Radical Polymerization

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This chapter introduces the fundamental concepts of radical polymerization. Typical monomers, initiators, and transfer and termination reagents are discussed. Furthermore, the kinetic equations, the degree of polymerization, and molar mass distribution are derived.

9.1 Mechanism

During radical polymerization, initially (start) a radical (species with a single electron), which arises from, for example, the decay of peroxides or azo compounds (▣ Fig. 9.9), adds to the C=C double bond of a monomer, resulting in a new radical extended by a monomer unit (▣ Fig. 9.1). If the radical that was extended by a monomer unit is able to add an additional monomer and to form a macro radical, it is referred to as *chain growth* (▣ Fig. 9.2).

This chain reaction is continued until two radicals meet and prohibit the addition of another monomer (▣ Figs. 9.3 and 9.13d$_1$) by, for example, forming a covalent bond (*combination*). Alternatively, the two radicals can be individually deactivated by *disproportionation* (▣ Fig. 9.13d$_2$).

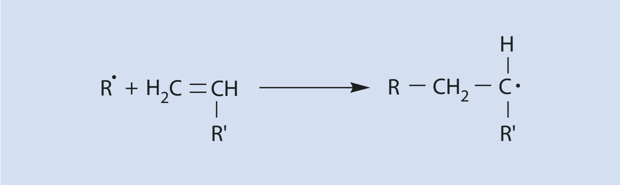
If the radical character of a macro radical is transferred to another moiety, and if this then becomes able to add an additional monomer, it is referred to as a transfer reaction (▣ Fig. 9.4).

These reaction types are discussed in detail in the following sections.

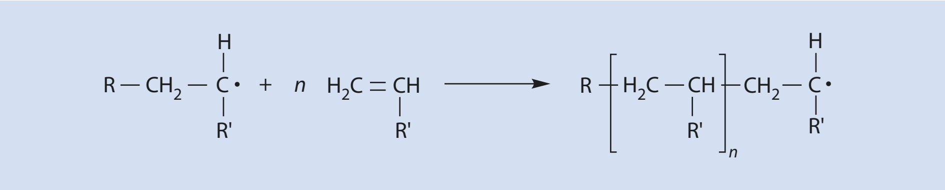
9.1.1 Typical Monomers

▣ Figure 9.5 shows the general structure of radically polymerizable monomers, R^1, R^2, and R^3, which are mostly H (▣ Table 9.1). R^4 are usually substituents that stabilize the growing radicals.

▣ **Fig. 9.1** Reaction of a radical $R^{\bullet}$ with a monomer $H_2C{=}CHR'$



$$R^{\bullet} + H_2C{=}\underset{R'}{\underset{|}{CH}} \longrightarrow R-CH_2-\overset{H}{\overset{|}{\underset{R'}{\underset{|}{C}}}}\bullet$$



$$R-CH_2-\overset{H}{\overset{|}{\underset{R'}{\underset{|}{C}}}}\bullet + n\ H_2C{=}\underset{R'}{\underset{|}{CH}} \longrightarrow R\left[H_2C-\underset{R'}{\underset{|}{CH}}\right]_n CH_2-\overset{H}{\overset{|}{\underset{R'}{\underset{|}{C}}}}\bullet$$

▣ **Fig. 9.2** Formation of a macro-radical

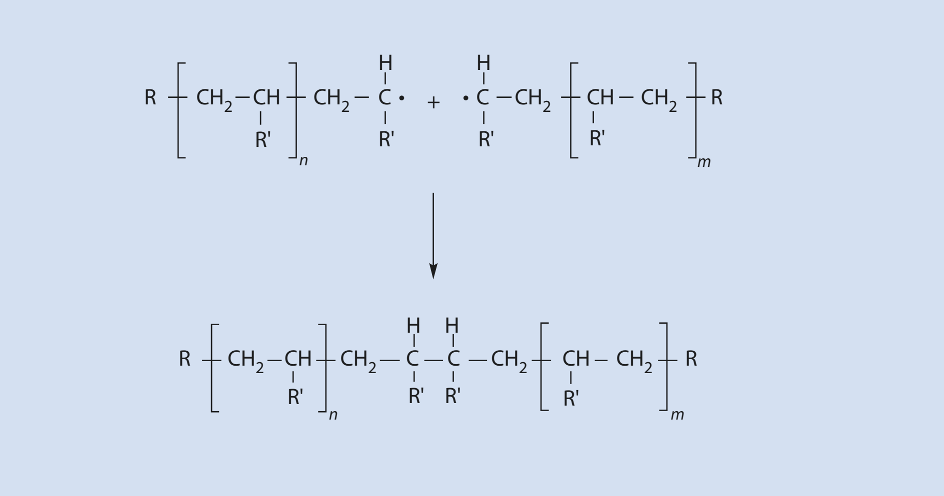


Fig. 9.3 Termination of chain growth by radical combination

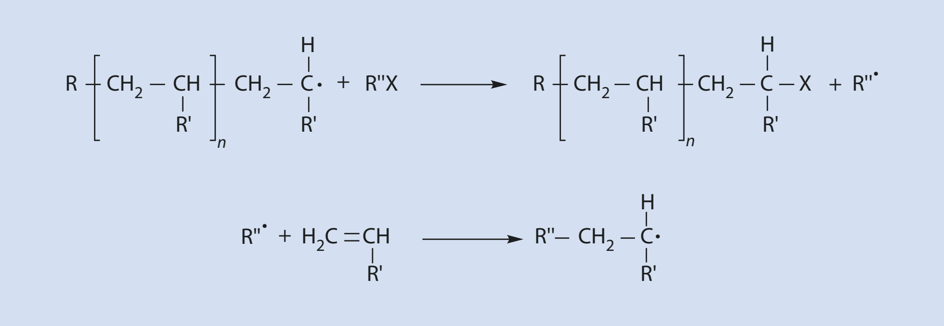
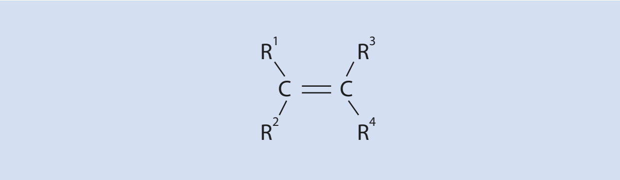


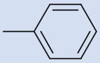
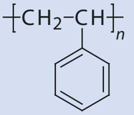
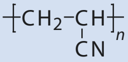
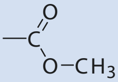
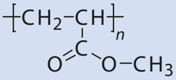
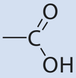
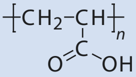
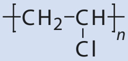
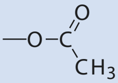
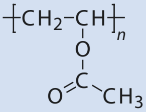
Fig. 9.4 Example of chain transfer

Fig. 9.5 General structures of monomers which polymerize radically



Generally, alkenes with other substitution patterns, such as 1,1- and 1,2-disubstituted alkenes, are , apart from some exceptions such as methyl methacrylate (MMA), more difficult to polymerize radically or they do not polymerize at all via a radical mechanism.

Table 9.1 Typical examples for radically polymerizable monomers of the structure $H_2C=CHR'$

Monomer	*R′*	Polymer
Ethene	$-H$	$\left[CH_2-CH_2 \right]_n$
Styrene		
Acrylonitrile	$-C\equiv N$	 $\left[CH_2-\underset{CN}{CH} \right]_n$
Acrylic acid methyl ester		
Acrylic acid		
Vinyl chloride	$-Cl$	 $\left[CH_2-\underset{Cl}{CH} \right]_n$
Vinyl acetate		

9.1.2 Radical Sources

Radical polymerizations are triggered by reactive species that have an unpaired electron (radicals). Such radicals can result from, for instance, the influence of light (visible or ultraviolet light) on neutral compounds (◘ Fig. 9.6). Another means of creating radicals involves the photochemical decay of special substances (*photoinitiators*) (◘ Figs. 9.7 and 15.7).

Radicals can also be created by γ- and β-radiation (◘ Fig. 9.8). In such a system, not only radicals but also anions and cations are created, and the respective chain growth reactions can proceed either via radicals, anions, or cations, or the different growing mechanisms can compete with each other.

Compounds that decompose to yield radicals during moderate heating (50–100 °C) are also frequently used as radical sources. The best-known radical sources are organic peroxides and azo compounds; industrially, organic peroxides are most often used (◘ Fig. 9.9).

Fig. 9.6 Photochemical activation of a monomer

$$M \xrightarrow{h\nu} M^{\bullet}$$

Fig. 9.7 Photochemical decomposition of benzoin ether

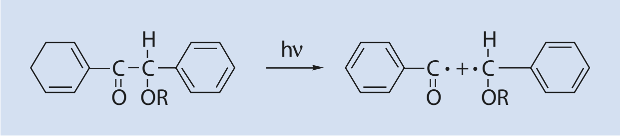


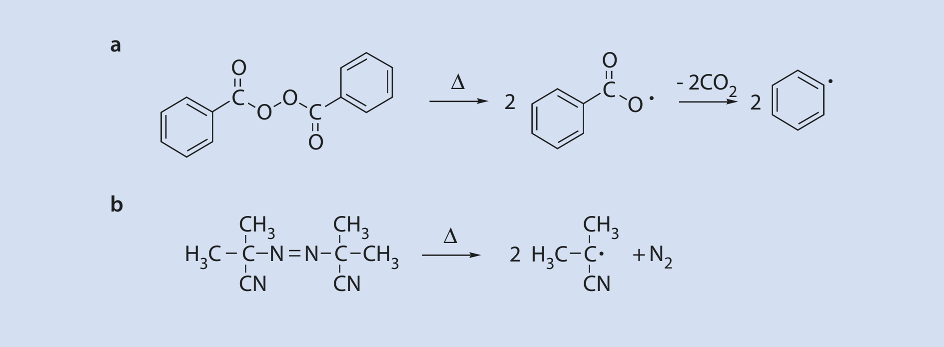
Fig. 9.8 Creation of radicals with high energy radiation. (**a**) γ-Radiation. (**b**) β-Radiation

a

$$AB \xrightarrow[-e^-]{\gamma} AB^{+\bullet} \longrightarrow A^+ + B^{\bullet}$$

b

$$AB + e^- \longrightarrow AB^{-\bullet} \longrightarrow A^{\bullet} + B^-$$



$$H_3C-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-CH_3 \xrightarrow{\Delta} 2\ H_3C-\overset{CH_3}{\underset{CN}{C}}\bullet \ + N_2$$

Fig. 9.9 Radicals from (**a**) dibenzoyl peroxide and (**b**) azo-bis-isobutyronitrile (AIBN)

Furthermore, redox reactions that proceed via radical intermediates can be used to initiate a radical polymerization (Fig. 9.10). In the literature, particularly in the patent literature, various combinations of oxidizing agents (e.g., peroxides, chlorates, hypochlorites, and permanganates) and reducing agents (e.g., sulfites, thiosulfates, sulfinic acid, and hydrazine) are suggested for this purpose. The major advantage of such redox systems is their ability to function at lower temperatures. Such systems have become irreplaceable for polymerizations where water is either the solvent or the dispersant.

It is also possible for monomers to polymerize simply by warming, known as *thermal polymerization*. This is, however, restricted to two monomers, namely, styrene and MMA. The list of thermally polymerizable monomers was originally longer. Upon closer investigation, however, with the exception of styrene and MMA, impurities have been identified as the radical source and thus responsible for the polymerization.

