Step-Growth Polymerization

The synthetic processes of producing polymers from their monomers can be divided into step-growth and chain-growth polymerization. These two polymer formation reactions (◘ Figs. 8.1 and 8.2) are fundamentally different in their mechanisms, intermediate products, the way the molar mass increases as a function of monomer conversion, and the activation energy of their elementary steps.

8.1 Differences Between Step-Growth and Chain-Growth Polymerizations

The basic characteristics of these two reaction types are illustrated by reference to the synthesis of polystyrene from styrene (◘ Fig. 8.1) and nylon 6.6 from 1.6-hexamethylene diamine and adipic acid (◘ Fig. 8.2).

As already briefly introduced in ▶ Chap. 1, one industrially significant polymerization mechanism involves the transformation of a double bond into two single bonds, as shown in ◘ Fig. 8.1.

Such polymerization of unsaturated compounds can be caused by radicals (▶ Chap. 9), ions (▶ Chaps. 10 and 12), or transition metal catalysts (▶ Chap. 11). During the radical polymerization of styrene, an initiating radical adds to the double bond of monomeric styrene and creates a styryl radical. This in turn can attack another styrene molecule. Because the reaction always leads to a chain terminating with a styryl radical, it can occur several thousand times before it ends. Because of its chain reaction character, such a process is referred to as a chain-growth polymerization. Such chain-growth polymerization have various distinguishing characteristics:

◘ **Fig. 8.1** Polymerization of a double bond using styrene (polystyrene) as an example
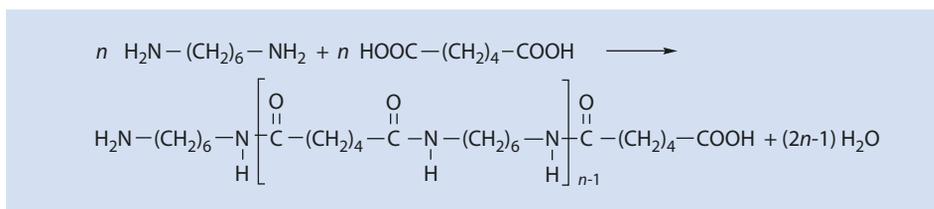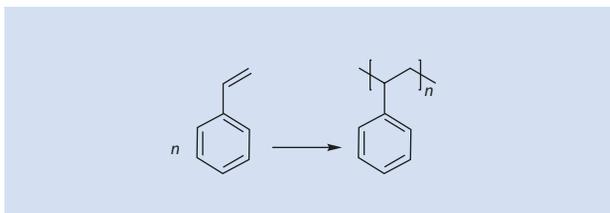
◘ **Fig. 8.2** Synthesis of a polyamide from 1.6-hexamethylene diamine and adipic acid
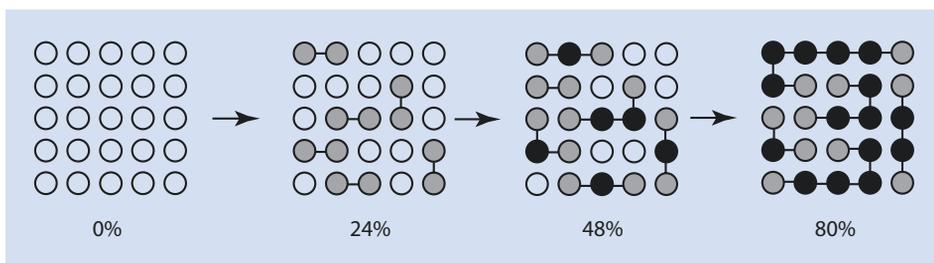
Fig. 8.3 A visualization of a polycondensation at 0 %, 24 %, 48 %, and 80 % functional group conversion. *White balls* represent monomers which have not reacted yet, *gray balls* those monomers which have reacted at one of their two active groups, and *black balls* are those molecules which have reacted at both ends

- It is initiated by a highly reactive particle.
- Only a small portion of the molecules in the process are actively involved in the polymerization process (in this case, the growing styryl terminated radicals). The remaining molecules are unreactive; that is, they can only react with radicals but not with themselves.
- The chain grows quickly (generally within a matter of seconds) to a high molar mass

A typical example of step-growth polymerization is the synthesis of nylon 6.6 from 1.6-hexamethylene diamine and adipic acid (Fig. 8.2). This polymerization is activated by heat, which causes dehydration. There is no chemical initiator. In contrast to chain-growth polymerization, it is impossible to differentiate between active and passive particles. A new monomer results from each individual reaction step and has the same reactivity as the original monomers. Further monomer conversion depends solely on statistical probabilities. All intermediate products are stable and can be isolated. In contrast to chain-growth polymerization, it takes considerable time for polymers with a high molar mass to form. Figure 8.3 illustrates this. Step-growth polymerizations in which a small molecule is a reaction byproduct are also termed "polycondensations."
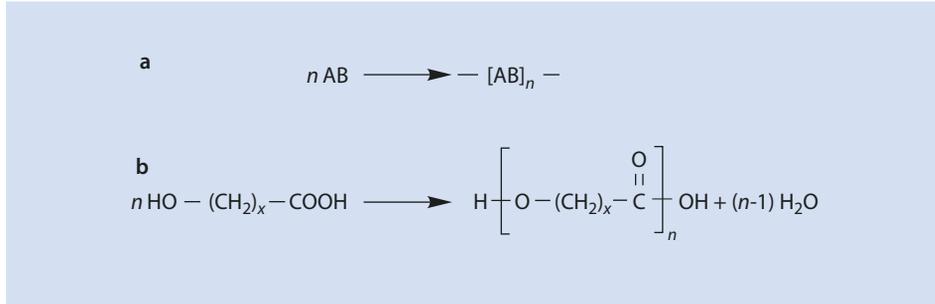
The example in Fig. 8.3, shows that, even with a conversion of 80 % of the functional groups, there are five "polymer chains" with "degrees of polymerization" of 3, 4, 5, 6, and 7. Not until very high conversions do the oligomers formed condense to chains with a high molar mass. The quantitative details of such processes are given in ▶ Sect. 8.2.

Step-growth polymerization is distinguished by the following characteristics:
- An initiation in the sense of the radical polymerization described above does not take place.
- All molecules are equally reactive and involved in the polymerization process. In particular, there are no chain-carrying reactive species with limited stability.
- Only at very high conversions are products with a high molar mass produced.

Step-growth polymerizations require that the monomers possess chemical functions that can form covalent bonds with each other. These functions can be united in the same molecule, such as ω-hydroxyl carboxylic acid, which can produce a polyester via dehydration (Fig. 8.4). Such a monomer is called an AB-monomer, where A and B represent the reactive groups. Alternatively, two di- or multi-functional molecules can react with each other to form the polymer (Figs. 8.2 and 8.5). Using similar terminology, such monomers are referred to as AA and BB.

A particular characteristic of the step-growth polymerization of two monomers AA and BB is the need to accurately adjust the stoichiometry of the reacting molecules if

a $n\ AB \longrightarrow - [AB]_n -$

b $n\ HO - (CH_2)_x - COOH \longrightarrow H \left[O - (CH_2)_x - \overset{\overset{O}{\|}}{C} \right]_n OH + (n\text{-}1)\ H_2O$

⬛ Fig. 8.4 Polymerization of an AB-monomer: (**a**) a general scheme and (**b**) the polymerization of a ω-hydroxyl carboxylic acid to a polyester as an example

⬛ Fig. 8.5 Generic diagram of the polymerization of AA- and BB-monomers

$n\ AA + n\ BB \longrightarrow -[AABB]_n-$
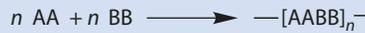
high molar masses are required. For example, if there is an excess of BB monomer, all the A-functionalities react and the oligomers are terminated with B groups, which cannot react with each other.

Given the criteria described here, polymerization reactions can be unambiguously classified into chain-growth and step-growth polymerization.

8.2 Molar Mass, Degree of Polymerization, and Molar Mass Distribution

The most important factors used to characterize macromolecules are the molar mass, the degree of polymerization, and the molar mass distribution. These characteristics depend on the polymerization mechanism of the macromolecules and on the degree of monomer conversion.

8.2.1 Degree of Polymerization and Molar Mass of Step-Growth Polymerizations

During the stepwise transformation of an AB-monomer or of a stoichiometric AA/BB-system into a polymer (⬛ Fig. 8.6), the molar mass is calculated by multiplying the molar mass of the components AB, AA and BB respectively, by the number n of repetitions in the polymer molecule:

$$M_{Polymer} = n(M_{AB}) \tag{8.1}$$

$$M_{Polymer} = n(M_{AA} + M_{BB}) \tag{8.2}$$

In (8.1) and (8.2), $M_{Polymer}$ represents the molar mass of the polymer, M_{AB} the molar mass of the monomer AB, and M_{AA} and M_{BB} the molar masses of the monomers AA and BB, respectively.

◘ **Fig. 8.6** A scheme of a step-growth polymerization

$$n \text{ AB} \longrightarrow - [\text{AB}]_n -$$

$$n \text{ AA} + n \text{ BB} \longrightarrow - [\text{AABB}]_n -$$

In a typical condensation reaction, for example an esterification of a dicarboxylic acid with a diol, the molar mass of the polymer decreases by $(2n-1)\cdot H_2O$ (and with AB-monomers such as a 6-hydroxy carboxylic acid by $(n-1)\cdot H_2O$).

The degree of polymerization, P_n, is identical to the number of repetitions n and is calculated as follows (▶ Sect. 3.1):

$$P_n = \frac{n_0}{n_t} \tag{8.3}$$

n_0 Initial number of molecules
n_t Number of molecules at time t

or:

$$P_n = \frac{c_0}{c_t} \tag{8.4}$$

c_0 Initial concentration of functional groups
c_t Concentration of functional groups[1] at time t

Because at a conversion, p:

$$p = \frac{c_0 - c_t}{c_0} = 1 - \frac{c_t}{c_0} \tag{8.5}$$

or

$$c_t = (1-p)\cdot c_0 \tag{8.6}$$

then P_n is given by

$$P_n = \frac{c_0}{c_0(1-p)} = \frac{1}{1-p} \tag{8.7}$$

This implies that only with high conversion rates (p almost 1) can sufficiently high degrees of polymerization be achieved (◘ Fig. 8.7).

If the concentration of the reactive groups is not stoichiometric, the degree of polymerization can be determined from the following considerations.

---

1   The concentration of the functional groups is the same as that of the existing molecules; the former is experimentally easier to access.

Fig. 8.7 Dependence of the degree of polymerization on conversion for a polycondensation
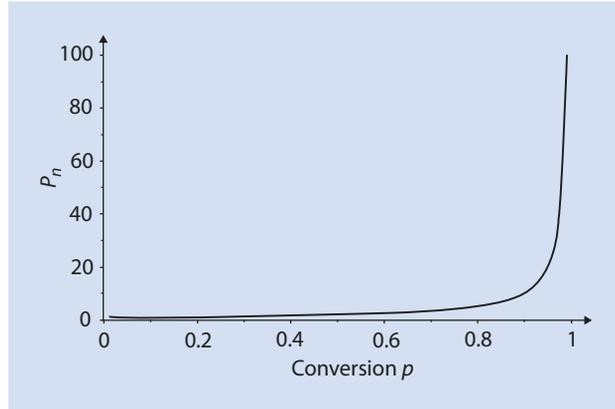
Because

$$P_n = \frac{n_0}{n_t}$$ (8.3)

the ratio of shortfall (A) to excess (B) is defined as the non-stoichiometric factor r:

$$\frac{n_A}{n_B} = r \le 1$$ (8.8)

n_A	Starting number of the functional groups A
n_B	Starting number of the functional groups B
$n_{A,t}$	Number of functional groups A at time t
$n_{B,t}$	Number of functional groups B at time t

From this it follows that r is always less or equal to 1.
From (8.3) and (8.8) we obtain

$$P_n = \frac{n_A + n_B}{n_{A,t} + n_{B,t}} = \frac{n_A\left(1 + \dfrac{1}{r}\right)}{n_{A,t} + n_{B,t}}$$ (8.9)

Because p represents the conversion of the functions A, unconverted A is given by

$$n_{A,t} = (1 - p)n_A$$ (8.10)

Because the conversion of B is limited by the non-stoichiometric factor r, the number of B functions is given by

$$n_{B,t} = (1 - rp)n_B$$ (8.11)

The total number of functions $n_{A,t} + n_{B,t}$ that have not been converted at time t is

$$n_{A,t} + n_{B,t} = (1 - p)n_A + (1 - rp)n_B$$ (8.12)

which, after rearrangement, gives

$$n_{A,t} + n_{B,t} = \frac{n_A}{r}\left(r - 2rp + 1\right)$$

(8.13)

Inserting this in (8.9) yields

$$P_n = \frac{n_A\left(1 + \dfrac{1}{r}\right)}{\dfrac{n_A}{r}\left(r - 2rp + 1\right)} = \frac{\dfrac{n_A}{r}\left(r+1\right)}{\dfrac{n_A}{r}\left(r - 2rp + 1\right)}$$

(8.14)

or the *Carothers equation*

$$P_n = \frac{r+1}{r - 2rp + 1}$$

(8.15)

In the case of exact stoichiometry of the functional groups, i.e., $r = 1$, (8.7) derived above is obtained:

$$P_n = \frac{2}{2 - 2p} = \frac{1}{1 - p}$$

With quantitative conversion of those active groups in the minority ($p = 1$, $r < 1$) it follows that the degree of polymerization is given by

$$P_n = \frac{r+1}{r - 2r + 1} = \frac{1+r}{1-r}$$

(8.16)

Thus, the degree of polymerization can be controlled by the conversion p, but also by the non-stoichiometry r. To limit the molar mass, non-stoichiometry is often induced by intentionally adding monofunctional elements. If [AA] < [BB], the degree of polymerization P_n of the polymer can be adjusted by (8.16). Furthermore, if AA is completely consumed, the polymer molecules are exclusively terminated by B groups which are available for subsequent reactions.

