2

In this chapter, the fundamentals and the most common methods and techniques for the synthesis, processing, characterization, and modification of macromolecular materials are described briefly, as an introduction to the special Chaps. 3, 4, and 5. The main emphasis is on the description of methods and techniques used in laboratories, but some examples from industrial practice are also mentioned.

2.1 Methods for Synthesis of Polymers

The formation of synthetic polymers is a process which occurs via chemical connection of many hundreds up to many thousands of monomer molecules. As a result, macromolecular chains are formed. They are, in general, linear, but can be branched, hyperbranched, or crosslinked as well. However, depending on the number of different monomers and how they are connected, homo- or one of the various kinds of copolymers can result. The chemical process of chain formation may be subdivided roughly into two classes, depending on whether it proceeds as a chain-growth or as a step-growth reaction.

2.1.1 Chain Growth Polymerizations

Chain growth polymerizations (also called addition polymerizations) are characterized by the occurrence of activated species (initiators)/active centers. They add one monomer molecule after the other in a way that at the terminus of each new species formed by a monomer addition step an activated center is created which again is able to add the next monomer molecule. Such species are formed from compounds which create radicals via homolytic bond scission, from metal complexes, or from ionic (or at least highly polarized) molecules in the initiating steps (2.1) and (2.2). From there the chain growth can start as a cascade reaction

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(propagation; 2.3) upon manifold repetition of the monomer addition and reestablishment of the active center at the end of the respective new product:

$$\mathrm{I} \longrightarrow \mathrm{I}^* \tag{2.1}$$

$$\mathrm{I}^* + \mathrm{M} \longrightarrow \mathrm{I{-}M}^* \tag{2.2}$$

$$\mathrm{I{-}M}^* + n\,\mathrm{M} \longrightarrow \mathrm{I}{-}\left[\mathrm{M}\right]_n{-}\mathrm{M}^* \quad (=\mathrm{P}^*) \tag{2.3}$$

Finally, growth of an individual macromolecule is arrested in either a termination or a transfer step (2.4) or (2.5)

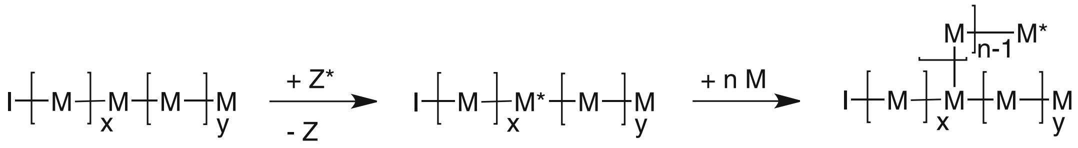
$$\mathrm{I}{-}\left[\mathrm{M}\right]_n{-}\mathrm{M}^* + \mathrm{S} \longrightarrow \mathrm{I}{-}\left[\mathrm{M}\right]_n{-}\mathrm{M} \quad (+\ \mathrm{S}') \tag{2.4}$$

$$\mathrm{I}{-}\left[\mathrm{M}\right]_n{-}\mathrm{M}^* + \mathrm{T} \longrightarrow \mathrm{I}{-}\left[\mathrm{M}\right]_n{-}\mathrm{M} + \mathrm{T}^* \xrightarrow[+\,n\,\mathrm{M}]{} \mathrm{T}{-}\left[\mathrm{M}\right]_{n-1}{-}\mathrm{M}^* \tag{2.5}$$

S: chain-terminating agent (stopper)

T: chain-transfer agent (solvent, monomer, initiator, polymer, regulator, . . .)

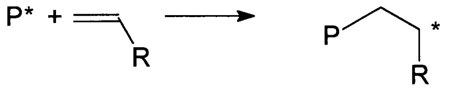
While termination leads to the irreversible disappearance of an active center, chain transfer results in the growth of a second chain while the first one is terminated. Here, the active center is transferred to another molecule (solvent, initiator, monomer, . . .) where it is able to initiate further chain growth. The resulting “dead” polymer, on the other hand, can continue its growth only when activated in a subsequent transfer step. Because this re-activation in general does not occur at the terminal monomer unit but somewhere in the chain, branched or cross-linked products will result:



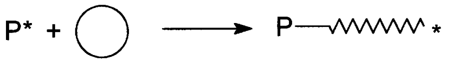
$$\mathrm{I}{-}\left[\mathrm{M}\right]_x{-}\mathrm{M}{-}\left[\mathrm{M}\right]_y{-}\mathrm{M} \xrightarrow[-\mathrm{Z}]{+\mathrm{Z}^*} \mathrm{I}{-}\left[\mathrm{M}\right]_x{-}\mathrm{M}^*{-}\left[\mathrm{M}\right]_y{-}\mathrm{M} \xrightarrow{+\,n\,\mathrm{M}} \mathrm{I}{-}\left[\mathrm{M}\right]_x{-}\overset{\mathrm{M}{-}\left[\mathrm{M}\right]_{n-1}{-}\mathrm{M}^*}{\mathrm{M}}{-}\left[\mathrm{M}\right]_y{-}\mathrm{M} \tag{2.6}$$

In conclusion, chain-growth polymerizations are typical chain-reactions involving a start-up step (initiation) followed by many identical chain-reaction steps (propagation) – stimulated by the product of the first start-up reactions. Transfer processes may continue until, finally, the active center disappears in a termination step.

Monomers appropriate for chain-growth polymerizations either contain double or triple bonds or are cyclic, having a sufficiently high ring strain



(2.7)

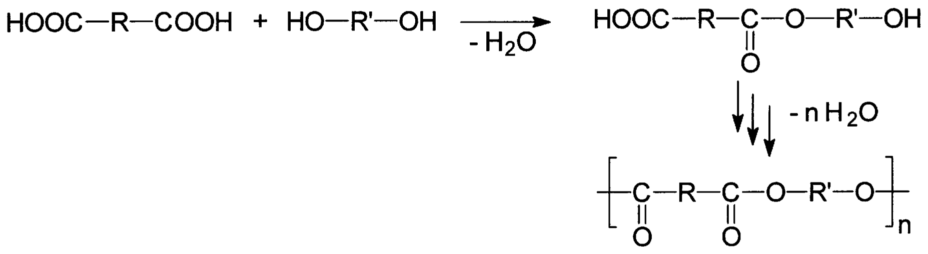


(2.8)

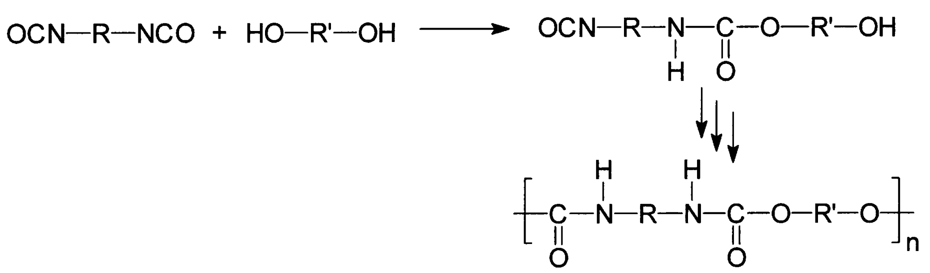
Depending on the nature of the active center, chain-growth reactions are subdivided into radicalic, ionic (anionic, cationic), or transition-metal mediated (coordinative, insertion) polymerizations. Accordingly, they can be induced by different initiators or catalysts. Whether a monomer polymerizes via any of these chain-growth reactions – radical, ionic, coordinative – depends on its constitution and substitution pattern. Also, external parameters like solvent, temperature, and pressure may also have an effect. Monomers able to grow in chain-growth polymerizations are listed in Table 2.2 of Sect. 2.1.4.

2.1.2 Step Growth Polymerizations

In step growth reactions, on the other hand, neither are specific activated centers present to force the connection of the monomers, nor does the process occur as a cascade reaction. Instead, the monomers are tied together in discreet, independent steps via conventional organic reactions such as ester-, ether-, amide-, or urethane formation. Depending on whether small molecules are set free in the connection step, one distinguishes between polycondensations Eq. 2.9 and polyadditions Eq. 2.10



$$\mathrm{HOOC{-}R{-}COOH + HO{-}R'{-}OH} \xrightarrow[-\,H_2O]{} \mathrm{HOOC{-}R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R'{-}OH} \xrightarrow{-\,n\,H_2O} \left[\mathrm{\underset{\underset{\displaystyle O}{\|}}{C}{-}R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R'{-}O}\right]_n \tag{2.9}$$



$$\mathrm{OCN{-}R{-}NCO + HO{-}R'{-}OH} \longrightarrow \mathrm{OCN{-}R{-}\underset{\underset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R'{-}OH} \longrightarrow \left[\mathrm{\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}R{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R'{-}O}\right]_n \tag{2.10}$$