Fig. 9.10 Radical formed during a redox reaction (*Fenton reagent*)

$$\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet}$$

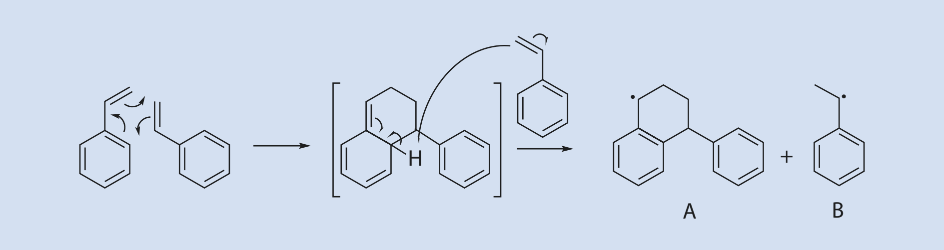


Fig. 9.11 Primary steps of the thermal polymerization of styrene

The thermal polymerization of styrene proceeds via a Diels–Alder adduct from which the radicals *A* and *B* emerge after reaction with an additional styrene molecule and H-transfer. The radicals are then able to initiate radical polymerization (Fig. 9.11).

9.2 Kinetics of Radical Polymerization

On the basis of the most precise mechanism, a radical polymerization can be divided into several individual reaction steps. A kinetic equation can be developed for every step, and from these the overall kinetics can be derived. The key question for the kinetics of radical polymerization is how the monomer concentration changes with time at a given temperature.

9.2.1 Basic Processes

The basic processes—initiation, growth, and termination—can be formally summarized by the scheme in Fig. 9.12. The initiator dissociates into two radicals at a given temperature with the rate constant k_d. These radicals, in the case of AIBN (**a**zo-bis-**i**so**b**utyro**n**itrile) (Fig. 9.9b), sufficiently stabilized by the nitrile group, are reactive enough to add to monomers (Table 9.1) with the rate constant k_i. The new radical $RM^\bullet$ adds additional monomers with the rate constant k_p. Depending on the temperature, termination can result from either radical combination (with k_t) or from disproportionation (with k_t') to a saturated chain RM_n^H and an unsaturated chain $RM_m^=$ (Figs. 9.12 and 9.13), or both termination reactions occur simultaneously. With an increase in temperature, termination by disproportionation generally becomes more important because $E_{A,disp.} > E_{A,comb.}$.

In Fig. 9.13 the individual steps—initiator decomposition, initiation, growth, and termination – are illustrated using the example of the AIBN-initiated polymerization of the monomer $CH_2{=}CHR'$.

In the following paragraphs, several limiting cases for the kinetics of radical polymerization are discussed.

Fig. 9.12 Formal scheme for a radical polymerization. *I* initiator, *R*$^•$ initiator radical, *M* monomer, *RM*$^•$ initiator radical extended by a single monomer unit, *RM*$_n^•$ initiator radical extended by *n* monomer units, RM$_n^H$ polymer with a saturated chain end, RM$_m^=$ polymer with an unsaturated chain end

$$
\begin{array}{lrl}
\text{Initiator decomposition} & \text{I} & \xrightarrow{k_d} 2\,\text{R}^• \\
\text{Start} & \text{R}^• + \text{M} & \xrightarrow{k_i} \text{RM}^• \\
\text{Propagation} & \text{RM}^• + (n\text{-}1)\,\text{M} & \xrightarrow{k_p} \text{RM}_n^• \\
\text{Termination} & \text{RM}_n^• + {}^•\text{M}_m\text{R} & \xrightarrow{k_t} \text{RM}_{n+m}\text{R} \\
 & & \xrightarrow{k'_t} \text{RM}_n^\text{H} + {}^{=}\text{M}_m\text{R}
\end{array}
$$

9.2.2 *R*$^•$ and *P*$^•$ are Equally Reactive

With the simplified assumption that all radicals have the same reactivity independent of their chain length ($R^• \equiv \text{RM}^• \equiv \text{RM}_n^• \equiv P^•$), the scheme in Fig. 9.12 can be simplified as follows (Fig. 9.14).

We then have

$$\frac{d\left[P^•\right]}{dt} = 2k_d\left[I\right] - k_t\left[P^•\right]^2 \tag{9.1}$$

With the assumption of a quasi-stationary state adapted from Bodenstein[1] it follows that

$$\frac{d\left[P^•\right]}{dt} = 0 \tag{9.2}$$

The radicals are consumed at the same rate at which they are created. For the radical concentration $[P^•]$ the following applies:

$$\left[P^•\right] = \sqrt{\frac{2k_d\left[I\right]}{k_t}} \tag{9.3}$$

Because termination by combination and disproportionation cannot be kinetically distinguished, k_t here is the average rate constant for both types of termination.

The monomer is only consumed by the growing chains, and thus the monomer consumption over time is a direct measure of the rate of polymerization v_{br} (▶ see (9.4)). (This assumption is not completely correct because monomer is also consumed by initiation (the first growth step) (Fig. 9.12). However, the amount of monomer consumed in the initial step of chain growth is very small compared with that consumed during polymerization to give chains many hundreds of monomer units long.)

$$-\frac{d\left[M\right]}{dt} = k_p\left[M\right]\left[P^•\right] \tag{9.4}$$

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[1] The concept of a quasi-stationary state involves the assumption that the change in the concentration of intermediate products (here *P*$^•$) can be neglected when compared with changes in the concentration of educts (here *M*) and products (here *P*) (Frost and Pearson 1964)

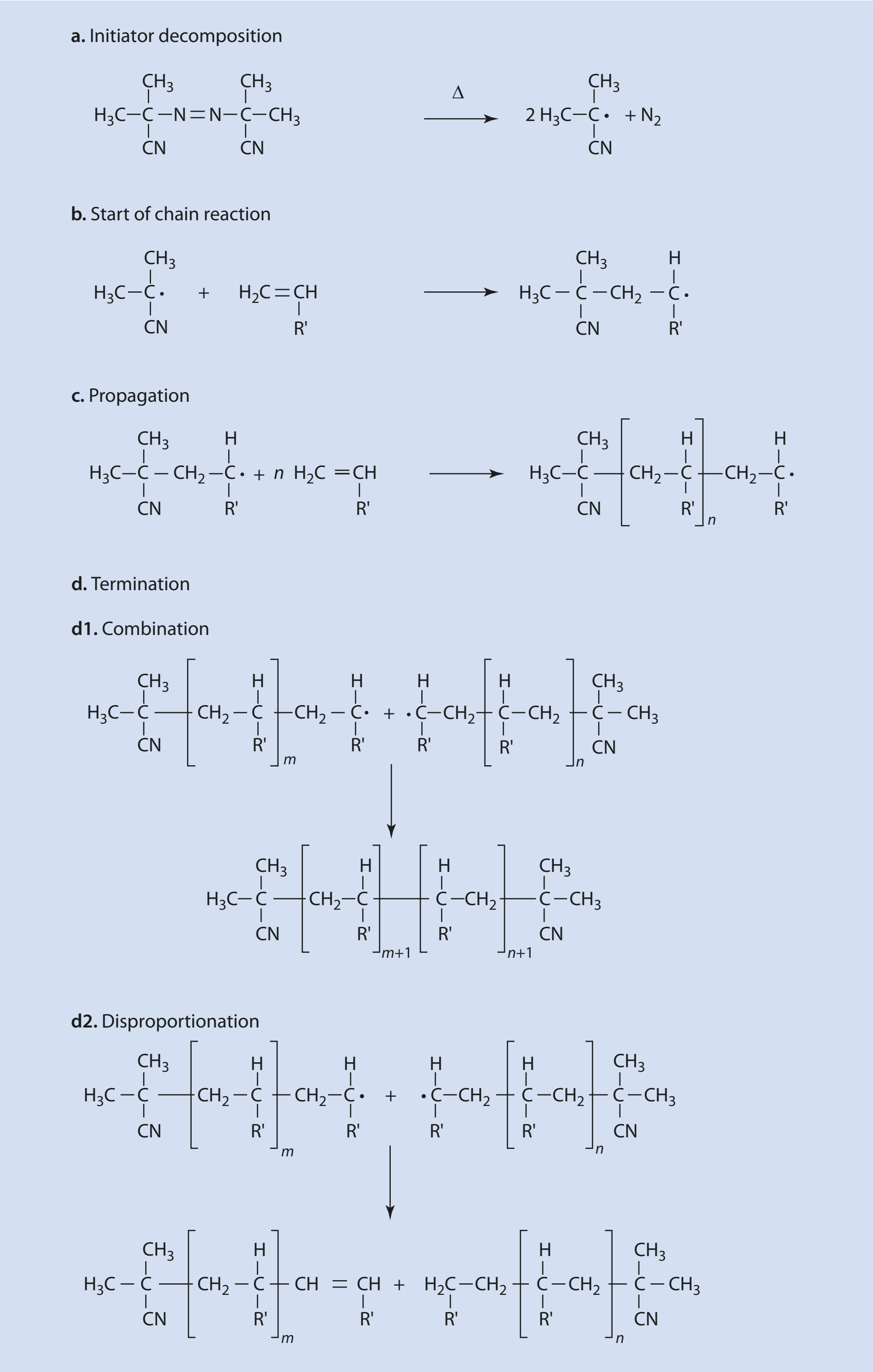

Fig. 9.13 Individual steps of the polymerization of a vinyl monomer $CH_2{=}CHR'$ initiated by AIBN (the elements of the last row correspond to RM_n^H and $RM_m^=$ in Fig. 9.12)

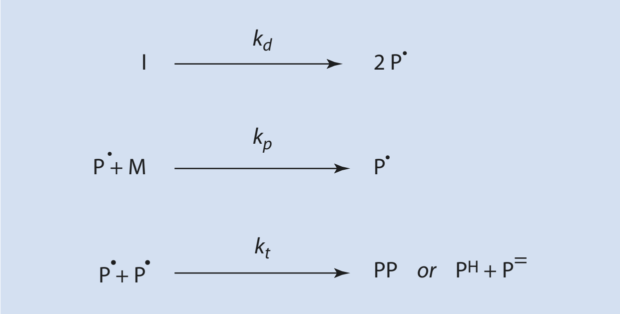

Fig. 9.14 Formal scheme for a radical polymerization with $R^\bullet \equiv P^\bullet$

Substituting (9.3) into (9.4) yields

$$-\frac{d[M]}{dt} = v_{br} = k_p \sqrt{\frac{2k_d[I]}{k_t}} \cdot [M] \tag{9.5}$$

This basic equation for radical polymerization describes the kinetics of polymerization for most vinyl monomers very well. Thus, the rate of polymerization can be controlled via the monomer and initiator concentrations as well as by the temperature (because of the temperature dependence of the rate constant; see ▶ Sect. 9.2.6).

9.2.3 Reactivities of $R^\bullet$ and $P^\bullet$ are Different

When the simplifying assumptions do not apply and $R^\bullet \neq P^\bullet$, but $RM^\bullet \equiv RM_2^\bullet \equiv RM_n^\bullet \equiv P^\bullet$, then ▫ Fig. 9.14 turns into ▫ Fig. 9.15.

