

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 9.13d₁) by, for example, forming a covalent bond (*combination*). Alternatively, the two radicals can be individually deactivated by *disproportionation* (■ Fig. 9.13d₂).

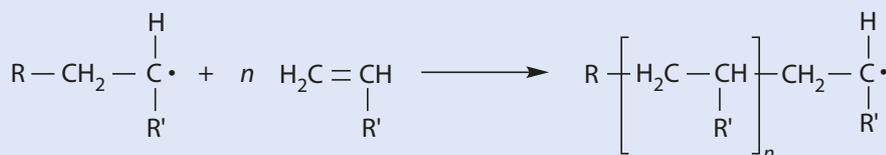
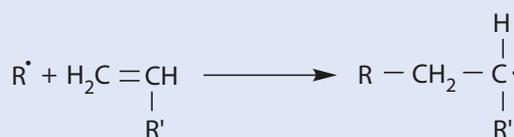
If the radical character of a macro radical is transferred to another moiety, and if this then becomes able to add an additional monomer, it is referred to as a transfer reaction (■ Fig. 9.4).

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 $H_2C=CHR'$



■ Fig. 9.2 Formation of a macro-radical

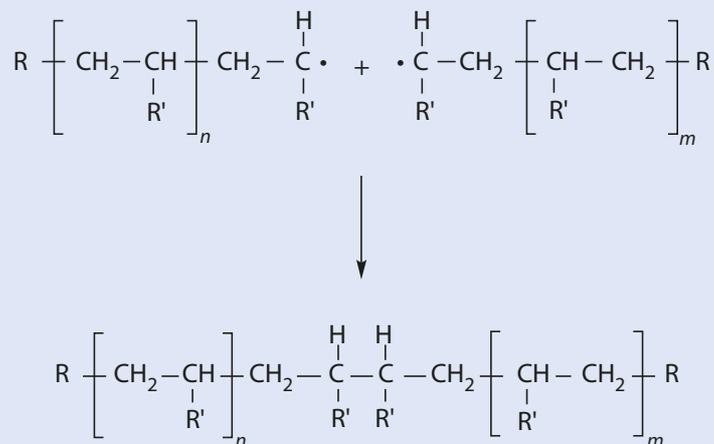


Fig. 9.3 Termination of chain growth by radical combination

9

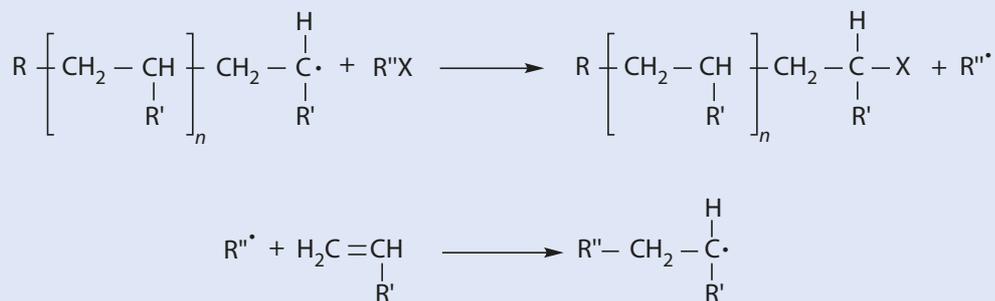
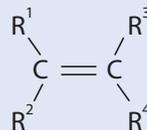


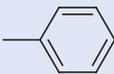
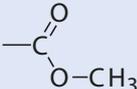
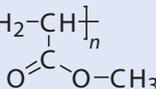
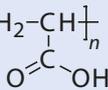
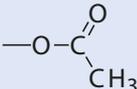
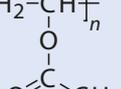
Fig. 9.4 Example of chain transfer

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 $\text{H}_2\text{C}=\text{CHR}'$