According to (8.16) or ◘ Fig. 8.8, at a non-stoichiometry of $r = 0{,}975$, despite complete conversion ($p = 1$), the degree of polymerization is only 79 ($P_n = 79$). If the conversion is reduced to $p = 0.95$ with otherwise identical conditions, the degree of polymerization decreases to $P_n = 16$.

The Dependence of the Conversion on the Equilibrium Constant K

Because the esterification reaction is a typical organic equilibrium, it is important to know what conversion can actually be achieved. This is determined by the equilibrium constant K, given in molar concentration terms by

$$K = \frac{[RCOOR'][H_2O]}{[RCOOH][R'OH]}$$

(8.17)

◘ **Fig. 8.8** Dependence of the degree of polymerization on conversion at different stoichiometric ratios r for the polymerization of AA- with BB-monomers
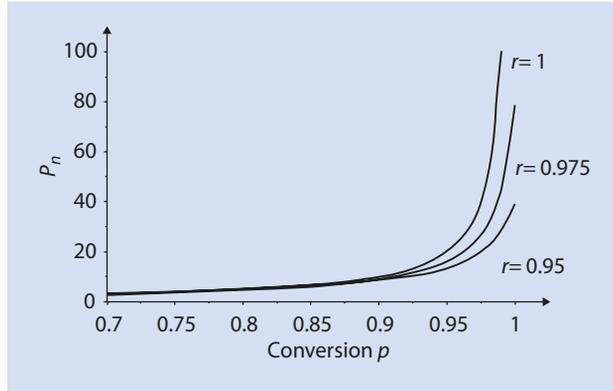
with

$$p = \frac{[RCOOR']}{[RCOOH]_0} = \frac{[H_2O]}{[RCOOH]_0} \qquad (8.18)$$

and

$$(1-p) = \frac{[RCOOH]}{[RCOOH]_0} = \frac{[R'OH]}{[RCOOH]_0} \qquad (8.19)$$

($[RCOOH]_0 = [R'OH]_0$: starting concentration of the educts; see also (8.6))
From (8.17)–(8.19):

$$K = \frac{p[RCOOH]_0 \cdot p[RCOOH]_0}{(1-p)[RCOOH]_0 \cdot (1-p)[RCOOH]_0} = \frac{p^2}{(1-p)^2} \qquad (8.20)$$

Solving (8.20) for p yields

$$p = \frac{\sqrt{K}}{1+\sqrt{K}} \qquad (8.21)$$

and, at equilibrium

$$P_n = \frac{1}{1-p} = \frac{1}{1 - \dfrac{\sqrt{K}}{1+\sqrt{K}}} \qquad (8.22)$$

As an example, for $K = 5$ one can calculate $p = 0.69$ and $P_n = 3$.

Higher degrees of polymerization (at a constant K) can only be reached by shifting the equilibrium to the products side. The system adjusts, creating new products (reactants are consumed) to establish equilibrium (8.17). As a result, higher conversions and higher

�«» **Fig. 8.9** Interfacial condensation of a diacid chloride with a diamine to a polyamide

Fiber

Diamine in Water

Polymer film formation at the interface

Diacid chloride in organic solvent
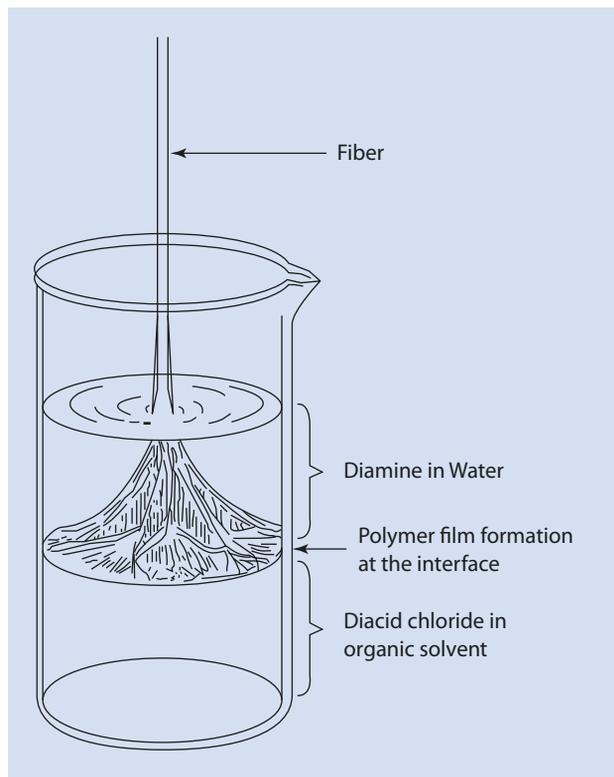
degrees of polymerization can be reached in accordance with the Carothers equation (see (8.15) or (8.7)).

To achieve high degrees of polymerization it is necessary to remove, as completely as possible, the water produced. Another option is to remove the resulting polymer, for instance by interfacial (�«» Fig. 8.9) or precipitation polymerization.

At the interface between the aqueous (containing the diamine) and organic phases (e.g., CCl_4 with diacid chloride) polyamide forms spontaneously and can be continuously removed. The polymeric film in the boundary layer forms a barrier for the reactants so that they only react with the chain ends of the polymers, and thus higher molar masses are achieved than with the more commonly employed melt condensation.

8.2.2 Molar Mass Distribution of Step-Growth Polymerization

The conversion of an AB-monomer into an $[AB]_P$ – polymer involves $(P-1)$ polymerization steps (e.g., esterifications). The probability that an A-group has reacted by time t corresponds to the conversion p $(0 \leq p \leq 1)$. The probability that an A-group has not reacted is thus $1-p$. The probability that a polymer molecule forms, with exactly P repeating units, requires not only $(P-1)$ reactions of the functional group A but also that one A-group does not react. With this the number n_P of these polymers is given by the product of the individual probabilities (in the following derivation note the distinction between P and p):

$$n_P = p^{P-1} \cdot n_t \tag{8.23}$$

n_P Number of molecules with degree of polymerization P

n_t Number of molecules remaining at time t

The sum of all n_P equals the number of molecules remaining, n_t:

$$\sum n_P = n_t \tag{8.24}$$

(All sums (Σ) in this chapter are considered over all elements, P)

From (8.3) and (8.7) it also follows that

$$n_t = n_0 \cdot (1-p) \tag{8.25}$$

where n_0 is the initial number of molecules.

Applying (8.25) to (8.23) yields

$$n_P = n_0 \cdot p^{P-1} \cdot (1-p) \tag{8.26}$$

For the weight fraction m_P it follows that

$$m_P = \frac{P \cdot n_P}{P_n n_0} = \frac{P n_P}{n_0}(1-p) \tag{8.27}$$

$$\sum m_P = 1 \tag{8.28}$$

Combining (8.26) and (8.27) gives

$$m_P = P \cdot p^{P-1} \cdot (1-p)^2 \tag{8.29}$$

◘ Figure 8.10 shows how the ratio n_P/n_0 and m_P shift with increasing conversion ($p=0.96$, 0.9875, 0.995) to higher degrees of polymerization P.

With the definition of the number average degree of polymerization, P_n:

$$P_n = \frac{\sum(n_P \cdot P)}{\sum n_P} = \sum\left(P \cdot \frac{n_P}{n_t}\right) \tag{8.30}$$
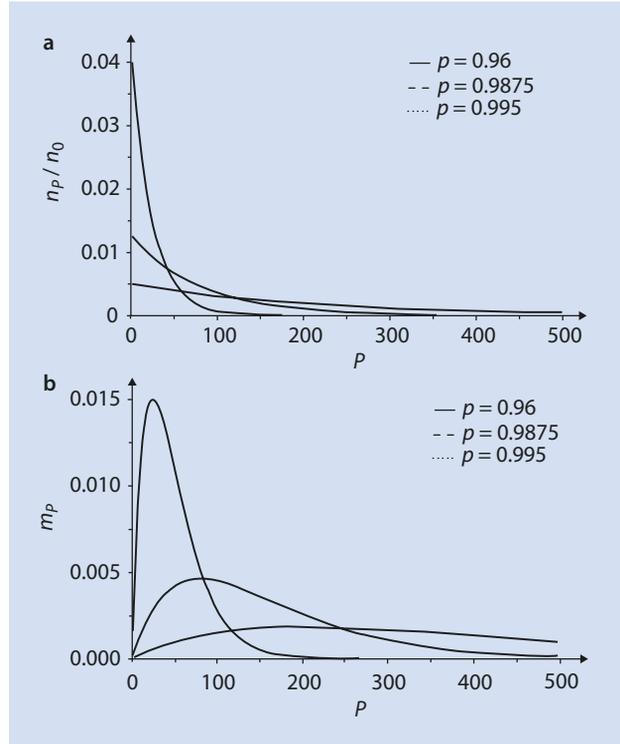
and from (8.23):

$$P_n = \sum\left(P \cdot p^{P-1}\right) \cdot (1-p) \tag{8.31}$$

can be derived.

According to progression theory:

$$\sum\left(P \cdot p^{P-1}\right) = \frac{1}{(1-p)^2}, \tag{8.32}$$

■ **Fig. 8.10** (**a**) n_P/n_0 and (**b**) m_P as a function of the degree of polymerization P. Calculated from (8.25) and (8.28)

so that the familiar Carothers equation (8.7) is found for P_n:

$$P_n = \frac{1}{1-p} \tag{8.7}$$

For the weight average degree of polymerization, P_w:

$$P_w = \sum \left(P \cdot m_P \right) \tag{8.33}$$

With (8.27) this gives

$$P_w = \sum \left(P^2 \cdot P^{P-1} \right) \cdot (1-p)^2 \tag{8.34}$$

Applying progression theory:

$$\sum \left(P^2 \cdot p^{P-1} \right) = \frac{1+p}{(1-p)^3} \tag{8.35}$$

We obtain for P_w:

$$P_w = \frac{1+p}{1-p} \tag{8.36}$$

For the polydispersity index (PDI) it follows:

$$PDI = \frac{P_w}{P_n} = \frac{1+p}{1-p} \cdot (1-p) = 1+p \tag{8.37}$$

As $p \rightarrow 1$ it follows from (8.37) that the PDI for an ideal step-growth polymerization (no secondary reactions, no ring formation) has the value 2 (8.38):

$$\frac{P_w}{P_n} = 2 \tag{8.38}$$

This PDI is the same as the PDI for radical polymerizations where termination is via disproportionation (▶ Sect. 9.3).

8.3 Linear, Branching, and Crosslinking Step-Growth Polymerizations

In this chapter, the extraction of linear polycondensates from AB-components and the reaction of AA- and BB-monomers, as well as of branched polycondensates from A_xB-components, is explained using the example of polyesters. Additionally, the conditions for crosslinking step-growth polymerization is introduced.

8.3.1 Monomers with Two Different Functional Groups

In general notation, an $[AB]_n$ – polymers originates from n AB-monomers. Corresponding to this schema, a polyester is derived from an ω-hydroxy carboxylic acid (HO–$(CH_2)_x$–COOH). However, the condition $x > 4$ must hold because for $x \leq 4$ the competing and alternative reactions shown in ◻ Figs. 8.11–8.13 are possible.

For $x = 1$ a lactide forms as the main product (◻ Fig. 8.11).

By means of anionic and cationic initiation or in the presence of special metal compounds (e.g., stannous octanoate), lactides undergo ring-opening polymerization (▶ Chap. 12).

When $x = 2$, heating produces mainly acrylic acid via dehydration (◻ Fig. 8.12).

When $x = 3$ or $x = 4$, lactones are the major products from the corresponding monomers (◻ Fig. 8.13).

In contrast, 6-hydroxyhexanoic acid ($x = 5$) can be converted into the corresponding polyesters without any problems (cf. ◻ Fig. 8.4).