The Bodenstein approach for the primary radical $R^\bullet$ is given by

$$\frac{d\left[R^\bullet\right]}{dt} = 2k_d[I] - k_i\left[R^\bullet\right][M] = 0 \tag{9.6}$$

This can be easily rearranged to

$$\left[R^\bullet\right] = \frac{2k_d[I]}{k_i[M]} \tag{9.7}$$

Again, it is assumed to a reasonable approximation that the monomer is consumed only by the growing chains and

$$-\frac{d[M]}{dt} = k_p[M]\left[P^\bullet\right] \tag{9.8}$$

For the determination of the unknown concentration $[P^\bullet]$, another Bodenstein approach is that

$$\frac{d\left[P^\bullet\right]}{dt} = k_i\left[R^\bullet\right][M] - k_t\left[P^\bullet\right]^2 = 0 \tag{9.9}$$

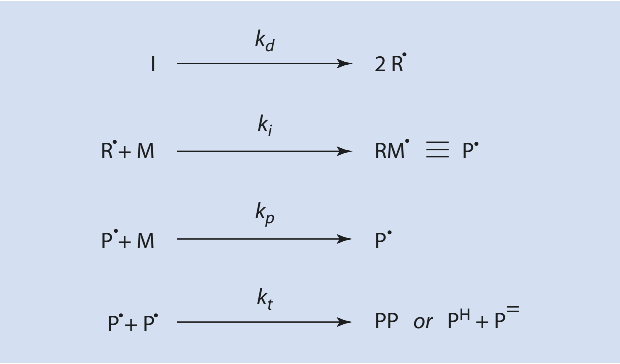

Fig. 9.15 Formal scheme of a radical polymerization with $R^{\bullet} \neq P^{\bullet}$ (the possibility of a reaction between $R^{\bullet}$ and $P^{\bullet}$ into $R{-}P$ is not considered)

So the molar concentration $[P^{\bullet}]$ is given by

$$\left[P^{\bullet}\right] = \sqrt{\frac{k_i\left[R^{\bullet}\right][M]}{k_t}} \tag{9.10}$$

If $[R^{\bullet}]$ is replaced in (9.10) by (9.7):

$$\left[P^{\bullet}\right] = \sqrt{\frac{k_i \cdot 2k_d[I][M]}{k_t \cdot k_i[M]}} = \sqrt{\frac{2k_d[I]}{k_t}} \tag{9.11}$$

and for the rate of polymerization after substituting (9.11) into (9.8):

$$-\frac{d[M]}{dt} = k_p\sqrt{\frac{2k_d[I]}{k_t}} \cdot [M] \tag{9.5}$$

In other words, differing reactivities of $R^{\bullet}$ and $P^{\bullet}$ cannot be determined kinetically.

9.2.4 Cage Effect

If one considers that the primary radicals from the decomposition of the initiator $R^{\bullet}$ are trapped by solvent molecules in a cage, it becomes clear why not all initially formed radicals initiate chain growth. Thus, the radicals first have to diffuse out of the cage (k_{diff}) in order to react with a monomer. However, they can also react with another primary radical if still in the cage (Fig. 9.16).

If, in addition, we assume that only the free radicals $R^{\bullet}_{free}$ are able to add to a monomer, the mechanism shown in Fig. 9.17 can be developed.

In this case, there are three unknown radical concentrations, $[R^{\bullet}_{cage}]$, $[R^{\bullet}_{free}]$, and $[P^{\bullet}]$. Consequently, the Bodenstein approach needs to be applied for each of these concentrations.

Cage Radicals $R^{\bullet}_{cage}$

Assuming the reaction process is as given in Fig. 9.17, the concentration of the radicals in the solvent cage $[R^{\bullet}_{cage}]$ changes with time. The radicals $R^{\bullet}_{cage}$ form in pairs in the cage, which means that, when a radical is present, the second exists inevitably in close proximity and does not need to diffuse into such a position. Thus, the recombination of radicals in

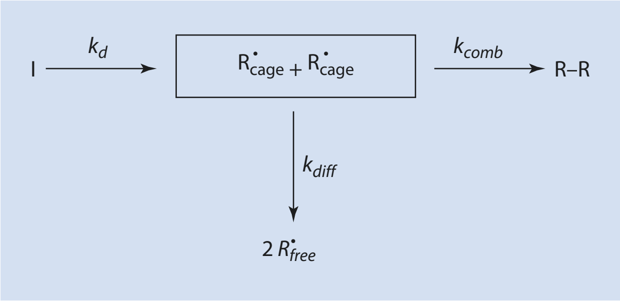

Fig. 9.16 Loss of radicals caused by the cage effect. *Frame* symbol for the cage

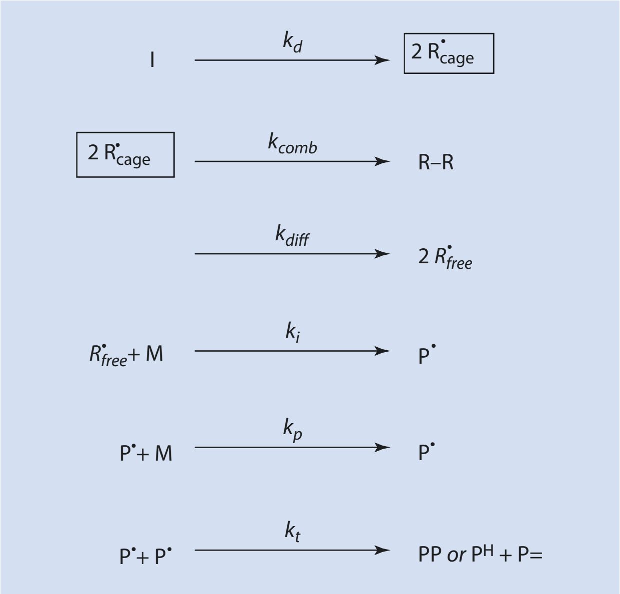

Fig. 9.17 Formal scheme for a radical polymerization including the cage effect

the solvent cage is of first order in radical concentration (Fig. 9.16) (9.12). In the equation the superscript 1 is included for emphasis:

$$\frac{d\left[R^{\bullet}_{cage}\right]}{dt} = 2k_d\left[I\right] - k_{comb}\left[R^{\bullet}_{cage}\right]^1 - k_{diff}\left[R^{\bullet}_{cage}\right] = 0 \tag{9.12}$$

Thus, it follows that

$$\left[R^{\bullet}_{cage}\right] = \frac{2k_d\left[I\right]}{k_{diff} + k_{comb}} \tag{9.13}$$

Free Radicals $R^{\bullet}_{free}$: Formation and Reaction

For the change of $[R^{\bullet}_{free}]$ with time, it follows from Fig. 9.17 that

$$\frac{d\left[R^{\bullet}_{free}\right]}{dt} = k_{diff}\left[R^{\bullet}_{cage}\right] - k_i\left[R^{\bullet}_{free}\right]\left[M\right] = 0 \tag{9.14}$$

Simple conversion yields

$$\left[R^\bullet_{free}\right] = \frac{k_{diff}\left[R^\bullet_{cage}\right]}{k_i\left[M\right]} \tag{9.15}$$

With (9.13) it follows that

$$\left[R^\bullet_{free}\right] = \frac{k_{diff}}{k_{diff}+k_{comb}} \cdot \frac{2k_d\left[I\right]}{k_i\left[M\right]} \tag{9.16}$$

Polymer Radicals $P^\bullet$: Fate and Definition of the Net Reaction Rate

The polymer radicals $P^\bullet$ are formed through the reaction of $R^\bullet_{free}$ with monomers and are destroyed by chain termination reactions. Hence, the following applies for the change of the radical concentration $[P^\bullet]$ with time:

$$\frac{d\left[P^\bullet\right]}{dt} = k_i\left[R\right]\left[M\right] - k_t\left[P^\bullet\right]^2 = 0 \tag{9.17}$$

and

$$\left[P^\bullet\right] = \sqrt{\frac{k_s\left[R^\bullet_{free}\right]\left[M\right]}{k_t}} \tag{9.18}$$

Using the definition of $[R^\bullet_{free}]$ from (9.16) gives

$$\left[P^\bullet\right] = \sqrt{\frac{k_i\left[M\right]}{k_t} \cdot \frac{k_{diff}}{k_{diff}+k_{comb}} \cdot \frac{2k_d\left[I\right]}{k_i\left[M\right]}} \tag{9.19}$$

Equation (9.19) can be simplified by introducing the efficiency f of the overall process producing polymerization active radicals:

$$f = \frac{k_{diff}}{k_{diff}+k_{comb}} \tag{9.20}$$

$$\left[P^\bullet\right] = \sqrt{\frac{f \cdot 2k_d\left[I\right]}{k_t}} \tag{9.21}$$

The efficiency of the initiator f can take values between 0 and 1. For AIBN, values of $f = 0.7$ are usually found, which means that that portion of the primary radicals already destroyed in the cage should not be neglected.

Combining (9.21) and (9.8) an expression for the overall rate of polymerization can be obtained:

$$-\frac{d\left[M\right]}{dt} = k_p \cdot \sqrt{\frac{f \cdot 2k_d\left[I\right]}{k_t}} \cdot \left[M\right] \tag{9.22}$$

and thus

$$v_{br} = -\frac{d[M]}{dt} \propto [M]^1 \tag{9.23}$$

$$v_{br} = -\frac{d[M]}{dt} \propto \sqrt{[I]} \tag{9.24}$$

The rate of polymerization v_{br} increases linearly with the monomer concentration (the highest possible $[M]$ is the molar concentration of the pure monomer) and with the square root of the initiator concentration.

9.2.5 Experimental Determination of the Rate of Polymerization

To determine the rate constants in (9.22), polymerizations are studied at low conversions ($[M]$ and $[I]$ are essentially constant so that $[M] \approx [M]_0$ and $[I] \approx [I]_0$) by first varying $[M]_0$ while keeping $[I]_0$ constant and then varying $[I]_0$ while keeping $[M]_0$ constant (◘ Fig. 9.18).

The rate of polymerization can be determined gravimetrically from the resulting polymer, because this is equal to the quantity of the monomer consumed. For this purpose, the polymer yield at a given time needs to be isolated. This is best achieved by adding the polymer solution drop by drop into a suitable precipitant agent.[2] The precipitated polymer is filtered, dried, and weighed and the weight converted into the amount of monomer polymerized. Gravimetry is a universal method for measuring conversion but it is time-consuming because only a single experimental data point is obtained for each experiment.

Alternatively, especially low conversions can be followed in a dilatometer (◘ Fig. 9.19). A dilatometer is a vessel of a known volume to which a capillary is attached. During polymerization, the total volume generally decreases because polymers usually have a higher density than monomers.[3] The volume reduction ΔV with time can be followed very exactly in the capillary. If the densities of the monomer and polymer being studied are known, the overall rate of polymerization can very easily be determined from the ΔV over time (for a sufficiently large range of monomer concentration $[M]$).

In specific cases, not only IR-, UV-, and ^{1}H-NMR-spectroscopy but also gas chromatography and other analytical methods can be used to follow the decrease in monomer concentration or the increase in polymer concentration.

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[2] For polystyrene methanol is a suitable non-solvent. Extensive information about solvents and non-solvents can be found, for example, in Brandrup and Immergut (1989).

[3] During the polymerization, the Van der Waals distances between monomer molecules are replaced by covalent bonds which are shorter so that the polymer usually has a greater density than the monomers.

