\right][M] = \overline{k_p}\left[C^-\right][M] \tag{10.14}$$

$k_{\pm}$	Rate constant of propagation for the ion pair
k_-	Rate constant of propagation for the free ions
$\overline{k_p}$	Average propagation rate constant
$[C^-]$	Total concentration of active polymer anions

$$\overline{k_p} = \frac{k_{\pm}\left[M_n^- Na^+\right]}{\left[C^-\right]} + \frac{k_-\left[M_n^-\right]}{\left[C^-\right]} \tag{10.15}$$

with

$$\left[M_n^- Na^+\right] = \left[C^-\right] - \left[M_n^-\right] \tag{10.16}$$

and the degree of dissociation α:

$$\alpha = \frac{\left[M_n^-\right]}{\left[C^-\right]} \tag{10.17}$$

then for $\left[M_n^- Na^+\right]$:

$$\left[M_n^- Na^+\right] = \left[C^-\right] - \alpha \cdot \left[C^-\right] = \left[C^-\right](1-\alpha) \tag{10.18}$$

Combining (10.13), (10.17), and (10.18) gives for K_D:

$$K_D = \frac{\alpha^2 \cdot \left[C^-\right]}{(1-\alpha)} \tag{10.19}$$

As the degree of dissociation α is usually significantly smaller than 1, $1-\alpha$ is close to 1 and

$$\alpha = \sqrt{\frac{K_D}{\left[C^-\right]}} \tag{10.20}$$

If α is small then the total concentration of the growing chains is essentially identical to the concentration of the ion pairs and

$$\left[M_n^- Na^+\right] = \left[C^-\right] \tag{10.21}$$

Thus, with (10.15), (10.17), and (10.21) one obtains for $\overline{k_p}$:

$$\overline{k_p} = k_\pm + k_- \alpha \tag{10.22}$$

By inserting (10.20) into (10.22) one obtains

$$\overline{k_p} = k_\pm + k_- \sqrt{\frac{K_D}{\left[C^-\right]}} \tag{10.23}$$

From a series of experiments with varying initiator concentration a plot of the mean propagation rate constant as a function of $1/\sqrt{\left[C^-\right]}$ (◘ Fig. 10.79) allows the determination of $k_\pm$ (from the intercept) and k_- (from the gradient, if K_D is known).

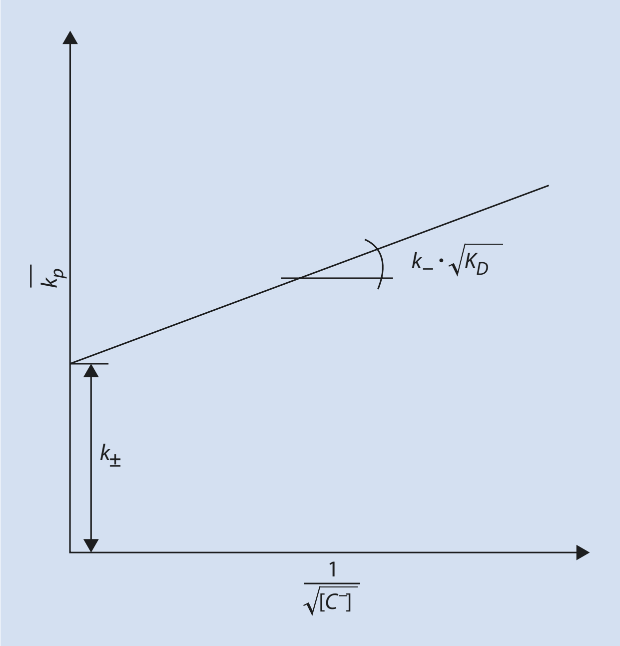
As discussed in ▶ Sect. 10.2.4.1, the addition of $NaB(Ph)_4$ completely suppresses the dissociation of the initiator and the growing chains (Gl. (10.13) and Gl. (10.21)). From (10.13), (10.17), and (10.22), and with $[M_n^- Na^+] = [C^-]$ (because of the shift in equilibrium produced by $NaB(Ph)_4$), one obtains

$$\overline{k_p} = k_\pm + k_- \cdot \frac{K_D}{\left[Na^+\right]} \tag{10.24}$$

A plot k_p vs. $1/[Na^+]$ allows $k_\pm$ and k_- to be determined using (10.24) (◘ Fig. 10.80).

Thus, with two alternative equations, all three constants K_D, $k_\pm$, and k_- can be determined. K_D can also be obtained independently from conductivity measurements.