8.3.2 Reaction of Two Different Monomers Each Having Two Identical Functional Groups

A typical example of this reaction type, where the respective polymer –$[AABB]_n$– is formed from AA + BB, is shown in ◻ Fig. 8.2. As described earlier, very high conversions and strict adherence to the stoichiometry are required for high molar masses (▶ Sect. 8.2.1).
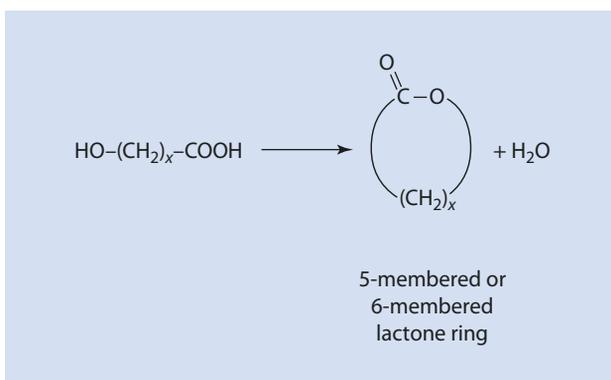
**Fig. 8.11** Synthesis of a lactide from hydroxyacetic acid

$$2\ HO{-}CH_2{-}COOH \longrightarrow \quad + 2\ H_2O$$
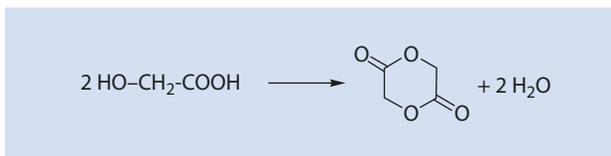
Fig. 8.12 Reaction of 3-hydroxypropionic acid to acrylic acid

$$HO{-}CH_2{-}CH_2{-}COOH \xrightarrow[-\ H_2O]{\Delta} \quad COOH$$
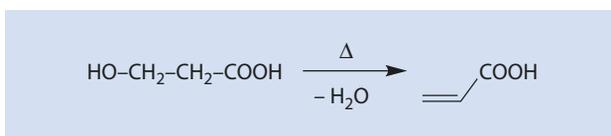
Fig. 8.13 Formation of the corresponding lactones from 4-hydroxybutanoic acid ($x=3$) or 5-hydroxypentanoic acid ($x=4$)

$$HO{-}(CH_2)_x{-}COOH \longrightarrow \quad + H_2O$$

$(CH_2)_x$

5-membered or
6-membered
lactone ring

Fig. 8.14 Formation of an AH-salt from 1.6-hexamethylene diamine (H) and adipic acid (A)
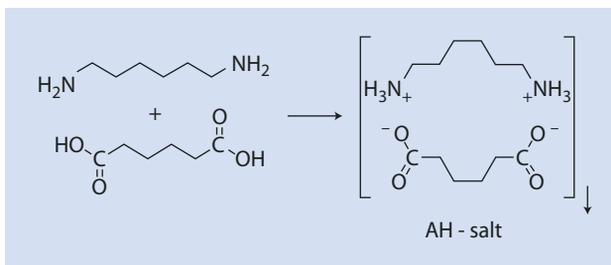
AH - salt

The problem of the stoichiometry of the reactants 1.6-hexamethylene diamine (AA) and adipic acid (BB) can be elegantly avoided by mixing the constituents beforehand and converting them into a so-called AH-salt that can be isolated in its solid state (Fig. 8.14). Here, both constituents are always exactly in the molar ratio 1:1.

By fusing in vacuo, the AH-salt can be dehydrated and converted into the corresponding polyamide 6.6 (Fig. 8.15).

Linear aliphatic polyamides are designated by numbering: either by using one number (e.g., polyamide 6 or polyamide 12) which indicates the number of C-atoms in the starting material (AB-monomer) or by using two digits (polyamide 6.6 or polyamide 6.12) when two starting materials are employed (AA and BB). The convention is that the first number gives the number of C-atoms in the diamine and the second number represents the number of C-atoms in the dicarboxylic acid.
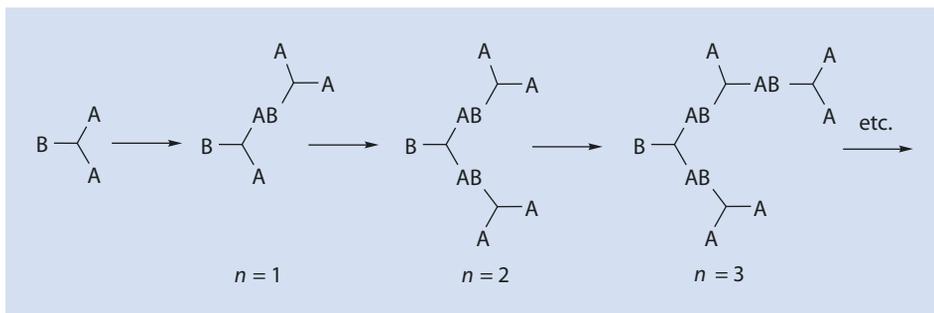
◘ **Fig. 8.15** Synthesis of polyamide 6.6 by fusion of the AH-salt

8.3.3 Polymers from A_xB-Monomers ($x \geq 2$)

A_2B-monomers can be converted into hyperbranched polymers through self-condensation. Such polymers have drawn not only scientific but also industrial attention in recent times, particularly as the polymerization of such A_xB-monomers ($x \geq 2$) cannot lead to crosslinking (► Sect. 1.3) (Flory 1952; Turner et al. 1993). These hyperbranched polymers are related to the so-called *dendrimers*. However, *dendrimers* have a perfect architecture which hyperbranched polymers do not. The latter are cheaper to produce. Schematically, an A_2B-monomer reacts as illustrated in ◘ Fig. 8.16.

The total number of free functionalities A (free A) in the polymer can be calculated from the overall functionality f in the A_xB-monomer ($f = 3$ for A_2B) and the number of links n with the formula (8.39) (◘ Table 8.1).

$$\text{Free A} = \underbrace{(f-1)}_{\substack{\text{Number of} \\ \text{function A} \\ \text{in the monomer}}} \cdot \underbrace{(n+1)}_{\substack{\text{Repeating units} \\ \text{in each} \\ \text{polymer molecule}}} - \underbrace{n}_{\substack{\text{Number of} \\ \text{reacted A} \\ \text{functional groups}}} = (n+1) \cdot f - 2n - 1 \tag{8.39}$$

The branching coefficient α specifies the probability of a functional group of one branching unit linking with another branching unit and thus, in hyperbranched systems, corresponds to the probability p_A that a randomly chosen A has reacted:

$$\alpha = p_A \tag{8.40}$$

Because the number of reacted A and B is equal, it follows that

$$p_A(f-1) = p_B = p \quad (f-1 = x \text{ in } A_xB) \tag{8.41}$$

Here p_B is the probability that B has reacted and P is the probability of the reaction of A with B. With (8.41), (8.40) can be transformed into (8.42):

$$\alpha = \frac{p}{f-1} \tag{8.42}$$

■ **Fig. 8.16** Formation of hyperbranched polymers from A_2B-monomers

■ **Table 8.1** Number of free A per polymer molecule as a function of reacted A, n (A_2B-monomer, $f=3$)	
n	Free A
1	3
2	4
3	5
4	6
⋮	⋮
20	22

For an A_2B-monomer ($f=3$) the relation (8.43) can be obtained from (8.42) at complete conversion ($p=1$):

$$\alpha = \frac{1}{2} \quad (\text{for } f = 3 \text{ and } p = 1) \tag{8.43}$$

Only when B in A_2B has completely reacted (this practically never happens) is $\alpha = ½$. Because crosslinking only occurs when this limit value is exceeded, the resulting polymer is not cross-linked and therefore soluble and fusible.

It must always be assumed that all functionalities of one type (A or B), independent of the size of the molecule, are equally reactive and thus react statistically, and that no intramolecular rings form. Macromolecules with a functionality B and $(n+1) \cdot f - 2n - 1$ unreacted A-positions then develop from A_nB, where n is the number of links (see (8.39)).

■ Figure 8.17 shows the result of the self-condensation of two dihydroxybenzoic acid derivatives protected with different protecting groups (TMS protecting group/COCI; CH_3CO protecting group/COOH).

Because of their multifunctionality and good solubility, their low solution viscosities (resulting from the high degree of branching), and their low tendency to crystallization and entanglement formation compared with linear polymers, these polymers have potential applications in catalytic converter technology and medicine as substrates, as well as materials in their own right.
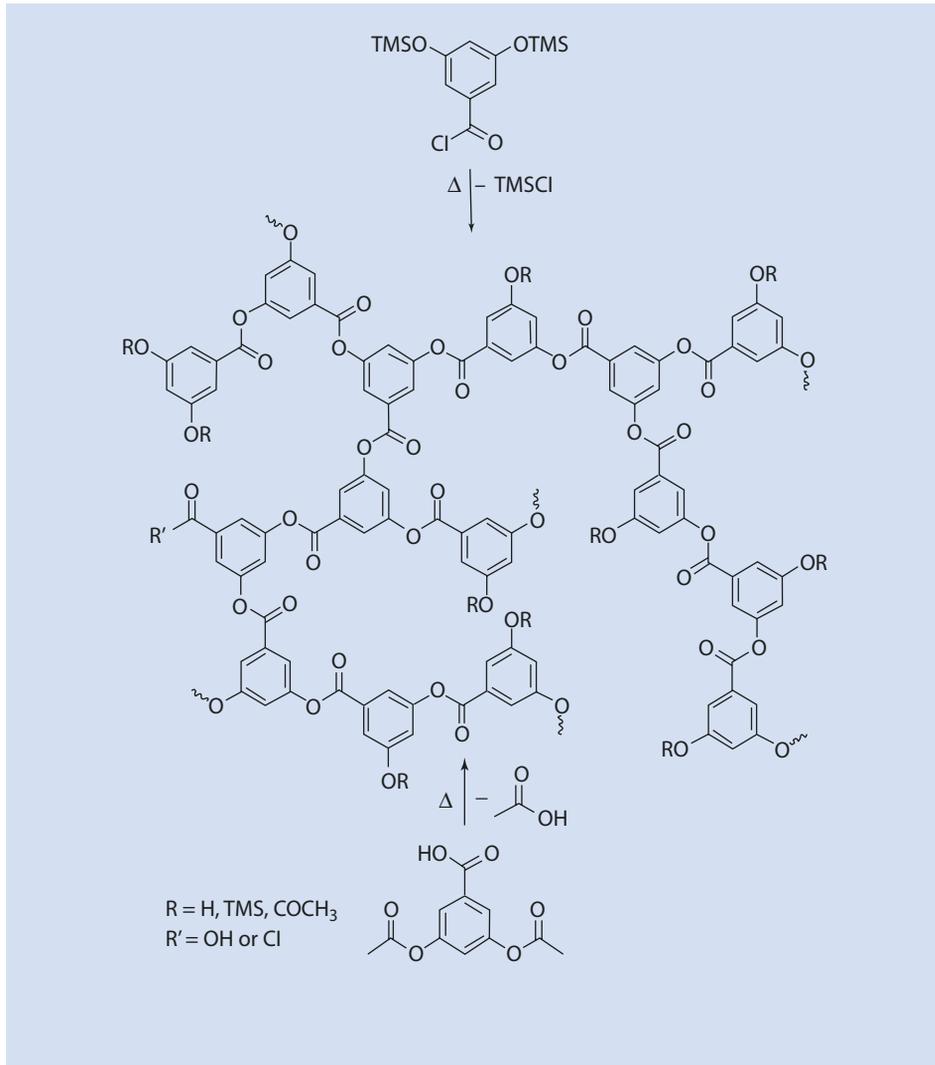
Fig. 8.17 Structure of a hyperbranched polyester based on two different monomers (TMS = trimethylsilyl)

8.3.4 Cross-Linking

The reaction of different monomers with more than two functional groups (e.g., the reaction of trifunctional alcohols with difunctional acids, ■ Fig. 8.18) with suitable stoichiometry of the functional groups eventually results in a three-dimensional network. Such networks have become indispensable materials because of their insolubility and their inability to melt.

◻ **Fig. 8.18** Formation of a network from di- and trifunctional monomers
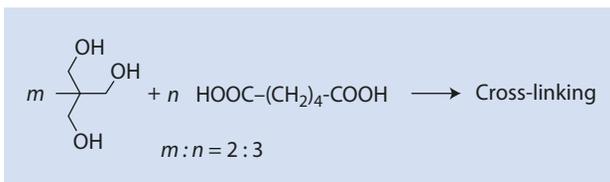
A cross-linked polymer is insoluble and does not melt; they can be distinguished from linear and branched polymers by solubility and melting tests.

From simple considerations, information as to when the polymer becomes a network, the so-called *gel point* can be obtained.

First, an average functionality $\bar{f}$ for the reaction mixture is defined as

$$\bar{f} = \frac{\sum n_j f_j}{\sum n_j} \qquad (8.44)$$

8

n_j Number of monomer molecules j
f_j Functionality of the monomer j

For the reaction shown in ◻ Fig. 8.18 ($m=2$ and $n=3$), (8.45) gives the average functionality:

$$\bar{f} = \frac{n_m \cdot f_m + n_n \cdot f_n}{n_m + n_n} = \frac{2 \cdot 3 + 3 \cdot 2}{2 + 3} = 2.4 \qquad (8.45)$$

With the definition for the conversion p of the difunctional reactant:

$$p = \frac{2(n_0 - n_t)}{\bar{f} \cdot n_0} \qquad (8.46)$$

n_0 Number of molecules (monomers) at time $t=0$
n_t Number of molecules (monomers + polymers) at time t
$2(n_0 - n_t)$ Number of functional groups which have reacted at time t
$\bar{f} \cdot n_0$ Average number of existent functional groups at time $t=0$.