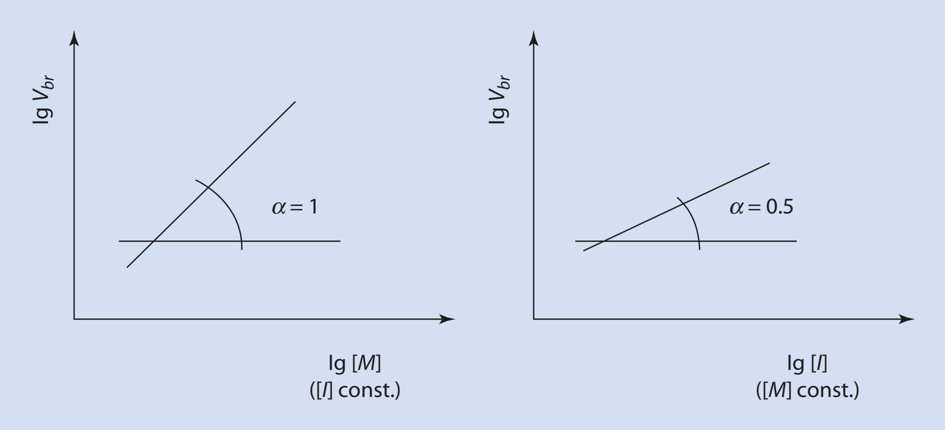
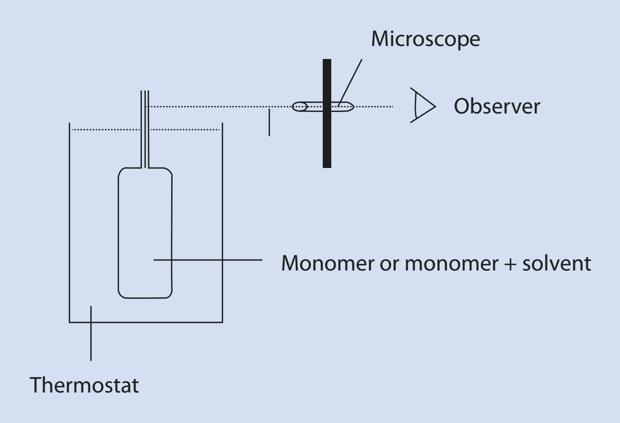


Fig. 9.18 Determination of the reaction order with respect to [*M*] and [*I*]

Fig. 9.19 Measuring the rate of polymerization using a dilatometer



9.2.6 Temperature Dependence of the Overall Rate of Polymerization

For the overall rate of polymerization (as already derived above):

$$v_{br} = k_p \cdot \underbrace{\sqrt{\frac{f \cdot 2k_d}{k_t}}}_{T-dependent} \cdot \underbrace{[M] \cdot \sqrt{[I]}}_{T-independent} \tag{9.22}$$

According to Arrhenius, if the efficiency *f* is assumed to be temperature independent:

$$\frac{d \ln v_{br}}{dT} = \frac{d \ln k_p}{dT} + \frac{1}{2} \cdot \frac{d \ln k_d}{dT} - \frac{1}{2} \cdot \frac{d \ln k_t}{dT} \tag{9.25}$$

or

$$\frac{E_{A,v_{br}}}{RT^2} = \frac{E_{A,p}}{RT^2} + \frac{1}{2} \cdot \frac{E_{A,d}}{RT^2} - \frac{1}{2} \cdot \frac{E_{A,t}}{RT^2} \tag{9.26}$$

Using the activation energies of the elementary steps:
$E_{A,p} \approx 20$ kJ/mol (applies for many monomers)
$E_{A,d} \approx 120$ kJ/mol (applies for AIBN)
$E_{A,comb.} \approx 0$ kJ/mol (applies for termination by combination)
$E_{A,disp.} \approx 10$ kJ/mol (applies for termination by disproportion)

It follows for termination by combination that

$$E_{A,v_{br}} \approx 20\,\mathrm{kJ/mol} + \frac{1}{2} \cdot 120\,\mathrm{kJ/mol} - 0\,\mathrm{kJ/mol} = 80\,\mathrm{kJ/mol} \tag{9.27}$$

If the rate constants for two temperatures, for example 80 °C and 90 °C, are calculated using this activation energy and the Arrhenius equation, it can be seen that the rate of polymerization almost doubles for this temperature increase of 10 °C. Thus, in addition to the concentration of monomer and initiator, temperature is a third crucial variable for the rate of polymerization.

9.3 Degree of Polymerization

The degree of polymerization P_n specifies how many monomer moieties make up one polymer chain (▶ Chap. 3, (3.11)):

$$P_n = \frac{M_n}{M_M} \tag{3.11}$$

M_n	number-average molar mass
M_M	molar mass of the monomer (equal to M_{RU}: molar mass of a repeating unit)

Similar to the mean values of molar mass M_n and M_w, it is also appropriate to distinguish between the different mean values, e.g., P_n and P_w, for the degree of polymerization.

9.3.1 Kinetic Chain Length and Degree of Polymerization

The kinetic chain length ν is a measure of the average number of monomer molecules which polymerize per initiating radical before chain growth is terminated. Thus, ν is determined by the ratio of the probabilities of chain growth p_p and the probability of the chain termination p_t or by the ratio of the rate of growth v_p to the rate of termination v_t:

$$\nu = \frac{p_p}{p_t} = \frac{v_p}{v_t} = \frac{k_p[M]\left[P^\bullet\right]}{k_t\left[P^\bullet\right]^2} = \frac{k_p[M]}{k_t\left[P^\bullet\right]} \tag{9.28}$$

From (9.3)

$$\left[P^\bullet\right] = \sqrt{\frac{2k_d\,[I]}{k_t}} \tag{9.3}$$

and it follows that

$$\nu = \frac{k_p\,[M]}{\sqrt{k_t \cdot 2k_d\,[I]}} \tag{9.29}$$

By rearranging

$$v_{br} = -\frac{d[M]}{dt} = k_p\,[M]\left[P^\bullet\right] \tag{9.8}$$

to obtain an expression for $[P^\bullet]$ and substitution into (9.28), the kinetic chain length as a function of the overall rate of polymerization can be obtained:

$$\nu = \frac{k_p^2 \cdot [M]^2}{k_t \cdot v_{br}} \tag{9.30}$$

With (9.30), it is now possible to determine the ratio $k_p{}^2/k_t$ as both the kinetic chain length ν and the overall rate of polymerization v_{br} can be determined experimentally with considerable accuracy.

There is a close correlation between the kinetic chain length and the degree of polymerization. Although the nature of the termination reaction (combination or disproportionation) is not considered when discussing the kinetic chain length, it is important for the degree of polymerization. For termination solely via disproportionation, the degree of polymerization P_n equals the kinetic chain length. On the other hand, a termination via combination joins two chains together so that the degree of polymerization is twice that for termination via disproportionation.

Termination by Disproportionation

$$P_n = \nu \tag{9.31}$$

and

$$P_n = \frac{k_p\,[M]}{\sqrt{k_t \cdot 2k_d\,[I]}} \tag{9.32}$$

Termination by Combination

$$P_n = 2\nu \tag{9.33}$$

or

$$P_n = 2 \cdot \frac{k_p\,[M]}{\sqrt{k_t \cdot 2k_d\,[I]}} \tag{9.34}$$

▣ **Table 9.2** Comparison of measured degree of polymerization P_n (osmotically determined) with the calculated kinetic chain length for the bulk polymerization of styrene at 50 °C (Henricí-Olivé and Olive 1969)

[AIBN] · 10^2 (mol/L)	$v_{Br} \cdot 10^5$ (mol/(L s))	ν	2ν	P_n
0.061	0.66	3600	7200	6800
0.122	0.96	2650	5300	5500
0.305	1.52	1670	3340	3570
1.83	3.57	655	1310	1380

The comparison of the measured degree of polymerization P_n with the calculated kinetic chain length ν for styrene leads to the conclusion that termination of polymerization occurs via combination (▣ Table 9.2).

From the definition of the degree of polymerization P_n (9.32) and (9.34) it follows that to increase the degree of polymerization, either the monomer concentration must be increased or the initiator concentration decreased. The greatest possible monomer concentration is the concentration of the pure substance. The effect of the temperature is more complex and is discussed in more detail in Sect. 9.3.2.

9.3.2 Temperature Dependence of the Degree of Polymerization

The defining equation for the degree of polymerization P_n (9.32) can be separated into temperature dependent and temperature independent terms:

$$P_n = \underbrace{\frac{k_p}{\sqrt{2k_t \cdot k_\mathrm{d}}}}_{T-dependent} \cdot \underbrace{\frac{[M]}{\sqrt{[I]}}}_{T-independent} \tag{9.32}$$

If one disregards the volume change of the system caused by a change in temperature, then the monomer and initiator concentrations are independent of temperature. For the effect of temperature on the degree of polymerization P_n, Arrhenius equations for the rate constants k_p, k_t, and k_d give

$$\frac{d \ln P_n}{dT} = \frac{d \ln k_p}{dT} - \frac{1}{2} \cdot \frac{d \ln k_t}{dT} - \frac{1}{2} \cdot \frac{d \ln k_d}{dT} \tag{9.35}$$

$$\frac{E_{A,P_n}}{RT^2} = \frac{E_{A,p}}{RT^2} - \frac{1}{2} \cdot \frac{E_{A,t}}{RT^2} - \frac{1}{2} \cdot \frac{E_{A,d}}{RT^2} \tag{9.36}$$

With the individual activation energies $E_{A,p}$, $E_{A,t}$ and $E_{A,d}$, which were already used for the calculation of $E_{A,v_{br}}$ (9.27), a value of −40 kJ/mol ((9.37) and (9.38)) can be determined for E_{A,P_n} (termination by combination):

$$E_{A,P_n} \approx 20\,\mathrm{kJ/mol} - \frac{1}{2} \cdot 0\,\mathrm{kJ/mol} - \frac{1}{2} \cdot 120\,\mathrm{kJ/mol} \tag{9.37}$$

$$E_{A,P_n} \approx -40\,\mathrm{kJ/mol} \tag{9.38}$$

From this it follows that the degree of polymerization decreases with increasing temperature (negative E_{A,P_n}). On simple reflection we see that qualitatively identical results can be inferred because higher temperatures lead to a faster decomposition of the initiator and therefore more radicals are formed per unit time. As a result, given a constant monomer supply, the chains formed are shorter.

Thus, temperature is a third critical variable, in addition to the monomer and initiator concentrations, for the average degree of polymerization. In addition, it is possible to control the degree of polymerization by adding transfer agent to the reaction mixture.

9.3.3 Regulation of Degree of Polymerization by Transfer

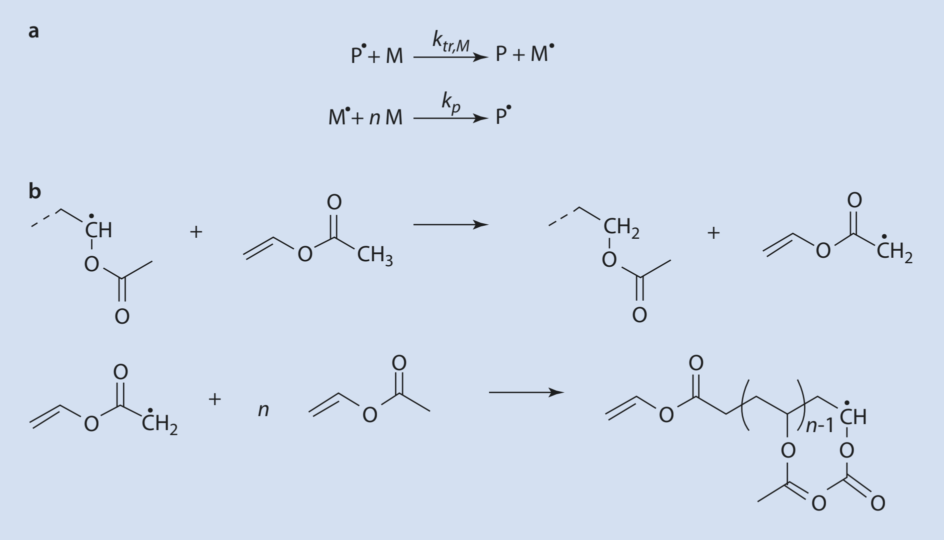
Reagents which can assume the radical nature of a growing chain and then start a new chain growth are referred to as *regulators*, *chain transfer agents*, or simply *transfer agents*. Monomers (◘ Fig. 9.20 and ◘ Table 9.3), polymers (◘ Fig. 9.23), and solvents (◘ Figs. 9.21 and 9.22), and also intentionally added substances such as mercaptans and aldehydes, can serve as chain transfer agents (◘ Table 9.4).

Transfer to Monomer

$M^{\bullet}$ is able to start a new polymer chain by adding an additional monomer unit. A characteristic of transfer agents is that they terminate an individual chain but they do not affect v_{br} because a new polymer chain starts from the small radical molecule formed.