◘ **Fig. 10.79** Plot to determine the rate constants $k_\pm$ and k_-



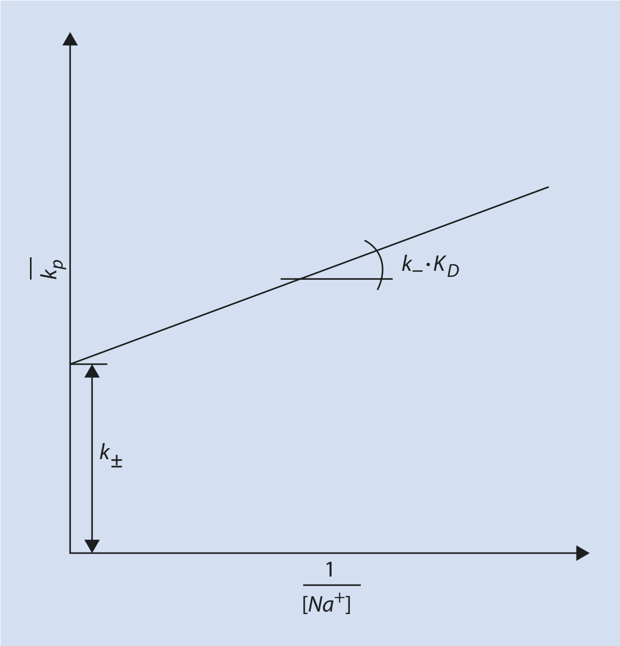


Fig. 10.80 Determine the rate constants $k_\pm$ and k_- from experiments with varying Na^+-concentration, e.g., by adding sodium tetraphenylborate (Kalignost)

The constants $k_\pm$ and k_- differ considerably. For the polymerization of styrene at 25 °C, initiated with sodium naphthalene in THF, the values

$$k_\pm = 80\,\mathrm{L}/(\mathrm{mol}\bullet\mathrm{s})$$
$$k_- = 65{,}000\mathrm{L}/(\mathrm{mol}\bullet\mathrm{s})$$

have been determined.

Thus, the rate of propagation for the free polystyryl ions is significantly faster than that for ion pairs.

10.2.4.2 Polymerization in Non-polar Solvents

The polymerization of monomers initiated by BuLi in non-polar solvents such as hexane is very slow. Initiation and chain growth occur initially at the same time so that an exact determination of the kinetics is not possible during this phase. If, however, the initiator is completely converted into oligomers (BuLi becomes M_nLi) and this initial solution is used for polymerization, we can empirically obtain the following relationship for monomer conversion:

$$-\frac{d[M]}{dt} = k_p[M]\sqrt{[M_nLi]} \tag{10.25}$$

The initial phase of polymerization with BuLi instead of M_nLi follows the empirically determined rule:

$$-\frac{d[BuLi]}{dt} = k_{st}[M]\cdot\sqrt[6]{[BuLi]} \tag{10.26}$$

k_{st} Start rate constant

These equations can be derived from the equilibria for the initiator and the growing chains given in ◘ Figs. 10.81 and 10.82), respectively.

Equation (10.26) can be analyzed experimentally by converting the remaining BuLi *n*-butane by adding water. The *n*-butane can then be determined, for example, by gas chromatography.

10.2.5 Ceiling Temperature

The rate of polymerization of α-methyl styrene decreases with increasing temperature and above a temperature of 61 °C polymerization ceases completely. The reason for this is the reversibility of the propagation reaction, and the relative rates of polymerization and depolymerization (◘ Fig. 10.83).

From ◘ Fig. 10.83 one can develop for the conversion of monomer with time:

$$-\frac{d[M]}{dt} = k_p [M]\left[M_n^-\right] - k_{dp}\left[M_{n+1}^-\right] \tag{10.5}$$

Again, making the assumption that

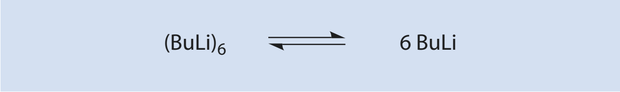
$$\left[M_n^-\right] = \left[M_{n+1}^-\right] \tag{10.8}$$

at equilibrium and with (10.5):

$$-\frac{d[M]}{dt} = \left(k_p [M] - k_{dp}\right)\left[M_n^-\right] = 0 \tag{10.5a}$$

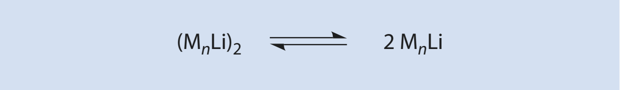
The temperature at which $k_p[M] - k_{dp} = 0$ and polymerization stops is referred to as the *ceiling temperature* (T_c) (◘ Fig. 10.84). This equilibrium can be determined for anionic polymerization because, in ideal cases, no termination takes place. However, principally, this equilibrium is independent of the type of polymerization.