Monomer	R'	Polymer
Ethene	—H	$\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$
Styrene		$\text{-(CH}_2\text{-CH)}_n\text{-}$ 
Acrylonitrile	—C≡N	$\text{-(CH}_2\text{-CH)}_n\text{-}$ CN
Acrylic acid methyl ester		$\text{-(CH}_2\text{-CH)}_n\text{-}$ 
Acrylic acid		$\text{-(CH}_2\text{-CH)}_n\text{-}$ 
Vinyl chloride	—Cl	$\text{-(CH}_2\text{-CH)}_n\text{-}$ Cl
Vinyl acetate		$\text{-(CH}_2\text{-CH)}_n\text{-}$ 

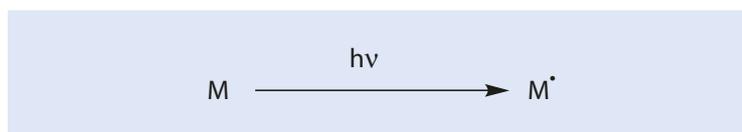
9.1.2 Radical Sources

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).

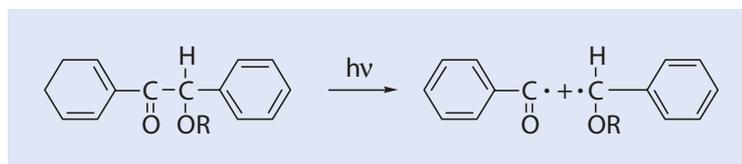
Radicals can also be created by γ - and β -radiation (■ Fig. 9.8). In such a system, not only radicals but also anions and cations are created, and the respective chain growth reactions can proceed either via radicals, anions, or cations, or the different growing mechanisms can compete with each other.

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).

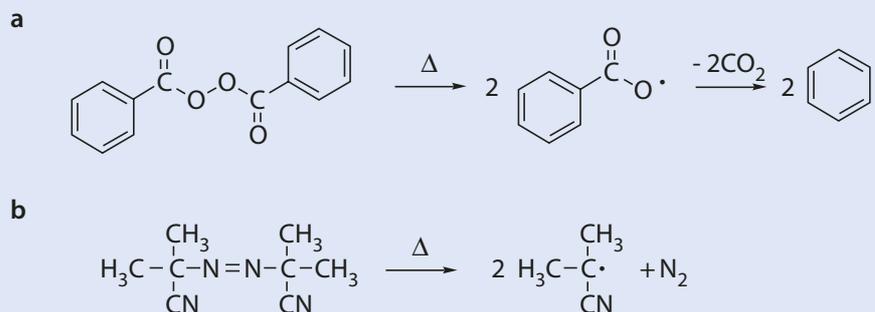
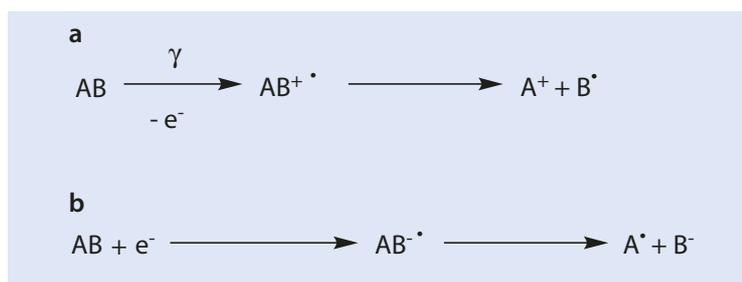
■ Fig. 9.6 Photochemical activation of a monomer