The general approach for determining the degree of polymerization from the rate of the transfer reaction is

$$P_n = \frac{v_p}{v_t + \sum v_{tr}} \tag{9.39}$$



◘ **Fig. 9.20** Chain transfer to monomer: (**a**) general scheme and (**b**) vinyl acetate as an example

Table 9.3 Transfer coefficients C_M for selected monomers (Brandrup and Immergut 1989)

Monomer	$C_M \cdot 10^4$
Acrylamide	0.5
Acrylonitrile	0.26
Ethylene	0.4–4.2
Styrene	0.3–0.6
Vinyl acetate	1.75–2.8
Vinyl chloride	10.8–16

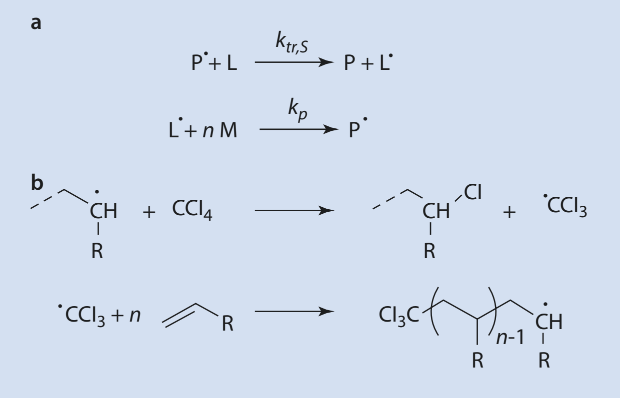


Fig. 9.21 Chain transfer to solvent: (**a**) general scheme and (**b**) CCl_4 as an example

where v_{tr} represents the rate of the transfer reaction and v_p and v_t represent the growth and termination rates, already introduced above. If the only transfer is transfer to monomer ($v_{tr,M}$ = rate of transfer to monomer) then

$$P_n = \frac{v_p}{v_t + v_{tr,M}} \tag{9.40}$$

By substitution for the different process rates as described by the formal kinetics of the processes described in Figs. 9.14 and 9.15, and with the rate of the transfer to monomer which results from Fig. 9.20, one obtains

$$P_n = \frac{k_p [M][P^\bullet]}{k_t [P^\bullet]^2 + k_{tr,M} [M][P^\bullet]} \tag{9.41}$$

This can be transformed into the more useful (9.42) without a sum in the denominator:

$$\frac{1}{P_n} = \frac{k_{tr,M}}{k_p} + \frac{k_t [P^\bullet]}{k_p [M]} = \frac{1}{P_{n,0}} \tag{9.42}$$

where $P_{n,0}$ is the degree of polymerization when no transfer or other chain length limiting reactions apart from transfer to monomer occur.

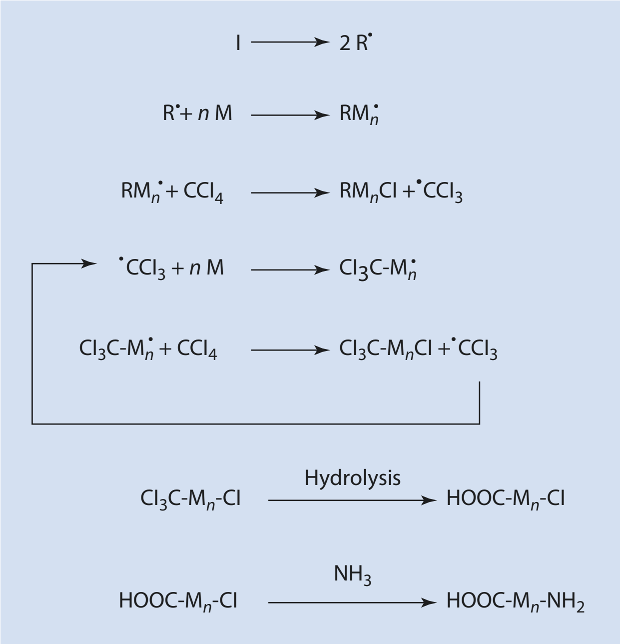


Fig. 9.22 Reaction scheme to form terminally functionalized polymers by chain transfer to CCl_4 solvent and subsequent hydrolysis followed by reaction with ammonia

Table 9.4 Transfer constants C_S for selected solvents and regulators for the polymerization of styrene at 60 °C (Brandrup and Immergut 1989)

Solvent	$C_S \cdot 10^4$
Benzene	0.023
Toluene	0.125
Isopropyl benzene	0.82
Chloroform	3.4
Carbon tetrachloride	110
Carbon tetrabromine	22 000
n-Butyl mercaptan	210 000

Substitution of (9.3) for $[P^\bullet]$ gives

$$\frac{1}{P_{n,0}} = \frac{k_{tr,M}}{k_p} + \frac{\sqrt{2k_d \cdot k_t}}{k_p} \cdot \frac{\sqrt{[I]}}{[M]} \tag{9.43}$$

Thus a plot of $1/P_n$ against $\sqrt{[I]}/[M]$ allows the transfer coefficient $C_M = k_{tr,M}/k_p$ to be determined from the intercept.

The transfer to monomer is intrinsic, inevitable, and is often called *direct chain transfer*. Compared to acrylamide, it plays a significant role for monomers such as vinyl acetate and vinyl chloride (Table 9.3).

Transfer to Solvent and Regulator

The same approach can be used as above for transfer to monomer (◘ Fig. 9.20). The reaction of polymer radicals with CCl_4 serves as a good example (◘ Fig. 9.21).

For a system in which both transfer to monomer and transfer to solvent take place, (9.39) can be written as

$$P_n = \frac{v_p}{v_t + v_{tr,M} + v_{tr,S}} \tag{9.44}$$

The new additive term, $v_{tr,S}$, the rate of transfer to solvent appears in the denominator. The reciprocal of (9.44) yields (9.45) or (9.46):

$$\frac{1}{P_n} = \frac{k_t\left[P^\bullet\right]^2 + k_{tr,M}\left[P^\bullet\right][M] + k_{tr,S}\left[P^\bullet\right][S]}{k_p\left[P^\bullet\right][M]} \tag{9.45}$$

$$\frac{1}{P_n} = \frac{1}{P_{n,0}} + C_S \cdot \frac{[S]}{[M]} \tag{9.46}$$

The rate constant ratio $k_{tr,S}/k_p$ is referred to as transfer coefficient C_S:

$$C_S = \frac{k_{tr,S}}{k_p} \tag{9.47}$$

A graph of $1/P_n = f([S]/[M])$ has the coefficient C_S as the gradient. In Table 9.4, some transfer coefficients for several solvents and the polymerization of styrene at 60 °C are compiled.

More important than the absolute numbers in this table, which not only depend on the monomer but also on the temperature, is the trend.

Mercaptans are thus highly effective regulators. Even very small amounts of mercaptan suffice to reduce drastically the molar mass of the resulting polymers. The kinetic analysis and reaction scheme are analogous to that for transfer to solvent (◘ Fig. 9.21).

An interesting application of transfer to solvent is the polymerization of styrene into CCl_4 which yields oligomers with a CCl_3 head group and a Cl terminal group. From these oligomers *α,ω*-amino acids can be synthesized (◘ Fig. 9.22).

Transfer to Polymer

Transfer to polymer leads to a branching of the main polymer chain and thus, in contrast to those transfer reactions discussed already, to an increase in molar mass (◘ Fig. 9.23).

9.4 Molar Mass Distribution

The macromolecules formed by chain growth have different chain lengths resulting from the kinetics of the processes which formed them (statistical sequence of start, growth, termination, and transfer). Thus, they are a mixture of molecules with a distribution of molar mass. This distribution has an important influence on their physical and material characteristics.

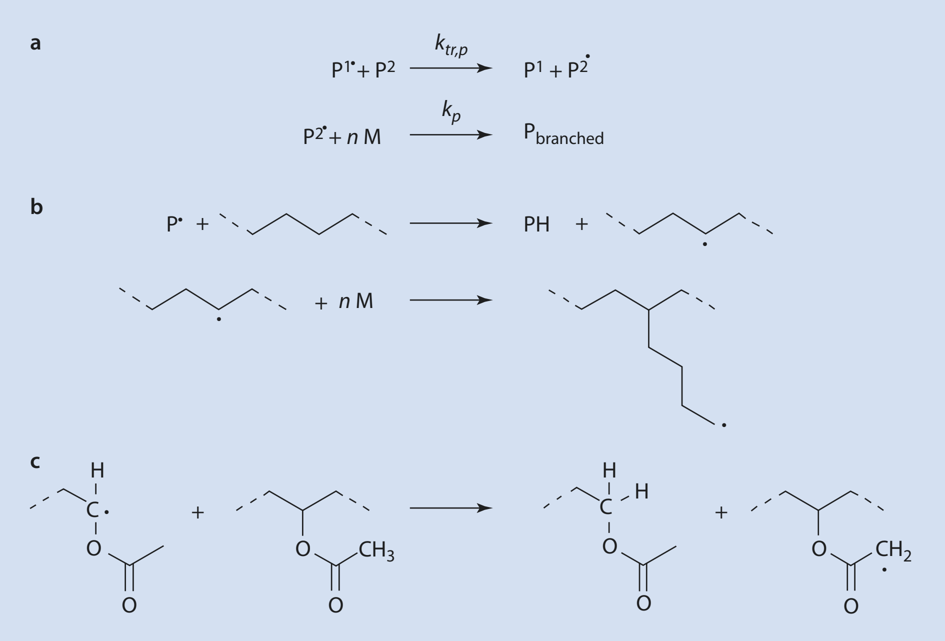


Fig. 9.23 Chain transfer to polymer: (**a**) general scheme, (**b**) polyethylene, and (**c**) polyvinyl acetate as examples

9.4.1 Molar Mass Distribution Resulting from Termination by Disproportionation

The numerical frequency n_P of those molecules that show a specific degree of polymerization P is proportional to the statistical probability Π_P that these molecules are formed:

$$n_P = const \cdot \Pi_P \tag{9.48}$$

n_P	Numerical frequency of the molecules with degree of polymerization P
Π_P	Statistical probability that the molecules are formed

Molecules with the degree of polymerization P result if propagation can continue unimpaired P times. Reactions that hinder propagation are transfer and termination. Thus, the probability α for a single propagation step is as follows:

$$\alpha = \frac{v_p}{v_p + v_t + \sum v_{tr}} \tag{9.49}$$

α	Probability for a single growth step
v_p	Rate of propagation
v_t	Rate of termination
v_{tr}	Rate of transfer

The transfer is not considered in the following so (9.49) can be simplified to

$$\alpha = \frac{v_p}{v_p + v_t} \tag{9.50}$$

With the definition for the kinetic chain length ν (9.51) and (9.28)

$$\nu = \frac{v_p}{v_t} \tag{9.51}$$

it follows that

$$\alpha = \frac{1}{1 + \frac{1}{\nu}} \tag{9.52}$$

Because $\nu \gg 1$ and $1/\nu \ll 1$ and making use of the MacLaurin's sequence:

$$\text{for } x \ll 1 : \frac{1}{1+x} = 1 - x + x^2 - x^3 \ldots \approx 1 - x \tag{9.53}$$

Thus:

$$\alpha = 1 - \frac{1}{\nu} \tag{9.54}$$

For the probability Π_P that the propagation continues consecutively P times so that molecules with the degree of polymerization P are formed, the following applies:

$$\Pi_P = \alpha_1 \cdot \alpha_2 \cdot \alpha_3 \ldots \cdot \alpha_P = \alpha^P \tag{9.55}$$

The combination of (9.48) and (9.55) yields (9.56):

$$n_P = const \cdot \alpha^P \tag{9.56}$$

From this it can be derived that

$$m_P = const \cdot M_P \cdot \alpha^P = const \cdot M_M \cdot P \cdot \alpha^P = A \cdot P \cdot \alpha^P \tag{9.57}$$

m_P	Frequency of the molecules in terms of mass (mass fraction) with the degree of polymerization P
M_P	Molar mass of the molecules with the degree of polymerization P
M_M	Molar mass of the monomers

From (9.57):

$$A = M_M \cdot const \tag{9.58}$$

For the general case:

$$\int_0^\infty m_P dP = 1 \tag{9.59}$$

so that

$$A \cdot \int_0^\infty P \cdot \alpha^P dP = 1 \tag{9.60}$$

or

$$A = \frac{1}{\int_0^\infty P \cdot \alpha^P dP} \tag{9.61}$$

The general solution of the integral is

$$\int_0^\infty P^n \cdot \alpha^P dP = \frac{n!}{(-\ln \alpha)^{n+1}} \tag{9.62}$$

Substitution of (9.62) into (9.61) (with $n = 1$) gives

$$A = \ln^2 \alpha \tag{9.63}$$

and for m_P (9.57):

$$m_P = \ln^2 \alpha \cdot P \cdot \alpha^P \tag{9.64}$$

This mass distribution function for the product of a polymerization where termination is via disproportionation gives the weight fraction of molecules with a degree of polymerization P (Schulz 1939; Flory 1953) (■ Fig. 9.24).