With the definition, given above, for the degree of polymerization P_n:

$$P_n = \frac{n_0}{n_t} \qquad (8.3)$$

it follows that

$$p = \frac{2}{\bar{f}} \left(1 - \frac{1}{P_n} \right) \qquad (8.47)$$

At the gel point, it holds that $P_n \to \infty$. The conversion required to reach the gel point can be derived as

$$p = \frac{2}{\bar{f}}$$

(8.48)

The conversion at the gel point as a function of the functionality of the reaction mixture is given in ◘ Table 8.2.

◘ Figure 8.19 clearly shows how the sharp rise of P_n shifts to lower conversions with increasing average functionality of the mixture.

Industrially important networks can be made, for example, from the reaction of diisocyanates with multifunctional alcohols or from reaction of triisocyanates with diols (◘ Fig. 8.20).

By varying the isocyanates and alcohols both with regard to structure and functionality, many and varied network properties can be achieved.

◘ **Table 8.2** Conversion required to reach the gel point depending on the functionality of the reaction mixture

$\bar{f}$	P
2	1.0000
2.1	0.9524
2.2	0.9091
2.3	0.8696
2.4	0.8333
3	0.6667
4	0.5000

◘ **Fig. 8.19** Influence of the functionality $\bar{f}$ on the degree of polymerization P_n
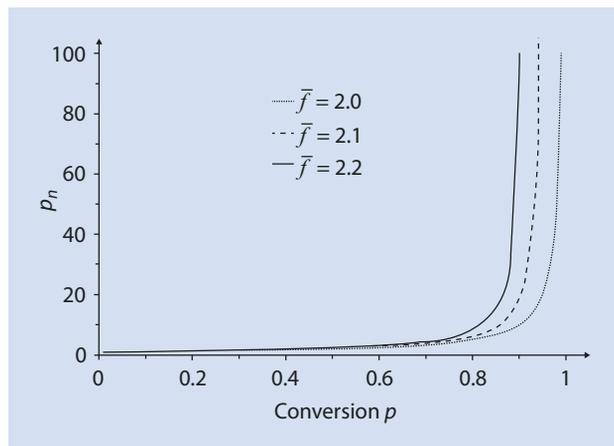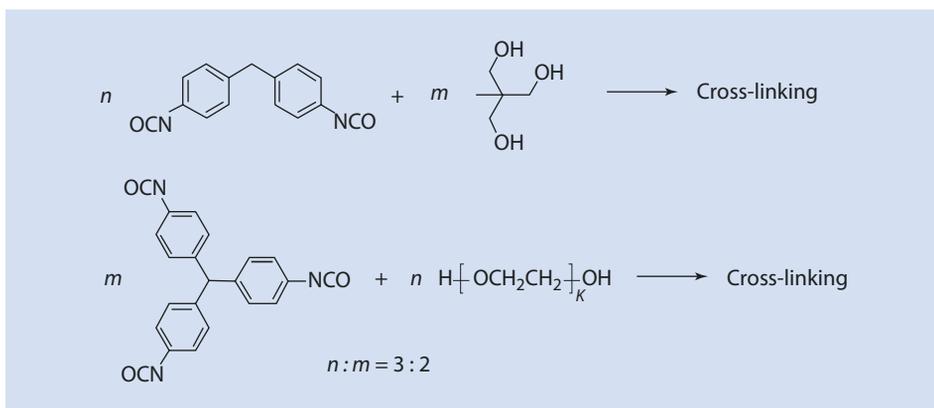
Fig. 8.20 Formation of polyurethane networks

Fig. 8.21 Condensation reaction of a carboxylic acid with an alcohol to give an ester

8.4   Kinetics of Step-Growth Polymerization

The fundamental kinetic theories of step-growth polymerization date back to P.J. Flory. These are based on the assumption that the individual reaction steps can be seen as reactions between the functional groups, and that the activity of these groups is independent of the size of the molecules. Using the example of the esterification, the processes and their consequences are explained (◘ Figs. 8.21 and 8.22). The fundamental propositions can also be applied to other step-growth polymerizations.

The reaction between a carboxylic acid and an alcohol results in an ester (◘ Fig. 8.21).

The ester formation can be subdivided into the stages illustrated in ◘ Fig. 8.22.

The attack by the alcohol (k_3) is the slowest and therefore determines the speed of the overall reaction. Thus, the overall rate, v_{br} is

$$v_{br} = -\frac{d[R'OH]}{dt} = -\frac{d[RCOOH]}{dt} = k_3 \left[RC^+ (OH)_2 \right] [R'OH] \tag{8.49}$$

From ◘ Fig. 8.22a it follows that

$$k_1 \cdot [RCOOH][HA] = k_2 \cdot \left[RC^+ (OH)_2 \right] \left[A^- \right] \tag{8.50}$$

a Protonation of the COOH-group

b Addition of alcohol

c Water elimination
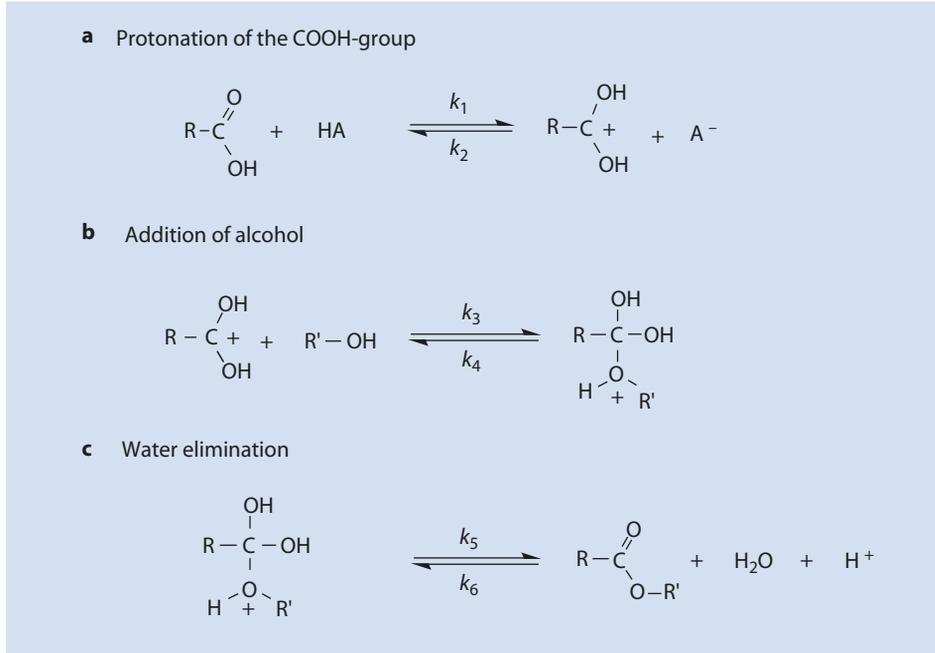
🔹 **Fig. 8.22** (**a–c**) Mechanism of acid-catalyzed ester formation by reaction of a carboxylic acid with an alcohol

which can be rearranged as

$$\left[RC^+(OH)_2 \right] = \frac{k_1}{k_2} \cdot \frac{[RCOOH][HA]}{[A^-]}$$

(8.51)

The term for the dissociation constant of the acid HA (8.52) can be rearranged to (8.53), and substitution in (8.51) then gives (8.54):

$$K_{HA} = \frac{[H^+][A^-]}{[HA]}$$

(8.52)

$$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_{HA}}$$

(8.53)

$$\left[RC^+(OH)_2 \right] = \frac{k_1}{k_2} \cdot \frac{[RCOOH][H^+]}{K_{HA}}$$

(8.54)

If (8.54) is combined with (8.49) one obtains (8.55) or (8.56):

$$-\frac{d[RCOOH]}{dt} = \frac{k_1 \cdot k_3}{k_2} \cdot \frac{[RCOOH][R'OH][H^+]}{K_{HA}} \tag{8.55}$$

$$-\frac{d[RCOOH]}{dt} = k'[RCOOH][R'OH][H^+] \tag{8.56}$$

whereby in (8.57)

$$k' = \frac{k_1 \cdot k_3}{k_2 \cdot K_{HA}} \tag{8.57}$$

Thus, the rate of the esterification depends linearly on the alcohol, carboxylic acid, and proton concentrations.

Esterification can either be self-catalyzed or externally catalyzed. For *self-catalysis* it holds:

$$[H^+] = [RCOOH] = [Kat] \tag{8.58}$$

Furthermore, with precise stoichiometry:

$$[RCOOH] = [R'OH] \tag{8.59}$$

With (8.58) and (8.59), (8.56) becomes

$$-\frac{d[RCOOH]}{dt} = k'[RCOOH]^3 \tag{8.60}$$

For simplification we put

$$[RCOOH] = c \tag{8.61}$$

and (8.60) becomes

$$-\frac{dc}{dt} = k'c^3 \tag{8.62}$$

By separating the variables and subsequent integration one obtains

$$\int_{c_0}^{c_t} \frac{dc}{c^3} = -k' \int_0^t dt \tag{8.63}$$

$$\left[-\frac{1}{2}\left(\frac{1}{c^2}\right) \right]_{c_0}^{c_t} = -\frac{1}{2}\left(\frac{1}{c_t^2} - \frac{1}{c_0^2} \right) = -k't + k' \cdot 0 \tag{8.64}$$

$$\frac{1}{c_t^2} - \frac{1}{c_0^2} = 2k't \tag{8.65}$$

It has already been shown that for the conversion p:

$$p = \frac{c_0 - c_t}{c_0} = 1 - \frac{c_t}{c_0} \tag{8.5}$$

or

$$c_t = (1 - p) \cdot c_0 \tag{8.6}$$

Thus, from (8.65):

$$\frac{1}{(1-p)^2 \cdot c_0^2} - \frac{1}{c_0^2} = 2k't \tag{8.66}$$

$$\frac{1}{c_0^2} \cdot \left(\left(\frac{1}{1-p} \right)^2 - 1 \right) = 2k't \tag{8.67}$$

$$\left(\frac{1}{1-p} \right)^2 = 2k't \cdot c_0^2 + 1 \tag{8.68}$$

Using Carothers' equation (▶ Sect. 8.2.1) for the degree of polymerization (8.7) one obtains (8.69):

$$P_n = \frac{1}{1-p} \tag{8.7}$$

$$P_n = \sqrt{2k't \cdot c_0^2 + 1} \tag{8.69}$$

As a first approximation for the case of self-catalysis, the average degree of polymerization increases with the square root of the time:

$$P_n \propto \sqrt{t} \tag{8.70}$$

For *external catalysis*, (8.56) and (8.59) also apply. If [H⁺] is replaced by [*Kat*] then one gets:

$$-\frac{d[RCOOH]}{dt} = k'[RCOOH][R'OH][Kat] \tag{8.71}$$

The catalyst concentration [*Kat*] and the rate constant k' can be consolidated to a new constant k'':

$$k'[Kat] = k'' \tag{8.72}$$

Thus, assuming the concentration of catalyst remains constant, the third-order, self-catalyzed reaction (8.62) becomes a second-order reaction:

$$-\frac{dc}{dt} = k''c^2 \tag{8.73}$$

By separating the variables and subsequent integration one obtains

◻ Fig. 8.23 Comparison of an externally catalyzed with a self-catalyzed polycondensation. *Squares* externally catalyzed, *triangles* self-catalyzed
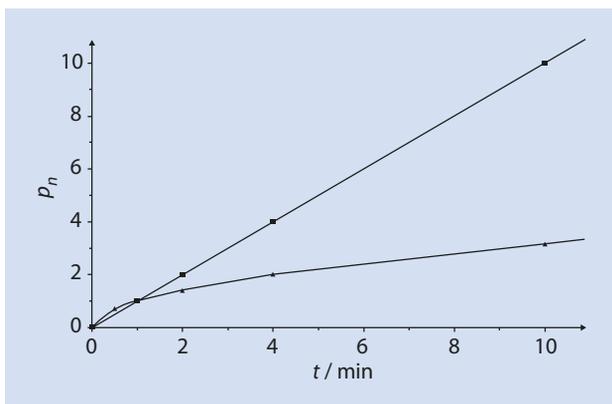
$$-\frac{dc}{c^2} = k''dt \tag{8.74}$$

$$-\int_{c_0}^{c_t} \frac{dc}{c^2} = k'' \int_0^t dt \tag{8.75}$$

$$-\left[-\frac{1}{c}\right]_{c_0}^{c_t} = \left[k''t\right]_0^t \tag{8.76}$$

$$+\left(\frac{1}{c_t} - \frac{1}{c_0}\right) = k''(t-0) \tag{8.77}$$

Combining this with (8.6) one obtains

$$\frac{1}{(1-p) \cdot c_0} - \frac{1}{c_0} = k''t \tag{8.78}$$

$$\frac{1}{c_0} \cdot \left(\frac{1}{1-p} - 1\right) = k''t \tag{8.79}$$

$$\frac{1}{1-p} - 1 = k''t \cdot c_0 \tag{8.80}$$

$$\frac{1}{1-p} = k''c_0 t + 1 \tag{8.81}$$

Finally, combining (8.81) with (8.7) one obtains

$$P_n = k''c_0 t + 1 \tag{8.82}$$

Because external catalysis leads to the average degree of polymerization increasing linearly with time, external catalysis is preferred over self-catalysis, where the degree of polymerization is proportional to the square root of time (◻ Fig. 8.23).