◘ **Fig. 10.81** Equilibrium between BuLi and the hexamer $(BuLi)_6$



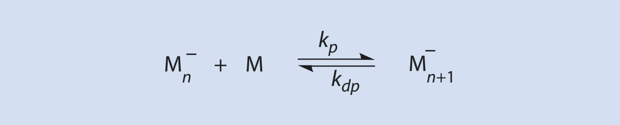
$$(\mathrm{BuLi})_6 \rightleftharpoons 6\ \mathrm{BuLi}$$

◘ **Fig. 10.82** Equilibrium between M_nLi and the dimer $(M_nLi)_2$



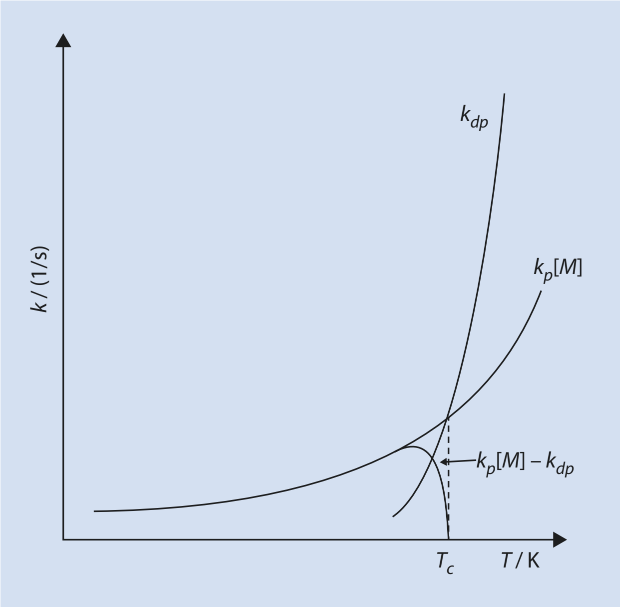
$$(M_n\mathrm{Li})_2 \rightleftharpoons 2\ M_n\mathrm{Li}$$

◘ **Fig. 10.83** Polymerization–depolymerization equilibrium



$$M_n^- + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^-$$

Fig. 10.84 Kinetic determination of the ceiling-temperature



Depolymerization has a larger activation energy than polymerization so that the increase of k_{dp} with increasing temperature is greater than that of k_p . To have the same dimensions, k_{dp} is compared to $k_p\ x\ [M]$ in Fig. 10.84. This does not change the basic assertion about the different temperature dependence of both partial reactions in Fig. 10.83.

As for every other chemical reaction, the basic thermodynamic equation also applies to the conversion of monomer into polymer:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10.27}$$

As well as this, the following applies for the free enthalpy of reaction ΔG:

$$\Delta G = \Delta G^0 + \mathrm{R}T \ln K \tag{10.28}$$

ΔG^0	Molar free enthalpy of polymerization
ΔH^0	Molar enthalpy of polymerization
ΔS^0	Molar entropy of polymerization
T	Reaction temperature
R	Gas constant

At equilibrium:

$$\Delta G = 0 \tag{10.29}$$

and from (10.28):

$$\Delta G^0 = -\mathrm{R}T \ln K \tag{10.30}$$

Combining the equilibrium constant K:

$$K = \frac{\left[M_{n+1}^{-}\right]}{\left[M_{n}^{-}\right][M]} \tag{10.7}$$

with the assumption

$$\left[M_{n+1}^{-}\right] = \left[M_{n}^{-}\right] \tag{10.8}$$

yields the very simple relationship

$$K = \frac{1}{[M]} \tag{10.31}$$

Inserting (10.31) into (10.30) gives

$$\Delta G^{0} = \mathrm{R}T \ln[M] \tag{10.32}$$

which, with (10.27), gives

$$\Delta H^{0} - T\Delta S^{0} = \mathrm{R}T \ln[M] \tag{10.33}$$

Thus, for the ceiling temperature:

$$T_c = \frac{\Delta H^{0}}{\Delta S^{0} + \mathrm{R} \ln[M]} \tag{10.34}$$

From (10.34) it can be seen that every monomer concentration is associated with a different ceiling temperature. A 1 M solution is usually viewed as the standard concentration in physical chemistry and at this concentration the ceiling temperature is given by

$$T_c = \frac{\Delta H^{0}}{\Delta S^{0}} \tag{10.35}$$

However, conventionally, ceiling temperatures are only discussed for polymerizations of pure monomers. The concentration c for pure α-methyl styrene is ($\rho = 0.940$ g/mL, $M = 118$ g/mol):

$$c = \frac{n}{V} = \frac{m}{M \cdot V} = \frac{\rho}{M} = \frac{940\ \mathrm{g/L}}{118\ \mathrm{g/mol}} = 7.966\ \mathrm{mol/L} \tag{10.36}$$