9.4.2 Molar Mass Distribution with Termination by Combination

The polymer molecules resulting from a termination via combination termination are composed of two polymer radicals. The degree of polymerization P can be obtained by the combination $1+(P-1)=P$; $2+(P-2)=P$ … $(P-2)+2=P$ and so on. Consequently, the number of combinations leading to the degree of polymerization P is $P/2$. The frequency of the xth combination $n_{P,x}$, is proportional to the product of the frequencies of the single chain lengths x and $P-x$:

$$n_{P,x} = const' \cdot \alpha^x \cdot \alpha^{P-x} = const' \cdot \alpha^P \tag{9.65}$$

$n_{P,x}$	Numerical frequency of the xth combination that leads to the degree of polymerization P
α^x	Probability of the formation of molecules with the degree of polymerization x
α^{P-x}	Probability of the formation of molecules with the degree of polymerization $(P-x)$

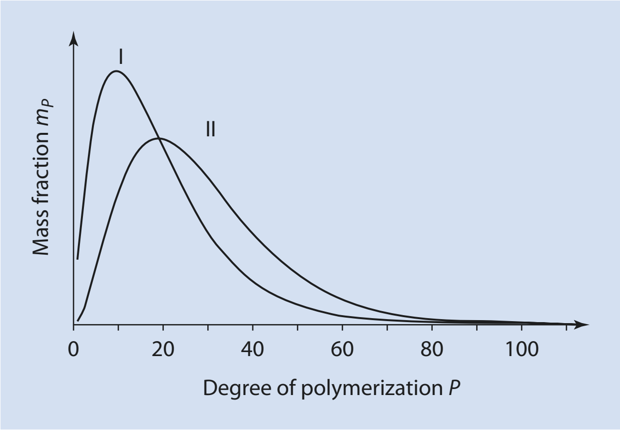


Fig. 9.24 Mass distribution function for $\nu = 10$, calculated from (9.63) and (9.69).
I Termination by Disproportionation,
II Termination by Combination

The numerical frequency n_P of the degree of polymerization is the sum of the individual frequencies $n_{P,x}$:

$$n_P = \sum_{x=1}^{x=\frac{P}{2}} n_{P,x} = const' \cdot \frac{P}{2} \cdot \alpha^P \tag{9.66}$$

In analogy to (9.57):

$$m_P = M_P \cdot const' \cdot \frac{P}{2} \cdot \alpha^P = M_M \cdot P \cdot const' \cdot \frac{P}{2} \cdot \alpha^P = A' \cdot P^2 \cdot \alpha^P \tag{9.67}$$

From (9.59) and (9.67) one obtains

$$\int_0^\infty m_P dP = 1 = A' \cdot \int_0^\infty P^2 \cdot \alpha^P dP \tag{9.68}$$

and with (9.62)

$$A' = -\frac{\ln^3 \alpha}{2} \tag{9.69}$$

So that with (9.67):

$$m_P = -\frac{\ln^3 \alpha}{2} \cdot P^2 \cdot \alpha^P \tag{9.70}$$

In Fig. 9.24, the values of m_P for termination by disproportionation (I) and combination (II) with an assumed kinetic chain length of $\nu = 10$ are plotted as a function of the degree of polymerization using (9.64), (9.70), and (9.54).

9.4.3 Average Degree of Polymerization and Non-Uniformity

The number-average P_n (9.71) and weight-average P_w (9.72) degrees of polymerization can be derived from the mass distribution functions and the equations for the number and weight-averages of the degrees of polymerization:

$$P_n = \frac{1}{\int_0^\infty \frac{m_P}{P}\, dP} \tag{9.71}$$

P_n Number-average of degree of polymerization

$$P_w = \int_0^\infty m_P \cdot P \cdot dP \tag{9.72}$$

P_w Weight-average of degree of polymerization

Derivation of the (9.71) and (9.72):

The number-average molar mass is defined as follows according to ▶ Chap. 3:

$$M_n = \frac{\sum n_p \cdot M_p}{\sum n_P}$$

From $M_P = M_M \cdot P$ and $m_P = n_P \cdot P$:

$$M_n = \frac{\sum \frac{m_p}{P} \cdot M_M \cdot P}{\sum \frac{m_P}{P}}$$

For the number-average degree of polymerization P_n it follows from $M_n = P_n \cdot M_M$ that

$$\frac{M_n}{M_M} = P_n = \frac{\sum m_P}{\sum \frac{m_P}{P}}$$

In integral notation one obtains

$$P_n = \frac{\int_0^\infty m_P dP}{\int_0^\infty \frac{m_P}{P} dP}$$

Because, by definition, $\int_0^\infty m_P dP = 1$ (see (9.59)), this results in (9.71).

Similarly, starting from the equation for the weight-average molar mass M_w:

$$M_w = \frac{\sum n_P \cdot M_P^2}{\sum n_P \cdot M_P}$$

One obtains (9.72) for the weight-average degree of polymerization P_w (9.72).

Termination by Disproportionation

Substituting (9.64) into (9.71) yields the number-average of degree of polymerization P_n:

$$P_n = \frac{1}{\ln^2 \alpha \int_0^\infty \alpha^P dP} \tag{9.73}$$

Using (9.62) it follows that

$$P_n = -\frac{1}{\ln \alpha} \tag{9.74}$$

For $\alpha \leq 1$, i.e., for large molar masses:

$$-\ln \alpha = 1 - \alpha \tag{9.75}$$

With (9.54) and (9.74) and (9.75) one obtains

$$P_n = \nu \tag{9.76}$$

From (9.72) and (9.64):

$$P_w = \ln^2 \alpha \int_0^\infty P^2 \cdot \alpha^P dP \tag{9.77}$$

With (9.62) it now follows that

$$P_w = -\frac{2}{\ln \alpha} \tag{9.78}$$

and substitution of (9.75) and (9.54) into (9.78) yields

$$P_w = 2\nu \tag{9.79}$$

With these equations for P_n (9.76) and P_w (9.79) and the definition of the non-uniformity U (9.80), one obtains (9.81):

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

$$U = \frac{2\nu}{\nu} - 1 = 1 \tag{9.81}$$

Thus, if polymerization is terminated by disproportionation, the non-uniformity $U = 1$.

Termination by Combination

A similar treatment can be applied for polymerizations terminated by combination. Thus, substitution of (9.70) into (9.71) for n yields

$$P_n = \frac{1}{\int \left(-\frac{\ln^3 \alpha}{2} \cdot \frac{P^2}{P} \alpha^P dP \right)} \tag{9.82}$$

From (9.62), (9.75), and (9.54) it follows that

$$P_n = -\frac{2}{\ln \alpha} = 2\nu \tag{9.83}$$

P_w can then be derived from (9.70) and (9.72):

$$P_w = \int \left(-\frac{\ln^3 \alpha}{2} P^3 \alpha^P dP \right) \tag{9.84}$$

Finally, using (9.62), (9.75), and (9.54) yields for P_w (9.85) and for U (9.86):

$$P_w = -\frac{3}{\ln \alpha} = 3\nu \tag{9.85}$$

$$U = \frac{3\nu}{2\nu} - 1 = 0.5 \tag{9.86}$$

If termination of polymerization takes place by combination, the non-uniformity of the polymer is given by (9.86)—$U = 0.5$.

Thus, the non-uniformity of the product of a polymerization terminated by combination is lower than that for polymers terminated by disproportionation. Because termination is generally not exclusively by one or other mode, the experimentally determined values for U lie between these limits. However, much higher values for U can be observed caused by transfer reactions.

In the scientific literature, the terms polydispersity and *polydispersity index PDI* (9.87) are often used instead of non-uniformity *U*:

$$PDI = \frac{P_w}{P_n} = U + 1 \tag{9.87}$$

9.5 Controlled Radical Polymerization (CRP)

The synthesis of block copolymers, i.e., of polymers with longer, alternating sequences of at least two different monomers, by the sequential addition of the different monomers, was a domain of ionic polymerization until 1985 (► Chap. 10). In the following sections methods a method of synthesizing such polymers via radical polymerization is introduced.

9.5.1 Comparison of Living and Radical Polymerization

A polymerization is considered as living when the rate of initiation is significantly greater than the rate of propagation and, additionally, when termination and transfer reactions are absent. The average degree of polymerization P_n can be determined at complete monomer conversion and for an initiator which is 100 % effective from the following relation:

$$P_n = \frac{[M]_0}{[I]_0} \tag{9.88}$$

$[M]_0$	Initial monomer molar concentration
$[I]_0$	Initial initiator molar concentration

Essentially ideal polymerizations, as living ionic polymerization are, yield products with narrow molar mass distributions (Poisson distribution; $M_w/M_n < 1.1$, ► Sect. 10.2.6). The active lifetime of the growing chains is "infinite"—i.e., these chains only stop growing when all the monomer is consumed. Additional monomer leads to additional chain growth and the molar masses increase proportional to conversion. Adding an alternative, skillfully selected monomer results in a block copolymer.

The reaction schemes for radical polymerization (initiation, propagation, termination, and transfer, Sect. 9.2.1) suggest that living radical polymerization should not exist. New chains are constantly started and growing ones terminated. The molar mass distributions are broad. As discussed above (► Sect. 9.4), $M_w/M_n \geq 2$ results if termination is by disproportionation and $M_w/M_n \geq 1.5$ if termination is by combination . Usually, it is therefore not possible to obtain block copolymers by radical polymerization simply by sequentially adding monomers (► Sect. 10.2.2.2).

In ◘ Table 9.5 the most important characteristics of living polymerization and of free radical polymerization are compared.

It would be of great scientific and technical value if free radical polymerizations were living. This would entail the ubiquitous irreversible termination and transfer reactions being curtailed or eliminated and the development of a suitable rapid, quantitative initiation so

Table 9.5 Characteristic differences between living polymerization and typical free radical polymerization

Living polymerization	Free radical polymerization
Block copolymers by sequential monomer addition	Block copolymers not possible
$M_w/M_n \approx 1.1$	$M_w/M_n \geq 1.5$ or ≥ 2.0
P_n increases linearly with conversion	P_n greatest at the start; decreases with increasing conversion because $P_n \sim [M]_t$
Sensitive to contaminations, extreme conditions, often $T < 0$ °C	Insensitive to contaminations, often $T > 70$ °C
Demanding, expensive technology, technically only used for specialties	Inexpensive technology, often used for technical processes

that all the chains grow simultaneously. If one compares the essential reaction for the formation of the polymer chain (v_p) with that responsible for the termination (v_t), it is apparent that both are dependent on the radical concentration but with different reaction orders:

$$v_p \sim \left[P^{\bullet}\right] \quad \text{first-order} \tag{9.89}$$

$$v_t \sim \left[P^{\bullet}\right]^2 \quad \text{second-order} \tag{9.90}$$

By reducing the radical concentration $[P^{\bullet}]$, the relative rate of the second-order reaction is reduced more than that of the first-order reaction. The rate of polymerization does decrease but not as much as the undesired termination reaction.