Fig. 8.24 Syntheses of PET and PBT via (**a**) polycondensation of terephthalic acid or (**b**) transesterification of terephthalic acid dimethyl ester with the respective diol
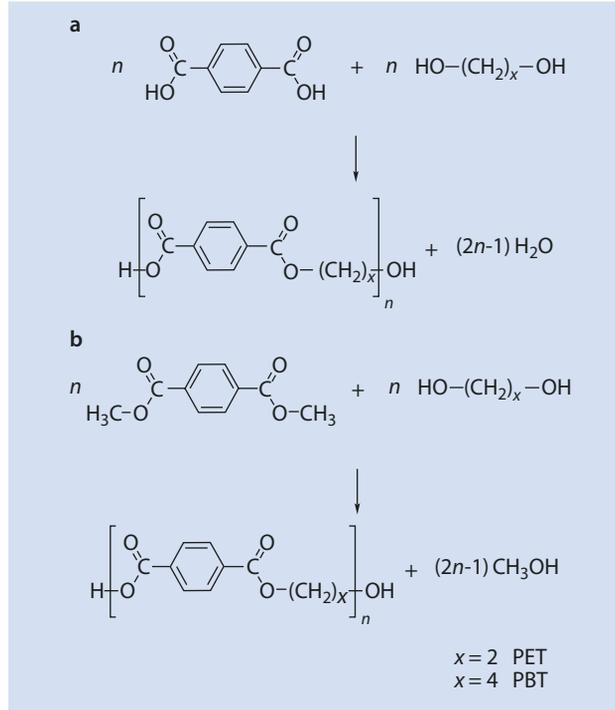
8.5 Typical Polycondensates

In this chapter the most important technological polycondensates, such as polyester, polycarbonates, and polyamides are introduced. Their synthesis, processing, and typical applications are described.

8.5.1 Polyester

Polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) belong to the most important polymers of this class. PET is used as a fiber and in the packaging sector, in particular as plastic bottles. PBT is used for high-quality construction materials, e.g., in the automobile and electrical industries. PET and PBT are available via reaction of terephthalic acid with ethylene glycol or with 1.4-butandiol, respectively, or through transesterification of terephthalic acid dimethyl ester with the respective diol (Fig. 8.24).

Typical trade names for PET are Arnite A (DSM), Rynite (DuPont), and Valox (SABIC).

PET crystallizes very slowly and can be partially crystalline or amorphous depending on the processing conditions.

A partially crystalline PET (PET-C) has medium strength, high stiffness and hardness, but relatively poor impact strength. Areas of application are in electrical (e.g., telephones, computers, switch parts, and spark plugs.) and mechanical engineering (e.g., bearings, gears, and pump parts). Moreover, it is also processed to make zippers, buttons, and furniture fittings. Amorphous PET (PET-A) is transparent at thicknesses up to 5 mm. Above 90 ° C it crystallizes and becomes opaque. Because of its good oxygen and carbon dioxide
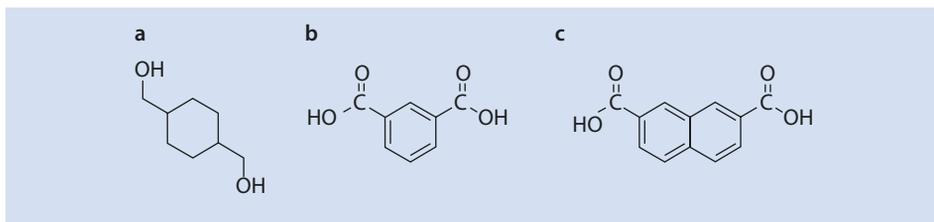
Fig. 8.25 Structural formula of (**a**) cyclohexane-1,4-dimethylol, (**b**) isophthalic acid, and (**c**) naphthalene-2,7-dicarboxylic acid

barrier properties, it is the preferred material for beverage containers. It is also used as a support material for thermal and magnetic typewriter ribbons, photographic film, and adhesive strips.

Typical trade names for PBT are Arnite T (DSM), Crastin (DuPont), Enduran (SABIC), Pocan (Lanxess), and Ultradur (BASF).

High dimensional stability, rigidity, abrasion resistance, and low creep deformation properties are the special attributes of PBT. Typical applications include sliding bearings, pulleys, couplings, and household appliances. By inclusion of bulky monomers such as cyclohexane-1,4-dimethylol (cyclohexane-1,4-dimethanol), as well as by partial substitution of terephthalic acid (benzene-1,4-dicarboxylic acid) with isophthalic acid (benzene-1,3-dicarboxylic acid) or naphthalene 2,7-dicarboxylic acid (Fig. 8.25), the crystallization tendency of PET and PBT can be suppressed and their transparency improved. This expands the range of applications to the packaging for hot foods.
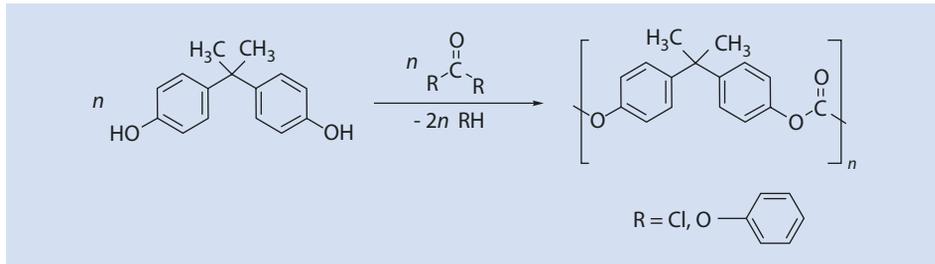
8.5.2 **Polycarbonates (PC)**

Polycarbonates are linear polyesters of carbonic acid. Well-known trade names of polycarbonates are Makrolon (Bayer Material Science), Lexan (SABIC), and Xantar (Mitsubishi). The industrially most important polycarbonate is produced from bisphenol A and phosgene or from diphenyl carbonate (Fig. 8.26).

The reaction of bisphenol A with diphenyl carbonate can be performed as a melt condensation; the crucial reaction here is a transesterification.

The reaction between bisphenol A and phosgene is carried out as an interfacial condensation. In this case, the phosgene is in the organic methylene chloride phase and the bisphenol A is present as the disodium salt in an aqueous alkaline solution. The reaction occurs at the phase boundary. A variant is homogeneous polymerization in pyridine.

By complete replacement of bisphenol A with other bisphenols (Fig. 8.27), important properties of the resulting polycarbonates, such as glass transition temperature and refractive index, can be varied. Polycarbonates from o,o,o′,o′-tetramethyl-bisphenols are very different from those with unsubstituted bisphenol constituents. They have higher glass transition temperatures and lower melt viscosities and hence are easier to process.

Typical fields of application worth mentioning are terminal strips, special plugs, baby bottles, parts for office machines, film and slide cassettes, optical data storage (CD), headlight reflectors, canopies, soundproof walls, and the side and rear windows of trucks and tractors.

Fig. 8.26 Synthesis of polycarbonates by polycondensation of bisphenol A with phosgene or diphenyl carbonate
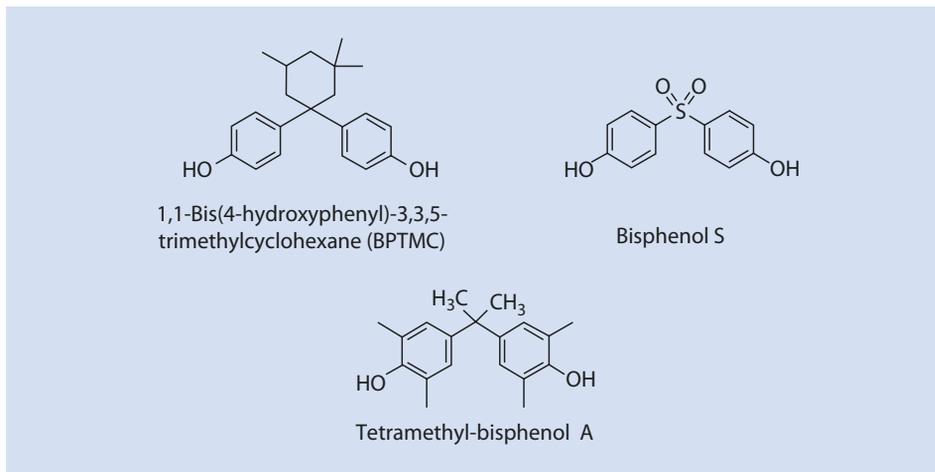
Fig. 8.27 Some alternative bisphenols for the preparation of polycarbonates

8.5.3 Polyestercarbonate (PEC)

By co-condensation of bisphenol A with terephthaloyl dichloride and phosgene, a polyestercarbonate is formed that has a higher heat resistance than the simple polycarbonate from bisphenol A and phosgene possesses. This is because of the partial substitution of CO by –CO–Ar–CO– units (◘ Fig. 8.28).

Typical applications for PECs are curling tongs, microwave dishes, headlight reflectors, and bobbins, where operating temperatures of 140–180 °C are possible and at the same time higher strengths are required. Examples of trade names are Lexan PPC (SABIC) and Ardel (BP-Amoco).

8.5.4 Aliphatic Polyamides (PA)

Polyamides can be prepared from a single component AB, e.g., 6-aminohexanoic acid or from the corresponding ε-caprolactam. Alternatively, they can be prepared from two components AA + BB, e.g., 1,6-hexamethylene diamine (1,6-diamino hexane) and adipic acid (butane-1,4-dicarboxylic acid) (◘ Fig. 8.29).
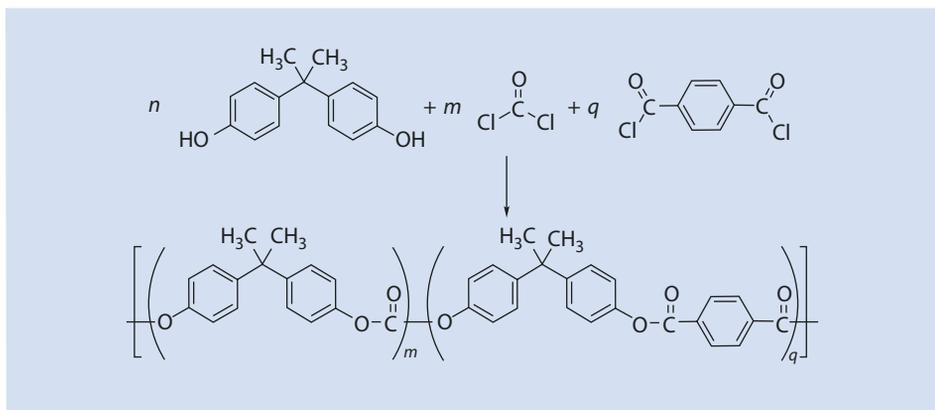
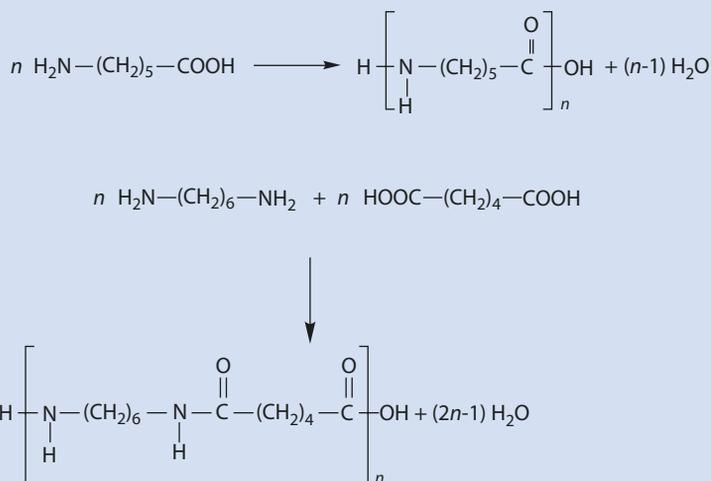**Fig. 8.28** Synthesis of a polyestercarbonate ($m + q = n$)

8

Fig. 8.29 Synthesis of (**a**) polyamide 6 and (**b**) polyamide 6,6

Polyamides are semi-crystalline. Hydrogen bonds between the amide groups of adjacent molecules are the reason for the elevated glass tranition temperatures compared to other non-polar polymers. Their high resilience, low coefficents of friction, and excellent wear properties are valued material properties. Table 8.3 contains selected examples of industrially interesting polyamides.