Living anionic polymerization is especially well suited for experimentally determining ceiling temperatures as the polymerization-depolymerization equilibrium is not disturbed by termination reactions. The polymerizations are carried out at different temperatures ($T < 60$ °C), allowing equilibrium to become established. The amount of polymer is then determined and from this the monomer conversion can be calculated. Solving (10.33) for $\ln[M]$ gives the basis for determining the ceiling temperature (◘ Fig. 10.85):

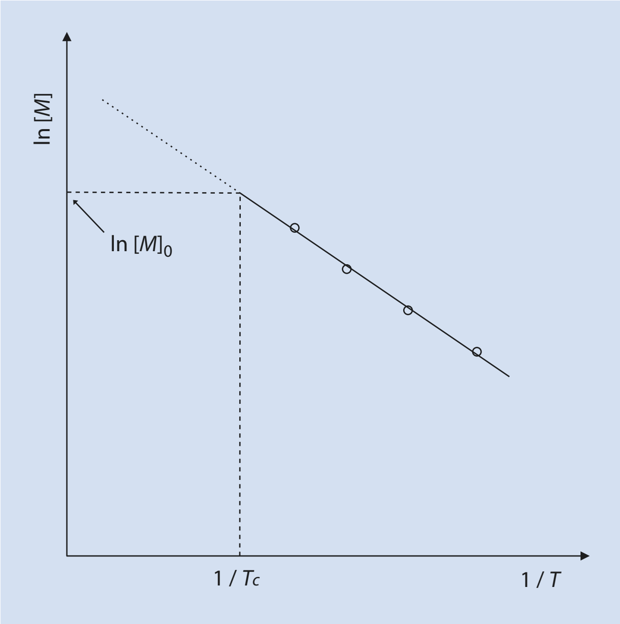


Fig. 10.85 Thermodynamic determination of the ceiling temperature. T_c ceiling temperature, $[M]_0$ concentration of pure monomer

$$\ln[M] = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \tag{10.37}$$

By plotting $\ln[M]$ against $1/T$ (Fig. 10.85), $\Delta H^0/R$ can be obtained from the gradient and $\Delta S^0/R$ from the intercept. Both ΔH^0 and ΔS^0 are negative. ΔH^0 is negative as a higher-energy monomer (π-bond) is converted into a lower-energy polymer (σ-bond). Negative values for ΔS^0 are the result of the loss of degrees of freedom for the polymer compared to the monomer.

From (10.34) it can be seen that at every polymerization temperature a minimum monomer concentration is necessary for polymerization to take place (Table 10.5).

10.2.6 Molar Mass Distribution from an Ideal (Living) Anionic Polymerization: Poisson Distribution

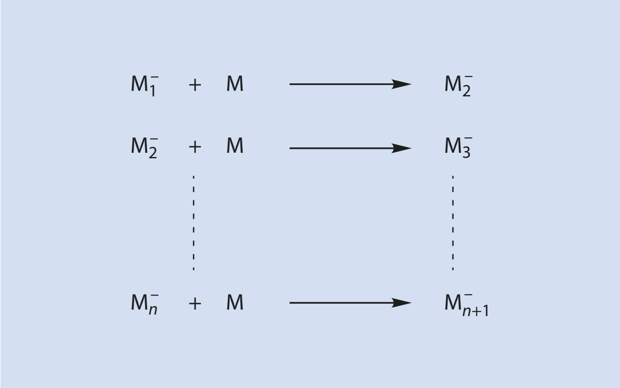
The term ideal anionic polymerization is used if the following conditions are met:

1. Every chain starts to grow at the same time, i.e., at time $t=0$ all active centers have identical degrees of polymerization, either $P=0$ or $P=1$. (This implies that the chains are initiated very rapidly and that the rate of initiation is much faster than the rate of propagation so that the time required for initiation is negligible.)
2. The number of growing chains remains constant during polymerization, i.e., there is no chain termination.
3. The chains are constructed out of a series of kinetically identical monomer units (Fig. 10.86).
4. Growth continues until the monomer has been completely converted or until it is intentionally stopped.

