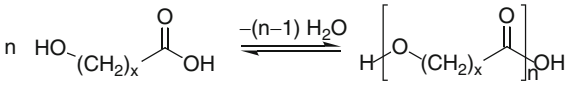
Synthesis of Macromolecules by Step Growth Polymerization

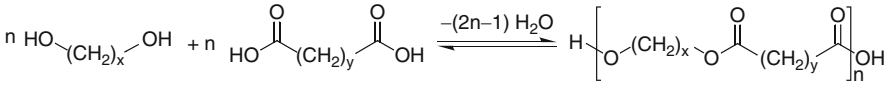
4

4.1 Condensation Polymerization (Polycondensation)

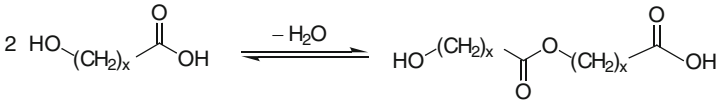
Condensation polymerizations (polycondensations) are stepwise reactions between bifunctional or polyfunctional components, with elimination of small molecules such as water, alcohol, or hydrogen and the formation of macromolecular substances. For the preparation of linear condensation polymers from bifunctional compounds (the same considerations apply to polyfunctional compounds which then lead to branched, hyperbranched, or crosslinked condensation polymers) there are basically two possibilities. One either starts from a monomer which has two unlike groups suitable for polycondensation (AB type), or one starts from two different monomers, each possessing a pair of identical reactive groups that can react with each other (AABB type). An example of the AB type is the polycondensation of hydroxycarboxylic acids:



An example of the AABB type is the polycondensation of diols with dicarboxylic acids:



The formation of a condensation polymer is a stepwise process. Thus, the first step in the polycondensation of a hydroxycarboxylic acid (AB type) is the formation of a dimer that possesses the same end groups as the initial monomer:



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The end groups of this dimer can react in the next step either with the monomeric compound or with another dimer molecule, and so on. The molecular weight of the resulting macromolecules increases continuously with reaction time, unlike many addition polymerizations, e.g., radical polymerizations. The intermediates that are formed in independent, individual reactions, are oligomeric and polymeric molecules with the same functional end groups as the monomeric starting compound. In principle, these intermediates can be isolated without losing their capability for further growth. Thus, all reactions

$$M_i + M_j \rightarrow M_{j+i}$$

can occur, where M_i, M_j denote oligomeric or polymeric species containing i, j monomeric units, respectively. The formation of a reaction scheme that takes into account the multitude of possible reactions between i-mers and j-mers, with different rate constants k_{ij}, and with the prevailing concentrations $[M_i]$ and $[M_j]$, would be extraordinarily complicated. If, however, one assumes that in each single step a reaction between an end group of the molecule M_i with an end group of the molecule M_j takes place in such a way that it is independent of i or j, the kinetic treatment of polycondensation is considerably simplified.

Thus, it is assumed that the reactivity is independent of molecular weight. This "principle of equal reactivity" holds true for both condensation and stepwise addition polymerizations. It means that there is no difference in the reactivity of the end groups of monomer, dimer, etc. and, therefore, that the rate constant is independent of the degree of polymerization over the total duration of reaction.

On this basis the kinetics of polycondensation were worked out a long time ago. The following points are of particular interest:

- Dependence of the average molecular weight on conversion,
- Dependence of the average molecular weight on the molar ratio of reactive groups,
- Dependence of the conversion and average molecular weight on the condensation equilibrium, and
- Exchange reactions such as transesterification or transamidation.

The progress of a polycondensation can be followed in a simple manner by analysis of the unreacted functional groups. If the reactive groups are present in equimolar amounts, which is generally desired (see below), it is sufficient to analyze for one of the two groups, for example, the carboxyl groups in polyester formation. If the number of such functional groups initially present is N_0, and the number at time t is N, the extent p of condensation is defined as the fraction of functional groups that have already reacted at that time:

$$p = \frac{N_0 - N}{N_0} \tag{4.1}$$

Multiplying p by 100 yields the conversion in %.