Polyamides are used in mechanical engineering, e.g., for gears, wheels, and bearings, and in the automotive industry as headlight housings, fuel lines, fenders, and intake pipes. In electrical engineering, they are indispensable as cable and wire sheathing. In the packaging sector, polyamides find a variety of uses as roasting bags, sausage casings, and coatings.

📍 Table 8.3 Selected examples of trade names and manufacturers of various polyamides	
Polyamide (PA)	**Trade mame (manufacturer)**
PA 6	Durethan B (Lanxess), Ultramid B (BASF), Akulon (DSM)
PA 11	Rislan B (Atofina)
PA 12	Grilamid (EMS), Rislan B (Atofina)
PA 4,6	Stanyl (DSM)
PA 6,6	Durethan A (Lanxess), Ultramid A (BASF), Minlon (DuPont)
PA 6,10	Ultramid S (BASF), Zytel (DuPont)
PA 6,12	Vestamid (Evonik), Zytel (DuPont)

The properties of the various types of polyamides are essentially determined by the hydrogen bonds between the amide bonds of neighboring macromolecules. Thus, for example, the melting temperature of elongated PA 6 is 222 °C, whereas the melting temperature of PA 6,6 is almost 40 °C higher, 260 °C. As shown in 📍 Fig. 8.30, polymer chains of PA 6,6 in a stretched state can form hydrogen bonds between the chains extremely well. An optimal arrangement can be achieved by moving the chains relative to each other during processing, for example, by drawing, until all the hydrogen bridges "snap" together.

In contrast, the main chain of PA 6 is less symmetric—the mirror plane that is present in PA 6,6 is missing. From 📍 Fig. 8.30 it is clear that the optimal formation of hydrogen bonds between the chains is only possible if the chains are facing away from each other. If both chains are facing in the same direction, the number of hydrogen bonds is reduced compared with PA 6.6. However, a complete "turn" of the polymer chains does not occur because of the high viscosity of the system as well as the entanglement of the individual chains (▶ Chap. 6).

8.5.5 Partially Aromatic and Aromatic Polyamides and Polyimides

Polyamides in which aliphatic units are partially replaced by aromatic moieties (📍 Fig. 8.31) are known as partially aromatic polyamides. They are superior to purely aliphatic polyamides with respect to their mechanical properties and their heat resistance. Typical commercial products are Ultramid T (BASF) and Durethan T (Lanxess). As a general abbreviation the convention is that, e.g., a polyamide synthesized from 1,6-hexamethylene diamine, adipic acid, and terephthalic acid is called PA 6/6 T.

Simple aromatic polyamides (polyaramides) are formed from aromatic components, e.g., from 1,4-, or 1,3-diaminobenzene and terephthalic acid (or terephthalic acid dichloride) or isophthalic acid (or isophthalic acid dichloride) (📍 Fig. 8.32).

These polymers are soluble in concentrated sulfuric acid and can be spun from it. Polyaramide fibers excel in their high rigidity, high impact resistance, high elongation, and good vibration absorption. The best-known applications are in the field of security
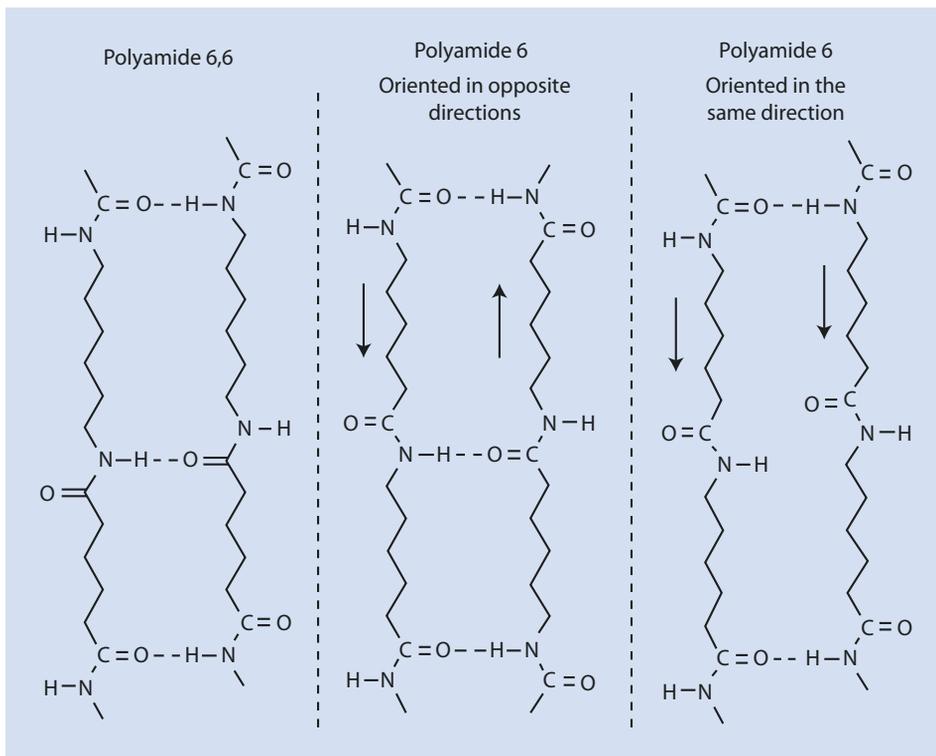
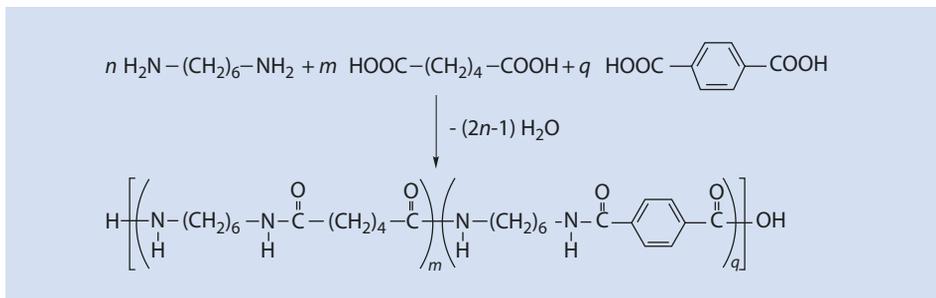**Fig. 8.30** Molecular arrangement and hydrogen bonds in PA 6.6 and PA 6

Fig. 8.31 Synthesis of a partially aromatic polyamide ($m + q = n$)

and safety (bullet-proof vests, armor for vehicles), but they are also used as a replacement for asbestos (in brake linings and gaskets) and as reinforcing agents (for fiber-optic cable, rubber materials, and sporting goods).

Because of their structure and the possibility of forming hydrogen bonds, these polymers have lyotropic liquid crystalline properties (■ Fig. 8.33; ▶ Chap. 20). This explains the

Fig. 8.32 Synthesis of aromatic polyamides

Kevlar (DuPont)

Nomex (DuPont)   X = OH, Cl
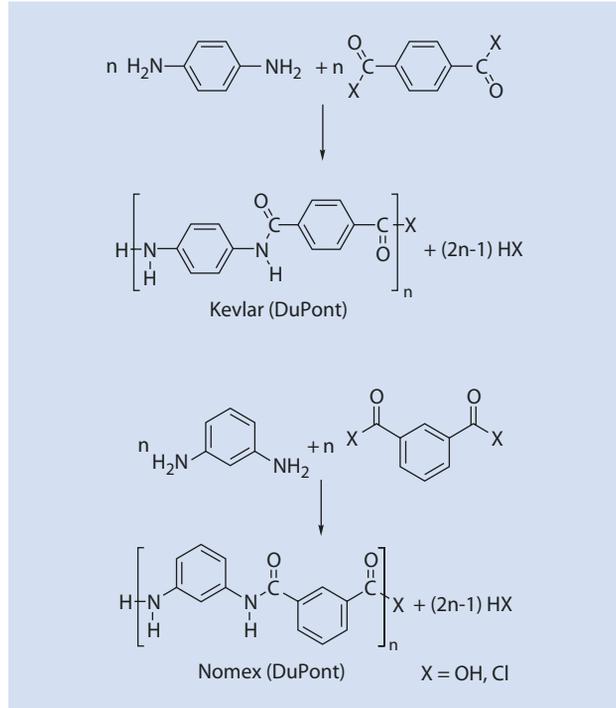
**Fig. 8.33** Two neighboring para-polyaramide chains with hydrogen bonds
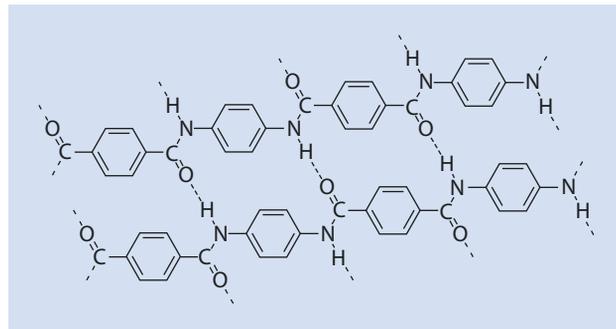
strong directional dependence of their mechanical properties (high-strength and resistance to bending in the direction of the polymer chains).

The synthesis of aromatic polyamides with an alternating sequence of NH- and CO-functions can be accomplished by employing 4-aminobenzoic acid but such polymers can also be synthesized indirectly via a Schotten–Baumann reaction (Fig. 8.34).

The direct path from 4-aminobenzoic acid to polymer is not useful because of partial decomposition of monomers at higher temperatures.

In contrast to the polyamides, the polyimides contain tertiary nitrogen atoms (imides) in the polymer chain. A polyimide is obtained, for example, by reaction of 1,3-diamino benzene with pyromellitic acid in two steps (Fig. 8.35).

◻ **Fig. 8.34** Formation of an aromatic polyamide from 4-aminobenzoic acid indirectly via the Schotten–Baumann reaction
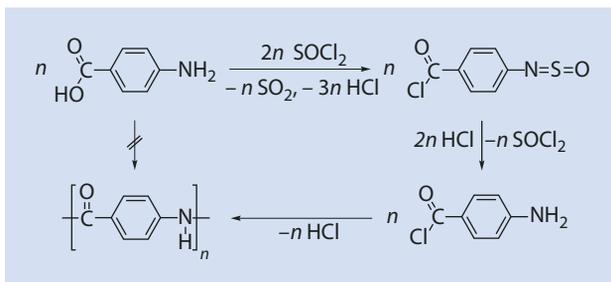
◻ **Fig. 8.35** Synthesis of a polyimide from diamino benzene and pyromellitic acid
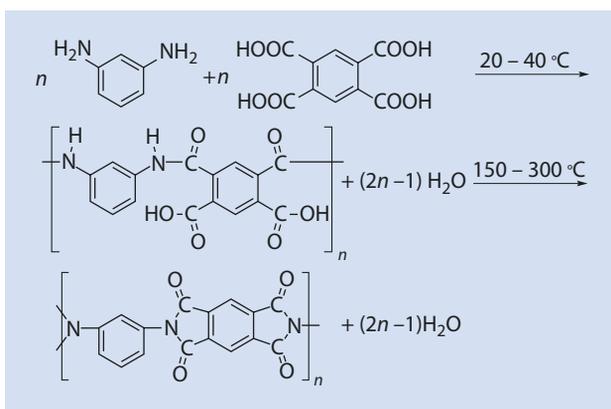
In the first step, a still soluble polyamide acid is formed, which is converted into the insoluble polyimide at elevated temperature. Polyimides, which are available in a variety of structural variations, are employed in the electronic industry as flexible cables and insulating films. Noteworthy properties are their fire resistance and good heat resistance.

8.5.6 Polymers of Isocyanates

Typical reactions of isocyanates which can be used for a stepwise synthesis of polymers are summarized in ◻ Fig. 8.36.

The most commonly used diisocyantes are shown in ◻ Fig. 8.37.

From the reaction of trifunctional isocyanates with di- or trifunctional alcohols, amines, or carboxylic acids, cross-linked, i.e., insoluble polymers are formed.

The diisocyanate polymerization reactions are characterized by a wide variety of available components (monomers and oligomers). The reactions often occur at room temperature and without the formation of by-products. By adjusting the stoichiometry, the molar masses can be controlled; the use of monomers with more than two functional groups leads to the formation of crosslinking points (▶ Sect. 8.3.4). The main areas of application are highly elastic foams (mattresses), rigid foams, and rigid and flexible molded parts with a compact outer skin (window frames, skis, steering wheels, shoe soles, etc.).
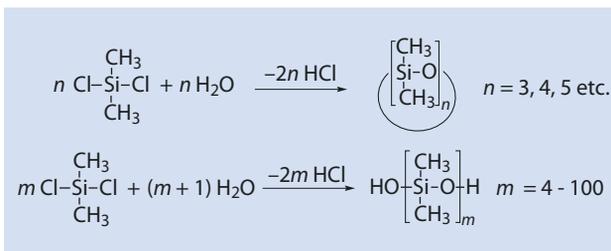
Fig. 8.36 Reaction of isocyanates with alcohols, amines and carboxylic acids

Fig. 8.37 Selection of commonly used diisocyanates (TDI: 2,4-tolyl diisocyanate (often a mixture of 2,4- and 2,6-isomers), NDI: 1.5-naphthyl diisocyanate, MDI: 4,4'-methylene diphenyl isocyanate, HDI: 1,6-hexamethylene diisocyanate)

8.5.7 Polysiloxanes

The complete hydrolysis of dimethyl dichlorosilane results in a mixture of cyclic compounds and hydroxyl-terminated oligomeric dimethyl siloxanes (■ Fig. 8.38).