Table 10.5 Limiting concentration for a selection of monomers at a polymerization temperature of 25 °C and the ceiling temperatures for the pure monomers

Monomer	$[M]_c$ (mol/L)	T_c (pure monomer) (°C)
Vinyl acetate	$1 \cdot 10^{-9}$	–
Methyl acrylate	$1 \cdot 10^{-9}$	–
Styrene	$1 \cdot 10^{-6}$	310
Methyl methacrylate	$1 \cdot 10^{-3}$	220
α-Methyl styrene	2.2	61

Fig. 10.86 Propagation of an ideal anionic polymerization



$$M_1^- + M \longrightarrow M_2^-$$
$$M_2^- + M \longrightarrow M_3^-$$
$$\vdots \qquad\qquad \vdots$$
$$M_n^- + M \longrightarrow M_{n+1}^-$$

5. The chains should only grow in one direction.
6. There is no chain transfer.

The molar mass distribution deviates considerably from those distributions derived above (► Sect. 9.5) as demonstrated below.

The change of the molar concentration of the active species with *a single* monomer unit per molecule ($P = 1$) with time is given by

$$\frac{d\left[M_1^-\right]}{dt} = -k_p\left[M\right]\left[M_1^-\right] \tag{10.38}$$

The change of the molar concentration of the active species with *two* monomer units per molecule ($P = 2$) with time is given by

$$\frac{d\left[M_2^-\right]}{dt} = k_p\left[M\right]\left[M_1^-\right] - k_p\left[M\right]\left[M_2^-\right] \tag{10.39}$$

By analogy, for $[M_n^-]$:

$$\frac{d\left[M_n^-\right]}{dt} = k_p\left[M\right]\left[M_{n-1}^-\right] - k_p\left[M\right]\left[M_n^-\right] \tag{10.40}$$

With every propagation step, monomer is consumed so that

$$-\frac{d[M]}{dt}=k_p[M]\sum_{n=1}^{\infty}\left[M_n^-\right] \tag{10.41}$$

According to condition (2) (above) the sum of all the active species is constant:

$$\sum_{n=1}^{\infty}\left[M_n^-\right]=const.=\left[C^-\right] \tag{10.42}$$

From (10.41) and (10.42):

$$-\frac{d[M]}{dt}=k_p[M]\left[C^-\right] \tag{10.43}$$

or

$$-\int_{[M]_0-[C^-]}^{[M]_t} d[M]=k_p\left[C^-\right]\int_0^t[M]dt \tag{10.44}$$

(One monomer unit has already reacted with each initiator molecule to become M_1^- at time $t=0$ so these must be deducted from $[M]_0$.)

Solving the left hand side of (10.44) yields

$$\frac{-\left([M]_t-[M]_0+\left[C^-\right]\right)}{\left[C^-\right]}=k_p\int_0^t[M]dt \tag{10.45}$$

The equation for the degree of polymerization P_n during an anionic polymerization, i.e., when not all the monomer has been converted to polymer ($[M]_t\neq 0$), is

$$P_n=\frac{[M]_0-[M]_t}{\left[C^-\right]} \tag{10.46}$$

$$P_n-1=\frac{[M]_0-[M]_t-\left[C^-\right]}{\left[C^-\right]} \tag{10.47}$$

From (10.45) and (10.47) if follows that

$$\frac{[M]_0-\left[C^-\right]-[M]_t}{\left[C^-\right]}=P_n-1=k_p\int_0^t[M]dt \tag{10.48}$$

Introducing the kinetic chain length ν, which denotes the number of monomer units which have been added to the chain started by the anion M_1^-:

$$\nu=P_n-1 \tag{10.49}$$

and from (10.48) one obtains

$$dv = k_p\left[M\right]dt \tag{10.50}$$

$$\frac{dv}{dt} = k_p\left[M\right] \tag{10.51}$$

From (10.51) and (10.38):

$$-\frac{d\left[M_1^-\right]}{\left[M_1^-\right]}\cdot\frac{1}{dt} = \frac{dv}{dt} \tag{10.52}$$

or

$$d\left[M_1^-\right] = -\left[M_1^-\right]dv \tag{10.53}$$

Similarly, from (10.39) and (10.50):

$$d\left[M_2^-\right] = \left[M_1^-\right]dv - \left[M_2^-\right]dv \tag{10.54}$$

and for the trimer:

$$d\left[M_3^-\right] = \left[M_2^-\right]dv - \left[M_3^-\right]dv \tag{10.55}$$

Thus, for an n-mer anion, from (10.40) and (10.50):

$$d\left[M_n^-\right] = \left[M_{n-1}^-\right]dv - \left[M_n^-\right]dv \tag{10.56}$$