■ Fig. 9.7 Photochemical decomposition of benzoin ether



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

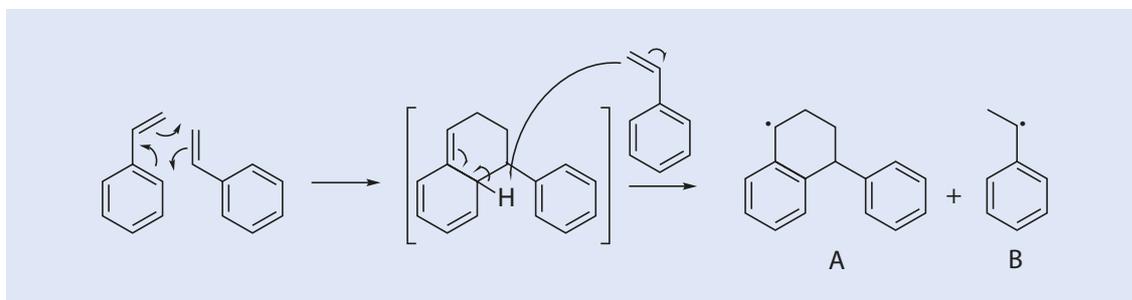


■ Fig. 9.9 Radicals from (a) dibenzoyl peroxide and (b) azo-bis-isobutyronitrile (AIBN)

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, sulfonic 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.

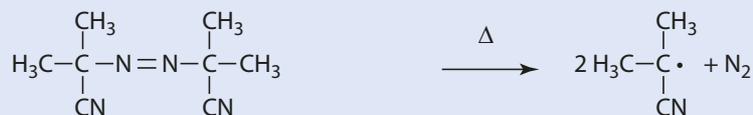
■ Fig. 9.10 Radical formed during a redox reaction (*Fenton reagent*)



■ 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).

a. Initiator decomposition



b. Start of chain reaction

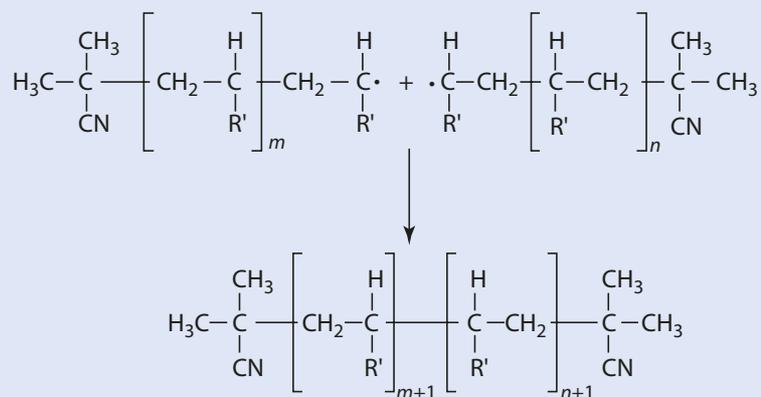


c. Propagation

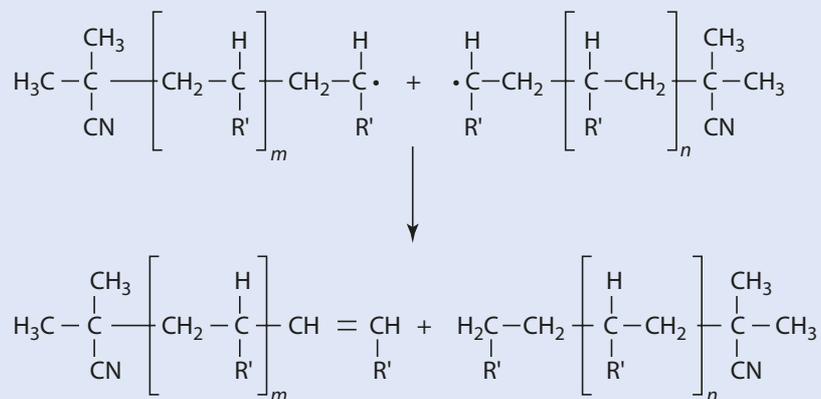


d. Termination

d1. Combination



d2. Disproportionation



■ Fig. 9.13 Individual steps of the polymerization of a vinyl monomer $\text{CH}_2=\text{CHR}'$ initiated by AIBN (the elements of the last row correspond to RM_n^{H} and RM_m^{H} in ■ Fig. 9.12)