By varying the hydrolysis conditions, the proportion of the cyclic compounds ($n = 3$, $n = 4$) can be controlled. The starting materials for the so-called equilibrium polymerization are cyclic compounds (▶ Chap. 12), whereas polycondensation is only possible with hydroxyl oligomers.

By adding a monchloro trialkyl silane, the molar mass of these polymers can be limited (■ Fig. 8.39).

α,ω-Dihydroxy polysiloxanes can be crosslinked by addition of trichloroalkyl silane or tetrachlorosilane (■ Fig. 8.40).

By varying the proportions of the reactants and by using different R, the properties of the networks can be widely varied.

Polysiloxanes are thermally stable and UV resistant. Because of the low intermolecular forces and the rotational capability of the Si-O-Si bond, they have a low glass transition temperatures.

Industrially used polysiloxanes are available as low-viscosity liquids, oils, fats, resins, and rubbers. Oils and fats are used as dielectrics, hydraulic oils, lubricants, and water repellents. Resins are required, for instance, for electrical insulation and protective coatings. Molded and extruded products as well as wire and cable insulation are made from silicone rubber.

Fig. 8.38 Hydrolysis of dimethyl dichlorosilane

$$n \; Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \; + \; n\,H_2O \xrightarrow{\;-2n\,HCl\;} \left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O \right)_n \quad n = 3, 4, 5 \text{ etc.}$$

$$m \; Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \; + \; (m+1)\,H_2O \xrightarrow{\;-2m\,HCl\;} HO\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O \right]_m H \quad m = 4 - 100$$

Fig. 8.39 Regulation of molar mass with monofunctional chloroalkyl silanes

$$HO\left[\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O \right]_n H \; + \; 2 \; Cl-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-R \xrightarrow{\;-2\,HCl\;} R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O\left[\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O \right]_n \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-R$$
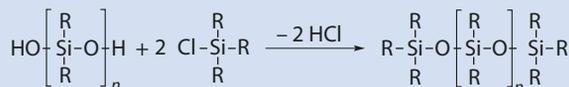
Fig. 8.40 Crosslinking of polysiloxanes with trichloro alkyl silane

$$k \; HO\left[\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O \right]_n H \; + \; m \; Cl-\underset{\underset{Cl}{|}}{\overset{\overset{R}{|}}{Si}}-Cl \xrightarrow{\;-x\,HCl\;} \text{Cross-linking}$$
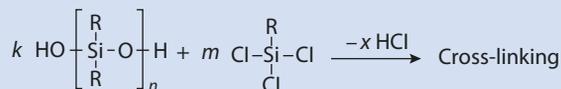
Fig. 8.41 Synthesis of a polyalkylene polysulfide

$$n \; Cl-(CH_2)_2-Cl \; + \; n \; Na_2S_x \longrightarrow \left[(CH_2)_2\text{-}S_x \right]_n + 2n \; NaCl$$

8.5.8 Selected Specialty Polymers

Here, examples of polymers that are also synthesized via a step-growth mechanism and which have achieved a certain economic importance are described. These include polyalkylene polysulfides, polyarylene sulfides, polysulfones, polyether ketones, and polyphenylene oxides.

8.5.8.1 Polyalkylene Polysulfides

The reaction of aliphatic dihalides with alkali metal polysulfides results in polymers with rubber-like properties. A typical reaction example is presented in ◘ Fig. 8.41.

Subsequently, when some of the S_x groups are split by a reducing reaction, liquid oligomers are formed that have SH groups at both ends and are can therefore be described as telechelic[2] (◘ Fig. 8.42).

In the telechelic molecules, S_x bonds remain that have not been split. The degree of division and thus the molar mass of the telechelic polymers can be controlled by the amount of reducing agent used.

By oxidation, for example with PbO_2 or quinone, the SH groups can be converted back into polysulfide bonds. Such materials, which have become known by their trade name, Thiokol, are used in large quantities for seals in the building industry, the automotive

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2   Telechelics are oligomers with well-defined functional end groups, with which further chemical reactions are possible.

Fig. 8.42 Synthesis of SH-terminated telechelic polymers by splitting the S_x groups
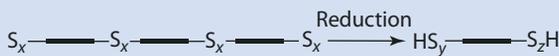
Fig. 8.43 Synthesis of polyphenylene sulfide

industry, and shipbuilding, where they are greatly appreciated for their oxygen and solvent resistance.

8.5.8.2 Polyarylene Sulfides

By reacting 1,4-dichlorobenzene in *N*-methyl pyrrolidone with Na_2S, polyphenylene sulfide (**Fig. 8.43**) can be obtained.

This polymer has become known by its trade name, Ryton (Chevron Phillips), and is very popular because of its exceptional mechanical properties, excellent dimensional stability, and insulating properties. The main fields of application are heat- and corrosion-resistant metal coatings and glass fiber reinforced injection molded parts.

8.5.8.3 Polysulfones

Polysulfones are thermoplastic construction materials that have a high strength, hardness, impact resistance, and chemical resistance. Their main fields of application are in the aerospace and electronics industries and in the household sector.

They can also replace die castings of zinc, bronze, and lead. Polysulfones can be produced via nucleophilic and electrophilic substitution reactions. **Figure 8.44** shows the nucleophilic attack of deprotonated bisphenol A on 4,4′-dichlorodiphenyl sulfone, i.e., one of the monomers already contains the sulfone group (**Fig. 8.44**).

Alternatively, polysulfones can be obtained by electrophilic substitution. Here, the sulfone group is formed by a Friedel–Crafts reaction of a sulfonic acid dichloride (**Fig. 8.45**).

Both synthetic methods are very varied because of the possible reactants.

8.5.8.4 Polyether Ketones

Entirely analogous to the polysulfones are the polyether ketones (PEK), which are available either by nucleophilic or by electrophilic substitution reactions (**Fig. 8.46**).

Polyether ketones are resistant to many organic and inorganic chemicals. Applications of PEK can be found in the automotive and aerospace industries and for high voltage as well as medical engineering (reusable, sterilizable, biocompatible, and transparent to X-rays).

8.5.8.5 Polyphenylene Oxides

Polyphenylene oxides (PPO) can be obtained by the oxidative dehydrogenation of 2,6-disubstituted phenols (**Fig. 8.47**).

Poly-2,6-dimethyl-1,4-phenylene oxide is completely miscible with polystyrene. This PPO and PPO/PS blends are used for electrical components. PPO are ideal materials for impellers, valves and flow meters. Surgical devices made of PPO can be easily sterilized in superheated steam. Additionally, PPO is a base material for heat-resistant connectors, insulators, and lamp bases.

Fig. 8.44 Synthesis of a polysulfone by nucleophilic substitution
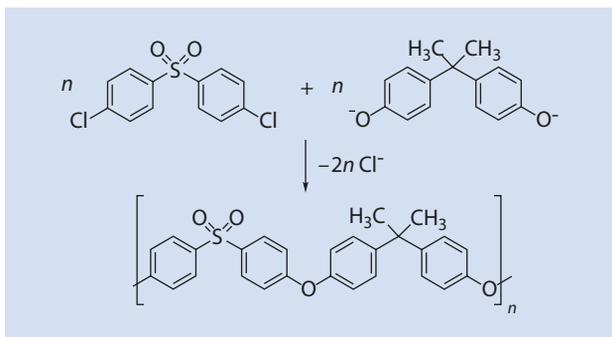
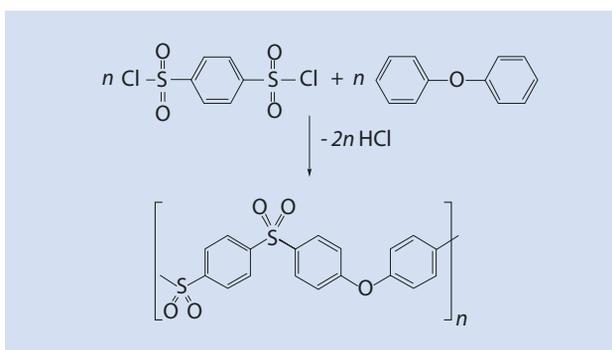**Fig. 8.45** Formation of a polysulfone by electrophilic substitution

Fig. 8.46 Synthesis of polyether ketones

Nucleophilic substitution:
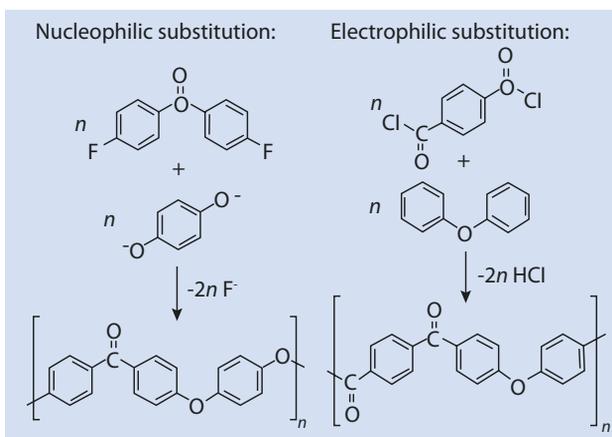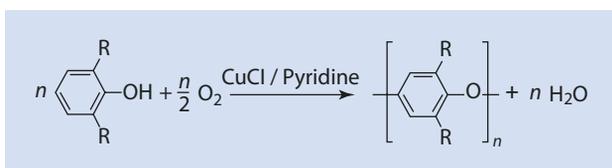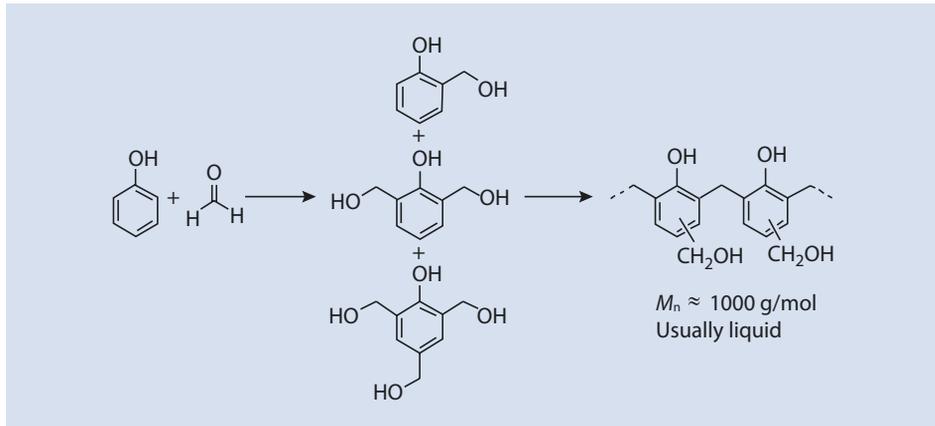
Electrophilic substitution:

Fig. 8.47 Synthesis of polyphenylene oxide by oxidative dehydrogenation

Fig. 8.48 Synthesis of resols (in a basic milieu, ratio of phenol : formaldehyde = 1:1.5)

8.6 Industrially Relevant Crosslinking Systems

As described in ▶ Sect. 8.3.4, polymers that are built up gradually can be cross-linked by using monomers with an average functionality of $\overline{f} > 2$, allowing them to be converted into insoluble three-dimensional networks. In this section, systems in which the cross-linking is carried out in two stages by reaction of a prepolymer (first stage) with a cross-linking agent (second stage) are discussed.

8.6.1 Phenolic Resins

Condensation of phenol with formaldehyde can yield low molar mass, soluble, often still liquid intermediate materials (prepolymers). By further reactions (e.g., by heating), these can be converted into networks that are insoluble and do not melt. These materials are among the oldest industrially used polymers. The condensation of phenol with formaldehyde in aqueous solution is pH-dependent. The prepolymers obtained in an alkaline medium are called *resols* (cross-linked products are called resins or *resites*) (■ Fig. 8.48). The prepolymers prepared in acidic solution are called *Novolac* (■ Fig. 8.49).

In an acidic environment, an excess of phenol is necessary, otherwise the polymerization cannot be controlled and no stable and storable intermediates are obtained. Novolac is usually solid at room temperature.

Cross-linking of resols is accomplished by heating. At 130 °C methylol phenols simply dehydrate (■ Fig. 8.50).

By contrast, at 150 °C, methyl groups are predominantly formed as formaldehyde and water are eliminated, (■ Fig. 8.51).

The crosslinking of Novolac is achieved by adding crosslinking agents, such as hexamethylene tetramine. This hydrolyzes to dimethylol amine and reacts with Novolac as shown in ■ Fig. 8.52.