Integration of (10.53) yields

$$\int\frac{d\left[M_1^-\right]}{\left[M_1^-\right]} = -\int dv \tag{10.57}$$

Solving (10.57) yields

$$\ln\left[M_1^-\right] = -v + const. \tag{10.58}$$

When $t=0$, $\nu=0$ and the constant can be calculated:

$$const. = \ln\left[M_1^-\right] \tag{10.59}$$

Because $[M_1{}^-]=[C^-]$ (when $t=0$), i.e., one monomer unit has already been added to the initiator:

$$const. = \ln\left[C^-\right] \tag{10.60}$$

By insertion into (10.59) one obtains for $t \neq 0$ and $[M_n^-] \neq [C^-]$:

$$\ln\left[M_1^-\right] = -\nu + \ln\left[C^-\right] \tag{10.61}$$

so that for $[M_1^-]$:

$$\left[M_1^-\right] = \left[C^-\right] \cdot e^{-\nu} \tag{10.62}$$

Insertion of (10.62) into (10.54) results in

$$d\left[M_2^-\right] = \left[C^-\right] \cdot e^{-\nu} d\nu - \left[M_2^-\right] d\nu \tag{10.63}$$

Integrating (10.63) by the method of integrating factors:

$$e^{\nu} \cdot d\left[M_2^-\right] = \left[C^-\right] d\nu - \left[M_2^-\right] \cdot e^{\nu} d\nu \tag{10.64}$$

whereby

$$e^{\nu} d\nu = d\left(e^{\nu}\right) \tag{10.65}$$

and substituting (10.65) into (10.64) gives

$$\left[C^-\right] d\nu = e^{\nu} d\left[M_2^-\right] + \left[M_2^-\right] d\left(e^{\nu}\right) \tag{10.66}$$

Using the integration rule (total differential):

$$x \cdot y = \int x \cdot dy + \int y \cdot dx \tag{10.67}$$

Equation (10.66) can be integrated ($x = e^{\nu}$; $dx = e^{\nu}\, d\nu = d(e^{\nu})$; $y = [M_2^-]$; $dy = d[M_2^-]$) and transformed into (10.68):

$$\left[C^-\right] \cdot \nu + \text{const.} = e^{\nu} \cdot \left[M_2^-\right] \tag{10.68}$$

const. = 0, because $[M_2^-]$ and $\nu = 0$ at $t = 0$ so that

$$\left[M_2^-\right] = \frac{\left[C^-\right] \cdot \nu}{e^{\nu}} \tag{10.69}$$

As deduced above (see (10.55)) for trimers:

$$d\left[M_3^-\right] = \left[M_2^-\right] d\nu - \left[M_3^-\right] d\nu \tag{10.70}$$

which, with (10.69) gives

$$d\left[M_3^-\right] = \frac{\left[C^-\right] \cdot \nu \cdot d\nu}{e^\nu} - \left[M_3^-\right] d\nu \tag{10.71}$$

After multiplication by e^ν one obtains

$$e^\nu \cdot d\left[M_3^-\right] + \left[M_3^-\right] \cdot e^\nu d\nu = \left[C^-\right] \cdot \nu \cdot d\nu \tag{10.72}$$

By analogy with (10.66), after integration one obtains

$$\left[M_3^-\right] \cdot e^\nu = \left[C^-\right] \cdot \frac{\nu^2}{1 \cdot 2} + const. \tag{10.73}$$

$const = 0$, as at $t = 0$, $[M_3^-] = 0$ and $\nu = 0$

$$\left[M_3^-\right] = \left[C^-\right] \cdot \frac{\nu^2}{2! \cdot e^\nu} \tag{10.74}$$

Extrapolating this approach one obtains for $[M_n^-]$:

$$\left[M_n^-\right] = \left[C^-\right] \cdot \frac{\nu^{n-1}}{(n-1)! \cdot e^\nu} \tag{10.75}$$

Thus, the mole fraction of n-mer anions M_n^- of the total ions$[C^-]$ generates a *Poisson* distribution :

$$\frac{\left[M_n^-\right]}{\left[C^-\right]} = \frac{\nu^{n-1}}{(n-1)! \cdot e^\nu} \tag{10.76}$$

The weight fraction of the n-mer anion m_P of the total weight m is then

$$w_P = \frac{m_P}{m} = \frac{\frac{\left[M_n^-\right]}{\left[C^-\right]} \cdot n \cdot M_0}{(\nu+1) \cdot M_0} = \frac{\nu^{n-1} \cdot n}{(n-1)! \cdot (\nu+1) \cdot e^\nu} \tag{10.77}$$