A reduction of $[P^{\bullet}]$ can be achieved by adding a stable radical $T^{\bullet}$ which reacts with the active end of a growing chain $P^{\bullet}$. By adding energy, $T^{\bullet}$ can be split off again so that the chain can continue growing. $T^{\bullet}$ itself should not be able to react with the monomer. This reaction between $P^{\bullet}$ and $T^{\bullet}$ should also be reversible (Fig. 9.25).

Free $P^{\bullet}$ can add additional monomers but, after every few growth steps, reacts with $T^{\bullet}$ and is transformed into the thermolabile P-T-species.

The concentration of the active chains is very small:

$$\frac{\left[P^{\bullet}\right]}{\left[P-T\right]} \leq 10^{-5} \tag{9.91}$$

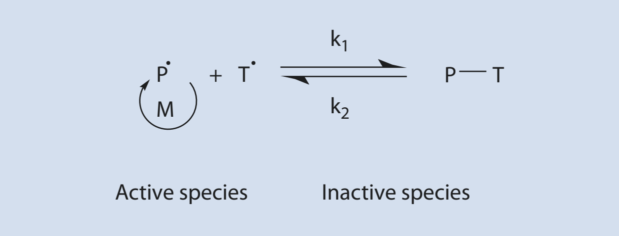
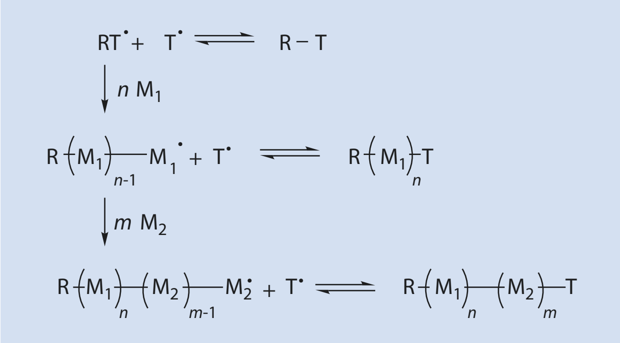


Fig. 9.25 Equilibrium between the active species $P^{\bullet}$ and the *dormant* species *P-T*

Fig. 9.26 Synthesis of block copolymers by controlled radical polymerization



If the exchange between dormant and active species takes place quickly enough, the active species only add a few monomer units and, if the next activation follows statistical rules, a linear increase in the degree of polymerization with conversion, typical of a living polymerization, can be observed. Through this reversible chain termination, this polymerization differs significantly from a true living polymerization (no termination), but also from a typical free radical polymerization (irreversible chain termination) and it is therefore better known as *controlled radical polymerization* (CRP). An important goal of CRP is to enable the synthesis of block copolymers (◘ Fig. 9.26).

The characteristics of a CRP are:

- Linear increase in the degree of polymerization with the conversion
- Low *PDI* ($PDI \leq 1.3$)
- High level of end functionalization (here end group *T*)
- Possibility of the synthesis of block copolymers
- Typical free radical polymerization insensitivity to contamination and water

The possibility of obtaining block copolymers that are inaccessible by ionic polymerization, as well as the insensitivity of the growing species to contamination and water, are obvious advantages of CRP. Prerequisites for the success of a CRP are a low concentration of $P^\bullet$ and a reversible chain termination with $T^\bullet$ which cannot start chains by itself. In the following Sects. 9.5.2, 9.5.3, 9.5.4, and 9.5.5, important CRP methods are introduced.

9.5.2 Dissociation-Combination-Mechanism

The dissociation combination mechanism involves the propagation of the polymer chains being interrupted by conversion to a stable radical $T^\bullet$ which is unable to trigger a radical polymerization by itself, as already shown in ◘ Fig. 9.25 (*p*ersistent *r*adical *e*ffect, PRE; ◘ Fig. 9.27), an equilibrium develops between “dormant” species *P*-*T* and growing radicals $P^\bullet$. The termination by combination of two growing polymer radicals ($P^\bullet$) should be reduced as much as possible (dashed arrow in ◘ Fig. 9.27).

The “termination” of the growing polymer chain with $T^\bullet$ is reversible. After the separation of $T^\bullet$, the polymer radical can add another monomer (◘ Fig. 9.29, example of the polymerization of styrene).

Fig. 9.27 Controlled radical polymerization by dissociation-combination-mechanism

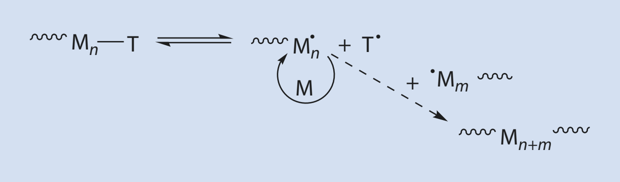


Fig. 9.28 Structural formula of TEMPO

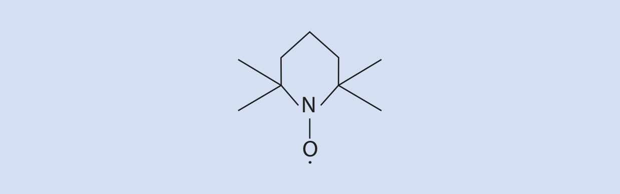
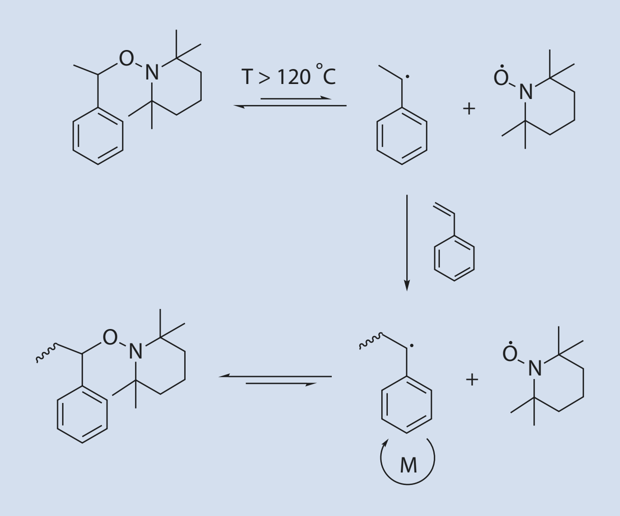
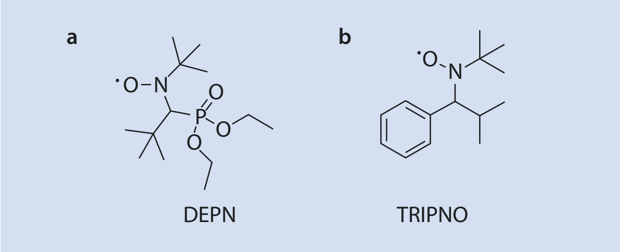


Fig. 9.29 Alkoxy amine as initiator of the controlled radical polymerization of styrene



An important class of materials for T• are the nitroxide radicals (Solomon et al 1985, Georges et al. 1993, Hawker et al. 2001, Benoit et al. 1999, 2000) and TEMPO ((2,2,6,6-**Te**tra**m**ethyl**p**iperidin-1-yl)**o**xyl) (Fig. 9.28) is the example which has been most often studied.

The initiation of CRP can take place with common initiators such as benzoyl peroxide and azobisisobutyronitrile in the presence of nitroxide radicals. It can, however, be initiated by special alkoxy amines (Fig. 9.29).



◘ **Fig. 9.30** Examples of *N*-oxide-radicals for the NMP-method. (**a**) *N*-*t*Bu-*N*-[1-**d**iethyl**p**hosphono-(2,2-dimethylpropyl)]-**n**itroxide (DEPN). (**b**) 2,2,5-**Tri**methyl-4-**p**henyl-3-aza-hexan-**n**itr**o**xide (TRIPNO)

Using CRP, polymers such as polystyrene, with a narrow molar mass distribution, can be synthesized. By these means, block copolymers can also be obtained (styrene/substituted styrene, styrene/methyl methacrylate, styrene/*N*-alkyl acrylamide, etc.). However, controlled radical polymerization occurs significantly slower than typical free radical polymerization. Another disadvantage is that, with the exception of TEMPO, alkoxy amines are not commercially available and these end groups are, for example, for the synthesis of telechelics, not easily converted into other interesting functional end groups.

Controlled radical polymerization in the presence of alkoxy amines can be found in the literature as NMP-method (**N**-oxide **m**ediated **p**olymerization) (Solomon et al. 1985; Georges et al. 1993; Hawker et al. 2001; Benoit et al. 1999, 2000).

◘ Figure 9.30 shows some more examples of *N*-oxide-radicals.

As well as styrene and various acrylates, monomers polymerizable using this method include acrylamides, acrylonitrile, and butadiene. Methacrylates form sterically demanding radicals so that controlled radical polymerization with such monomers via NMP is not possible. Whereas TEMPO requires polymerization temperatures of $T \geq 120$ °C, TRIPNO and DEPN (◘ Fig. 9.30) can be successful even at $T \geq 80$ °C. The NMP-method can be carried out as a solution but also as an emulsion polymerization (► Sect. 16.5).

Numerous statistical, block, and graft copolymers, as well as star and highly branched (co)polymers can be created by means of NMP.

9.5.3 Bimolecular Activation (Atom Transfer Radical Polymerization, ATRP)

At almost the same time as CRP was being developed, in 1995, Matyjaszewski and Sawamoto described radical polymerizations that involve a bimolecular initiation reaction and have become known as **a**tom **t**ransfer **r**adical **p**olymerizations (ATRP) (◘ Fig. 9.31).

As the Y (in ◘ Fig. 9.31) Cu(I)-(Wang and Matyjaszewski 1995), Ru(II)-(Kato et al. 1995), and also Fe(II)-, Ni(II)-, and Ni(0)-complexes can be employed. One well known example of ATRP is shown in ◘ Fig. 9.32.

The list of monomers that are polymerizable by means of ATRP includes styrene, various substituted styrenes, (meth-)acrylates, (meth-)acrylamides, acrylonitrile, and vinyl pyridine.

Typical initiators are depicted in ◘ Fig. 9.33.

Some of the diverse structures of the ligands which have been used are shown in ◘ Fig. 9.34.

Fig. 9.31 Scheme of a controlled radical polymerization through bimolecular activation

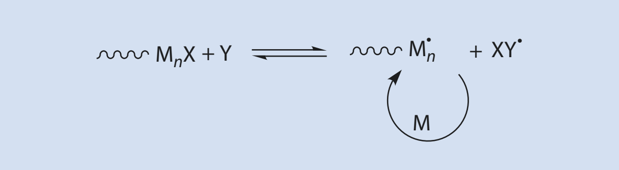
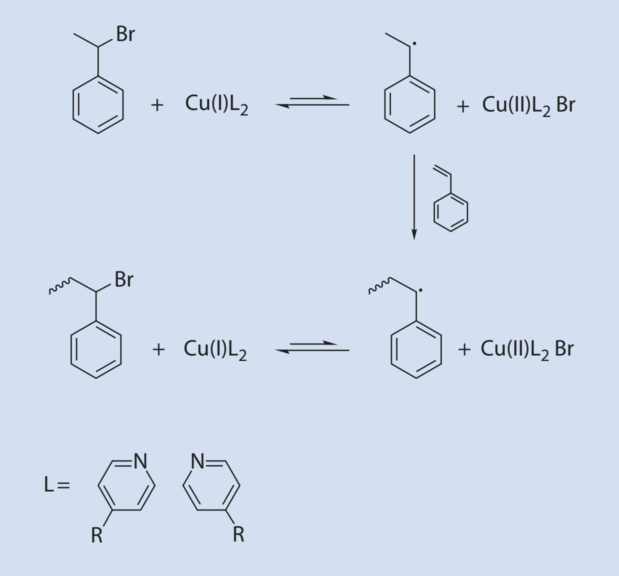


Fig. 9.32 ATRP of styrene, initiated with 1-bromoethyl benzene and Cu(I)-bis-(bipyridine)



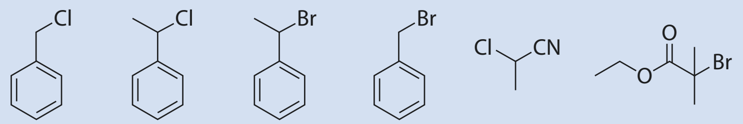
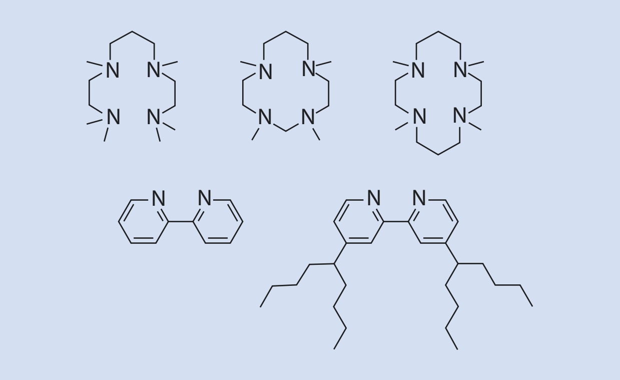


Fig. 9.33 Typical initiators for ATRP

Because the end group (e.g., X = Br) remains throughout the polymerization, it can be easily used for the synthesis of block copolymers (Fig. 9.35). To this end, monomer M_2 is added after the polymerization of monomer M_1 is complete.