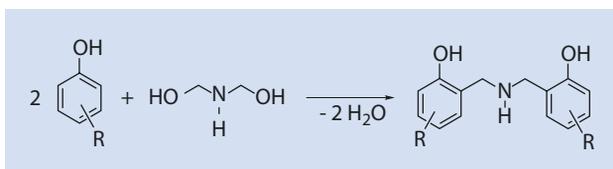**Fig. 8.49** Synthesis of Novolac (at pH ≤ 3, ratio of phenol:formaldehyde = 1:0.8)
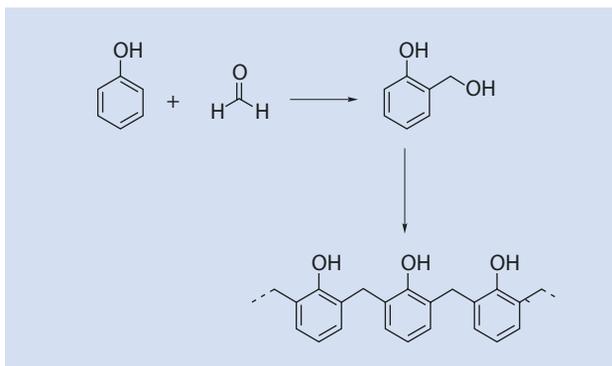
Fig. 8.50 Elementary step in the cross-linking of a resol by dehydration (T = 130 °C)
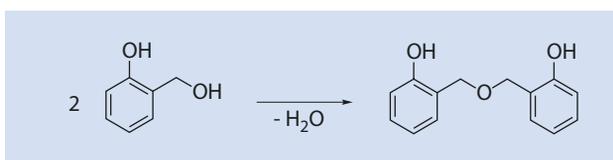
Fig. 8.51 Elementary step in the cross-linking of a resol by elimination of water and formaldehyde (T = 150 °C)
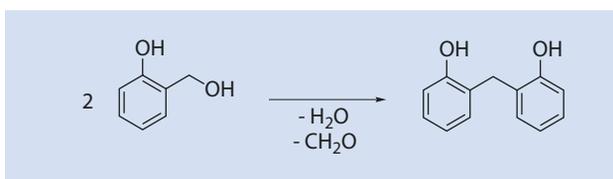
Fig. 8.52 The cross-linking of Novolac with dimethylol amine

Phenolic resins are used mainly as molding compounds with fillers. The hardened (cross-linked) resins are tough construction materials with good resistance to stress cracking. Webs of paper or tissues impregnated with phenolic resins can be processed into laminates.

8.6.2 Urea Resins

The reaction products of formaldehyde with urea (carbamide) are called urea resins. This reaction, which is a Mannich reaction, is pH-dependent.

In a neutral to slightly alkaline environment, well-defined products are created (■ Fig. 8.53).

Fig. 8.53 Conversion of urea with formaldehyde to urea resin precursors in a neutral to slightly alkaline environment
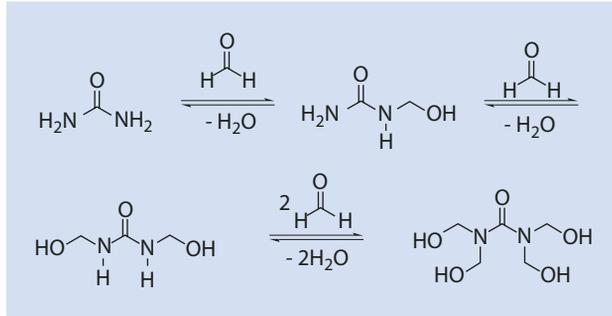
Fig. 8.54 Individual steps of the acid-catalyzed cross-linking of urea resin precursors
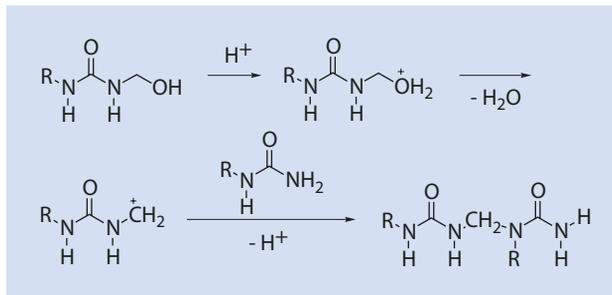
Fig. 8.55 Trimerization of urea in an acidic environment
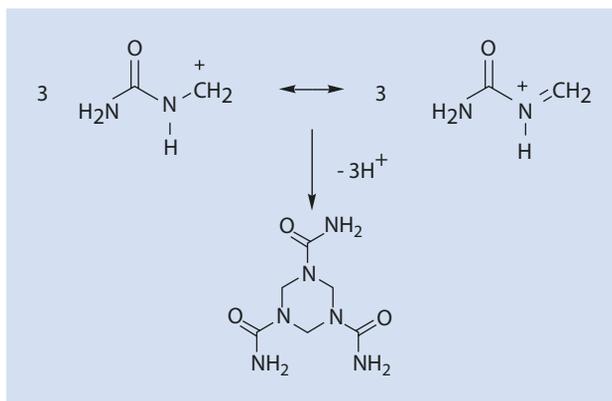
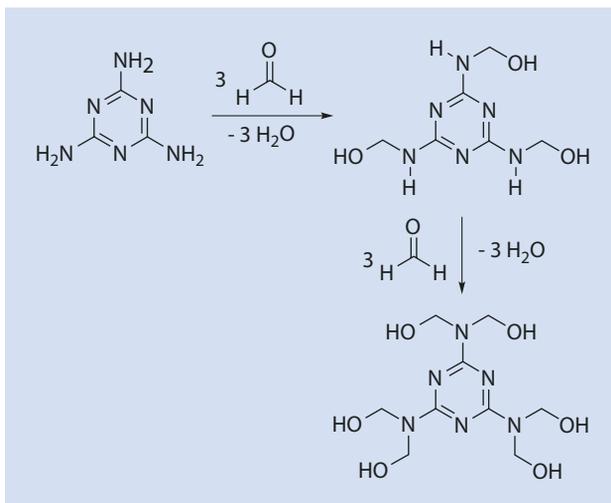In an acidic environment, cross-linked structures rapidly form (Fig. 8.54).

The cross-linking can be continued to incorporate all the $-NH_2$ groups. In addition, the carbenium ion can trimerize (Fig. 8.55).

Thereafter, the NH_2 groups can react further (as described above) and cross-link. The urea resins are similar in their properties and their applications to phenolic resins.

8.6.3 Melamine Resins

Melamine (1,3,5-triaminotriazine) and formaldehyde react stepwise to yield intermediates which have similar structures to those of urea resins (Fig. 8.56).

At elevated temperatures (140–160 °C), the molecules bridge and form a network (■ Fig. 8.57).

Cross-linked melamine resins have slightly better mechanical and thermal properties than both phenolic and urea resins. They are used especially for the production of light-colored or white components, instead of phenolic and urea resins which have a dark, natural color.
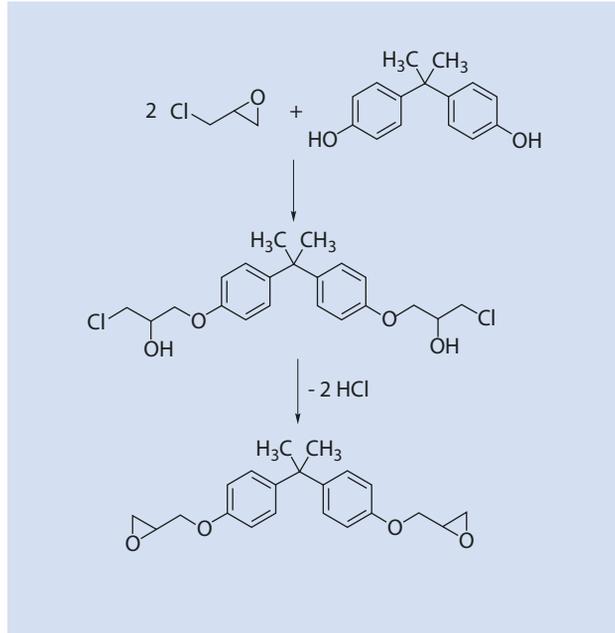
8.6.4   Epoxy Resins

Epoxy resins are produced by the reaction of low molar mass epoxy compounds with phenols (■ Fig. 8.58).

With a small excess of epichlorohydrin (epichlorhydrin:phenol < 2:1), higher molar mass epoxy resins are formed via multiple repetition of the reactions shown in ■ Fig. 8.58 (■ Fig. 8.59).

These prepolymers can be converted into networks either by stoichiometric reactions with acid anhydrides (heat or latent curing) or with primary or secondary amines (cold curing), but also catalytically with tertiary amines.

The first step of the cross-linking of the prepolymers is an esterification of the –OH group with an acid anhydride (■ Fig. 8.60a). In the second step, the resulting –COOH function opens an epoxide ring and connects two chains together in the intermolecular course of the reaction (■ Fig. 8.60b).
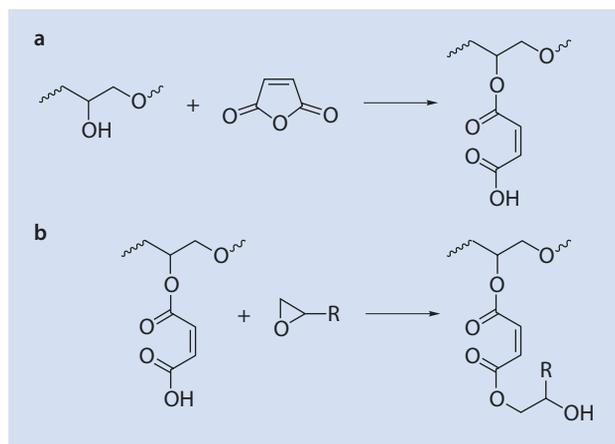
■ **Fig. 8.58** Condensation reaction of epichlorohydrin with bisphenol A
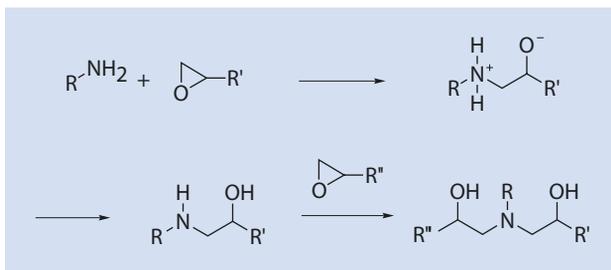

■ **Fig. 8.59** Structural formula of epoxy resin prepolymers
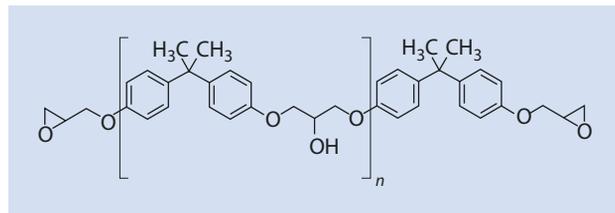
■ **Fig. 8.60** Mechanism of crosslinking of epoxy resin prepolymers with carboxylic acid anhydrides (heat curing)

Fig. 8.61 Reaction of epoxy resin prepolymers with primary amines (cold hardening); Cross-linking occurs when the components are multifunctional

Fig. 8.62 Catalytic curing of epoxy resin prepolymers with tertiary amines. Crosslinking occurs when the epoxy prepolymer is multifunctional, that is, at least two epoxy functional groups are present per molecule
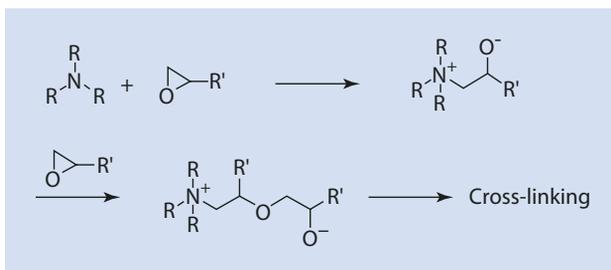
The first step of the curing of the prepolymers with primary amines is the opening of the oxirane ring. In the second step, the resulting secondary amine opens another oxirane ring (most likely from another chain). As with acid hardening (■ Fig. 8.60), primary amine curing is a stoichiometric reaction (■ Fig. 8.61).

The curing of oxirane polymers with tertiary amines is a catalytic process. The basic steps of this curing are shown in ■ Fig. 8.62.

Epoxy resins are high-quality, indispensable materials, which are often used in conjunction with reinforcing agents such as glass, carbon, or aramid fibers. The composites have tensile strengths and moduli greater than or equal to steel alloys. Areas of application are in electrical engineering (carrier material for printed circuit boards, printed circuits), the automotive industry (structural and body components), and sports articles (e.g., bicycle frames, skis, hockey, tennis rackets). By varying the starting components, the characteristic properties of these materials can be precisely adjusted to the particular requirements.

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Turner SR, Voit BI, Morey TH (1993) All-aromatic hyper branched polyesters with phenol and acetate end groups: syntheses and characterization. Macromolecules 26:4617–4623