Using this equation and the definition of the weight average, one obtains for the weight average of the degree of polymerization P_w:

$$P_w = \sum_n w_P \cdot n = \sum_n \frac{\nu^{n-1} \cdot n^2}{(n-1)! \cdot (\nu+1) \cdot e^\nu} =$$

$$= \frac{\nu^2 + 3\nu + 1}{\nu + 1} \tag{10.78}$$

By solving this equation using the series theory one obtains

$$P_w = \sum_n \frac{\nu^{n-1}\cdot n^2}{(n-1)!\cdot(\nu+1)\cdot e^{\nu}} = \frac{\nu}{(\nu+1)\cdot e^{\nu}}\sum_n \frac{\nu^{n-2}\cdot n^2}{(n-1)!} =$$
$$= \frac{\nu}{(\nu+1)\cdot e^{\nu}}\cdot\left(\nu+3+\frac{1}{\nu}\right)\cdot e^{\nu} = \frac{\nu^2+3\nu+1}{\nu+1}$$

The definition of the non-uniformity of a molar mass distribution (▶ Sect. 9.4.3) is

$$U = \frac{P_w}{P_n} - 1 \tag{9.80}$$

which (if $P_n = \nu + 1$ (10.49)) can be expanded to

$$U = \frac{\nu^2+3\nu+1}{(\nu+1)\cdot(\nu+1)} - 1 = \frac{\nu}{(\nu+1)^2} = \frac{P_n-1}{P_n^{\,2}} = \frac{1}{P_n} - \frac{1}{P_n^{\,2}} \tag{10.79}$$

Under ideal conditions, polymers with very narrow molar mass distributions are usually obtained during anionic polymerization. This is why anionic polymerization is used, for example, for the synthesis of polymer standards, e.g., for calibrating size exclusion chromatography (▶ Sect. 3.3.2).

From (10.79) it follows that non-uniformity decreases with an increase in the degree of polymerization.

From ◘ Fig. 10.87 and (10.79) it can be seen that a polymer from an anionic polymerization still contains chains with degrees of polymerization between $n = 30$ and $n = 80$ even when its inconsistency is $U = 0.02$, despite the fact that it has a considerably narrower molar mass distribution than a polymer from a radical polymerization with an identical kinetic chain length ($\nu = 50$).

At this point, it is important to draw the readers' attention to a comparison between the frequency distribution of the individual polymer fractions $x_i(P_i)$ and the weight fraction distribution $w_i(P_i)$, both as functions of the degree of polymerization P_i . The basic concept beneath the former is the mole fraction and for the latter the weight fraction. For a Poisson distribution, in analogy with (10.76) and (10.77) one gets:

$$x_i(P_i) = \frac{(P_n-1)^{P_i-1}}{\Gamma(P_i)}\exp(1-P_n) \tag{10.80}$$

$$w_i(P_i) = x_i(P_i)\frac{P_i}{P_n} \tag{10.81}$$

$x_i(P_i)$ describes the mole fraction of those polymer chain with a degree of polymerization P_i, $w_i(P_i)$ the corresponding weight fraction, P_n the mean degree of polymer-