ATRP can be applied to many radically polymerizable monomers. The reaction conditions are comparable to those for typical free radical polymerization but the polymerization temperatures for ATRP are significantly higher than normal for free radical polymerization. The molar masses are controlled by the $[M]/[I]$-ratio. Furthermore, polymers with narrow molar mass distributions can be obtained. The color of many metal complexes as well as their toxicity and the difficulty of their removal are disadvantages. Because here, as well as with NMP (▶ Sect. 9.5.2), the concentration of the active species must be very low, the rate of polymerization is comparatively slow despite the higher reaction temperatures.

Fig. 9.34 Selected ligands for the metal complexes used for ATRP



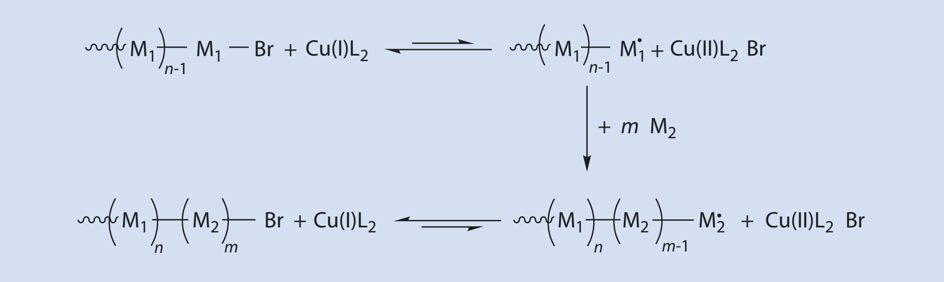


Fig. 9.35 Synthesis of poly(M_1-*Block*-M_2) by ATRP

9.5.4 Degenerative Transfer (RAFT)

The general description of degenerative transfer is illustrated in Fig. 9.36.

The best known method is the "***R**eversible **A**ddition **F**ragmentation and **T**ransfer*" method (RAFT) in which specific transfer reagents such as dithioester are added (Figs. 9.37 and 9.38) (Delduc et al. 1988).

If transfer occurs quickly and the transfer reagent is used in sufficient concentration ($[Transfer\ agent] > 10 \cdot [I]$), a free radical polymerization can relatively easily become a controlled radical polymerization.

RAFT has the following advantages compared to ATRP:

- No metals
- Milder conditions

Similar to ATRP, RAFT can be used for many vinyl monomers. However, complex research is required to find an appropriate dithioester for each monomer. Furthermore, colored and odor-intensive byproducts are common. Dithioester end groups are less easily converted into other interesting end groups and they are not particularly stable at higher temperatures or with respect to light.

Fig. 9.36 Controlled radical polymerization via degenerative transfer

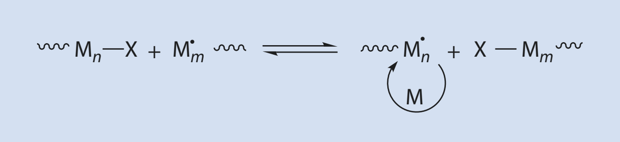


Fig. 9.37 Structure of the dithioester used for RAFT

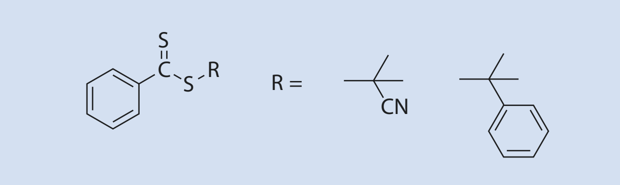
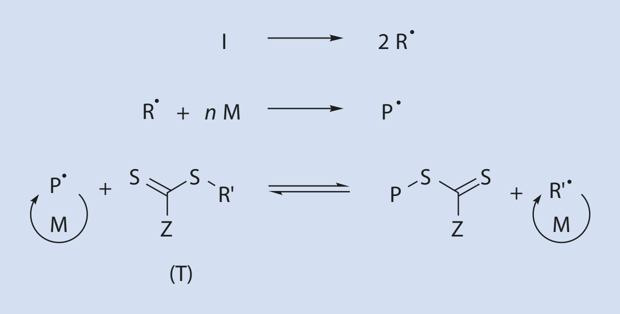


Fig. 9.38 Controlled radical polymerization by RAFT



9.5.5 Comparison of NMP, ATRP, and RAFT

Every CRP-system has advantages and disadvantages. The advantage of the NMP-system is that it is a purely organic system and that it is applicable for many monomers including acids. Disadvantages are the high reaction temperature and the lack of availability of the *N*-oxide-precursors as well as the difficult conversion of the end groups into more attractive groups. Furthermore, the *N*-oxide-radicals need to be used at the same concentration as the initiator.

For ATRP, only catalytic amounts of the metal complex transfer agents are required and many monomers are polymerizable using this method. The end groups (X = Br) are easily converted. Additionally, many potential initiators have simple structures and are commercially available. The principal disadvantages of ATRP are the color, the toxicity, and the difficulty of removing the metal residues.

RAFT is equally universally applicable as ATRP. However, only a few dithioesters are commercially available. Other disadvantages are the odor, color, and toxicity of the products, byproducts, or their decomposition products.

The industrial application of CRP has the following advantages:

- The technology is simple
- Block copolymers can be made by radical polymerization
- The molar masses are easily controllable and the molar mass distributions are narrow

Until now, the commercial application of CRP has been limited to niches because the disadvantages still prevail:

- Too slow (NMP, ATRP, RAFT)
- Too expensive (NMP, RAFT)
- Toxic, coloration, difficult to remove catalysts (ATRP)
- Colored products (ATRP, RAFT)
- Odor-intensive products (RAFT)

As a result, new methods devoid of these disadvantages are still being looked for.

9.5.6 Polymerization in the Presence of 1,1-Diphenylethylene (DPE-Method)

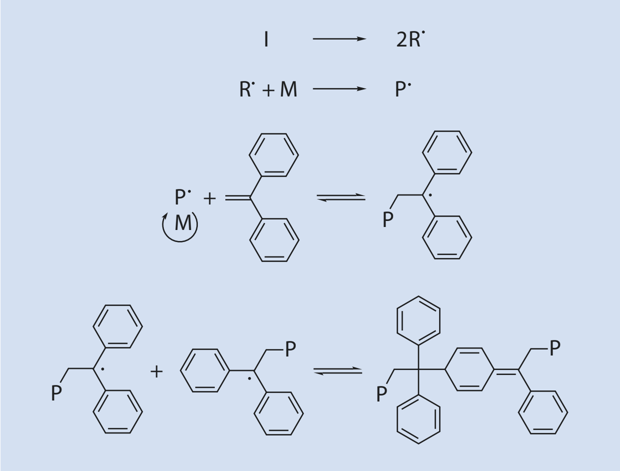
1,1-**Dip**henyl**e**thylene (DPE) is noted because even traces retard the rate of polymerization and reduce the molar mass of the resulting polymer (e.g., during the polymerization of styrene.). This effect can be explained as follows (◘ Fig. 9.39).

As soon as a 1,1-diphenylethylene adds to the growing chain, neither the monomer M nor an additional DPE can be added. There are two possibilities for this radical: either it eliminates a DPE again and adds further monomer units or it simply terminates by combination. The termination product is thermolabile; it can break open at the original link, eliminate DPE, and then, as described above, continue to propagate.

If the termination product is employed as an initiator for the polymerization of another monomer, one can obtain block copolymers in an elegant way (◘ Fig. 9.40).

This method is universally applicable to all monomers that are radically polymerizable (Raether et al. 2001; Wieland 2003) and block copolymers are easily synthesized from more than two different monomers.

◘ **Fig. 9.39** Effect of 1,1-diphenylethylene on radical polymerization



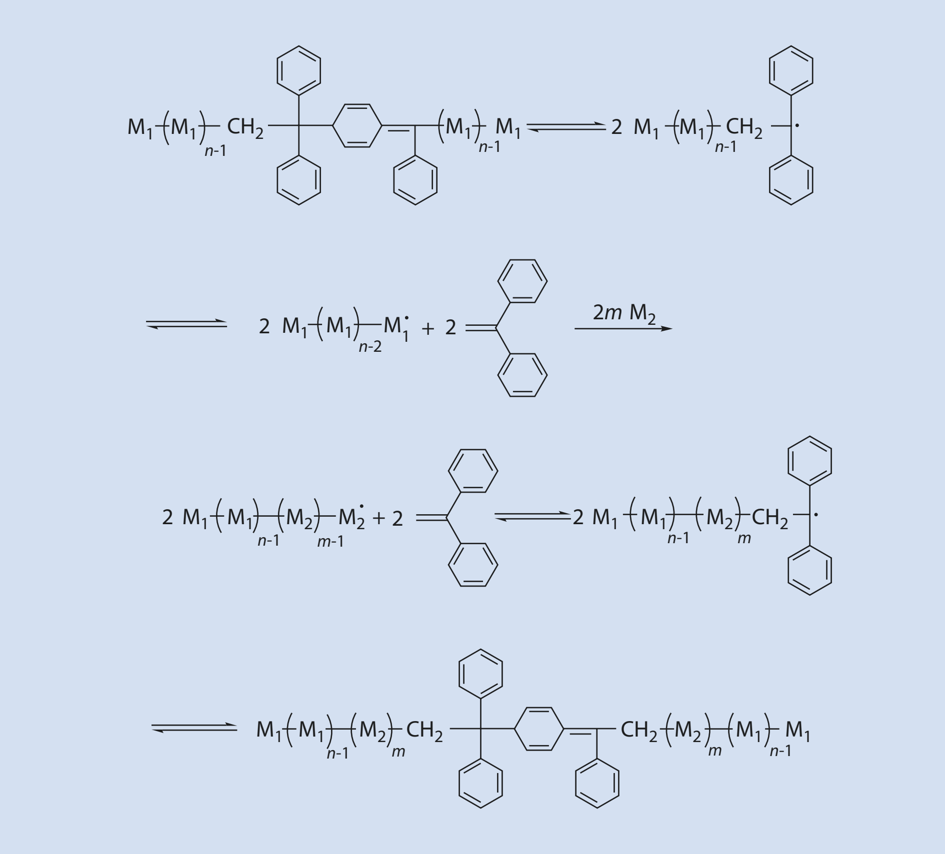


Fig. 9.40 Synthesis of a block copolymer from M_1 and M_2 by the DPE-method

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