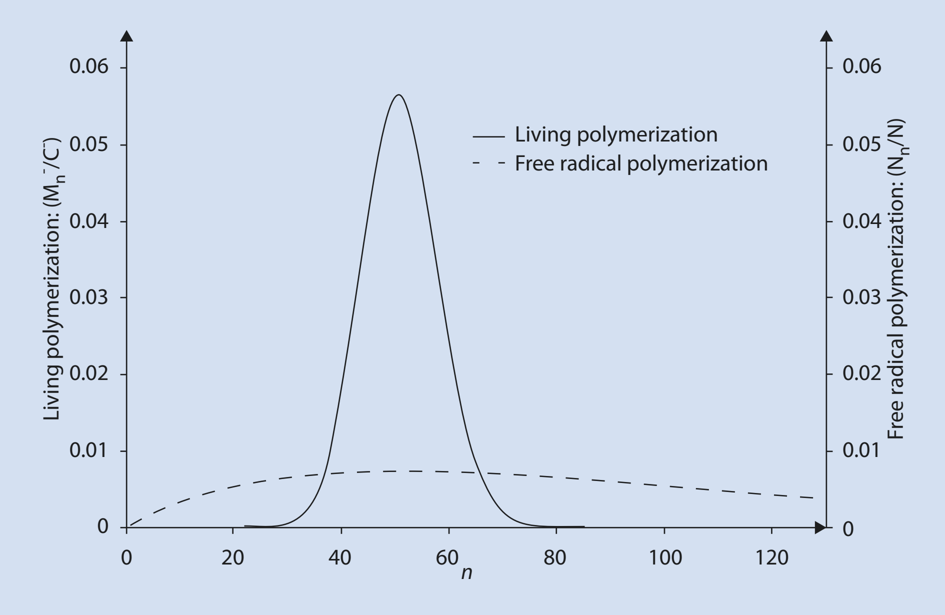


Fig. 10.87 Comparison of the number average distribution of *n*-mers from an anionic and a free radical polymerization. Anionic polymerization: M_n^- number of active chains with *n* repeating units, C^- total number of active chains; radical polymerization, N_n number of polymers with *n* repeating units, *N* number of all polymer chains; for both cases $\nu = 50$

ization (number average), and Γ the gamma function with the auxiliary variable k given by

$$\Gamma(P_i) = \int_0^\infty k^{P_i - 1} \exp(-k)\, dk \tag{10.82}$$

It should also be noted that for natural numbers:

$$(P_i - 1)! = \Gamma(P_i) \tag{10.83}$$

On the other hand, Schulz Zimm distributions are usually obtained from free radical polymerizations:

$$x_i(P_i) = \frac{\zeta^{\zeta+1}}{P_n^{\zeta}\Gamma(\zeta+1)} P_i^{\zeta-1} \exp\left(\frac{-\zeta P_i}{P_n}\right) \tag{10.84}$$

ζ describes the degree of coupling, i.e., the number of chains that grew independently and are terminated by combination:

$$\zeta = \frac{P_n}{P_w - P_n} \tag{10.85}$$

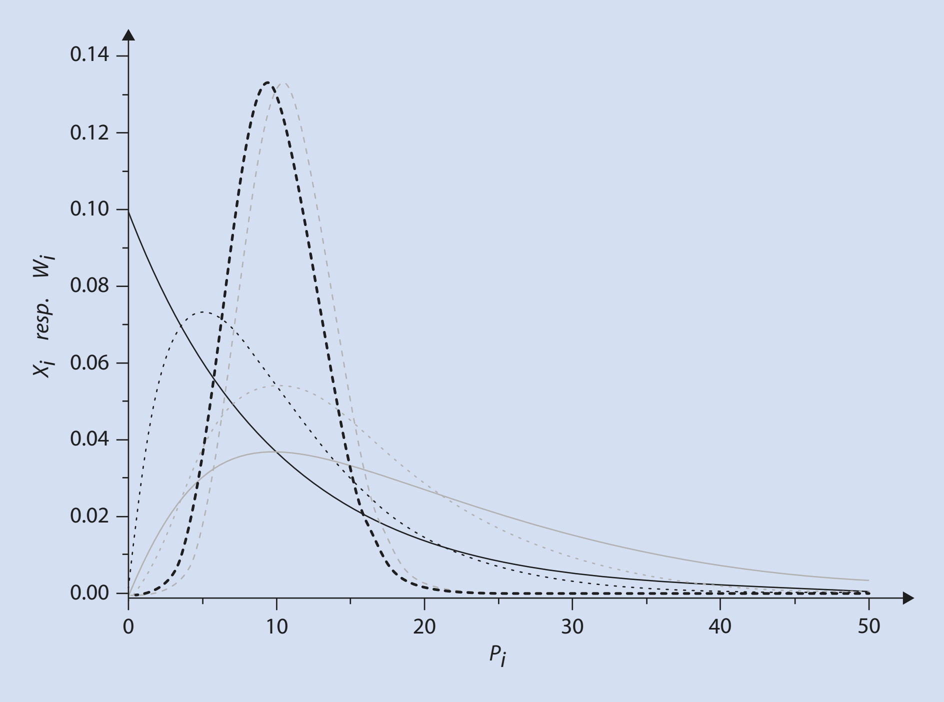


Fig. 10.88 Distribution functions with $P_n = 10$. *Dashed line:* Poisson-distribution, *full line:* Schulz–Zimm distribution with $\zeta = 1$, *dotted line:* Schulz–Zimm distribution with $\zeta = 2$. (black: mole/number fraction distributions x_i, gray: weight fraction distributions w_i)

P_w describes, as above, the weight average degree of polymerization. Where termination is solely by disproportionation $\zeta = 1$ (the resulting distribution is also called a Schulz Flory distribution). Where termination is by recombination $\zeta = 2$. Examples of the graphs of these functions are shown in Fig. 10.88.

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