Table 4.1 Degree of polymerization P_n and number-average molecular weight M_n (assuming a structural element of molecular weight 100) as a function of conversion in condensation and stepwise addition polymerizations

Conversion (%)	P_n	M_n
50	2	200
75	4	400
90	10	1,000
95	20	2,000
99	100	10,000
99.5	200	20,000
99.95	2,000	200,000

The number-average degree of polymerization P_n is defined as the number of structural units per polymer chain (N_0 = number of monomer molecules originally present, N = total number of molecules at the appropriate stage of reaction, including the as yet unconverted monomer molecules). Hence from Eq. 4.1 one obtains:

$$P_n = \frac{N_0}{N} = \frac{1}{1-p} \tag{4.2}$$

P_n is thus dependent on the conversion ($p \cdot 100$). This is illustrated by some numerical examples in Table 4.1.

From Table 4.1 it is clear that to attain the commercially interesting molecular weights of 20,000–30,000, the reaction must be driven to conversions of more than 99%.

The degree of polymerization P_n is affected not only by the yield, but also by the molar ratio of the reacting functional groups A and B. If N_A and N_B are the numbers of such groups originally present, and r is their ratio ($r = N_A/N_B$; $r \leq 1$), then the average degree of polymerization P_n can be expressed by modifying Eq. 4.2 to give Eq. 4.3:

$$P_n = \frac{1+r}{2 \cdot r \cdot (1-p) + 1 - r} \tag{4.3}$$

On equivalence of both functional groups A and B, which means $r = 1$, Eq. 4.3 reduces to Eq. 4.2.

If all the A groups have reacted (i.e., $p = 1$), Eq. 4.3 simplifies to:

$$P_n = \frac{1+r}{1-r} \tag{4.4}$$

In general, the effect of an excess of one component is greater, the higher the conversion. At 99% conversion the molecular weight is reduced to half its value by a 2% excess of one component; at 99.5% conversion the same effect is produced by

Table 4.2 Degree of polymerization P_n as a function of the ratio of the functional groups A and B in condensation and stepwise addition polymerizations (conversion 100% with respect to A, i.e., component A has completely reacted)

Excess of component B (mol%)	$r = N_A/N_B$	P_n
10	0.09	19
1	0.99	199
0.1	0.999	1,999
0.01	0.9999	19,999

a 1% excess. Some numerical examples are given in Table 4.2 for the effect of non-equivalence of components on the degree of polymerization (at 100% conversion of the lesser component).

Table 4.2 shows the importance of the exact equivalence of functional groups in polycondensation reactions, since even a 1 mol% excess of one of the two groups limits the maximum attainable degree of polymerization P_n to less than 200. For polycondensations of the AB type, e.g., hydroxycarboxylic acids or amino acids, this equivalence is automatic since the monomer contains both groups. On the other hand, for polycondensations of the AABB type, e.g., between diols and dicarboxylic acids, a small excess of one component causes the reaction to come to a halt when only the end groups of the component present in excess are left because these are unable to react with each other.

Even if both functional groups are present in equivalent amounts at the beginning of reaction, this equivalence can be disturbed during the course of reaction by evaporation, sublimation, or side reactions of one of the reaction partners. A monofunctional compound that can react with one of the bifunctional reaction partners acts in the same way as an excess of a bifunctional component. Therefore, high purity of the monomers is absolutely essential in the preparation of high-molecular-weight polymers by condensation and stepwise addition polymerization. On the other hand, this also means that it is possible to regulate precisely the average molecular weight of the polymer formed either by using a controlled excess of one component or by addition of a monofunctional compound.

The effects described by Eqs. 4.1, 4.2, 4.3, and 4.4 apply to both stepwise addition and condensation polymerizations. In polycondensation, two further factors must be considered: The condensation equilibrium and the exchange reactions. The *condensation equilibrium* limits the conversion and hence the average molecular weight. As in the case of esterification of monofunctional compounds, the corresponding polycondensations are to be treated as equilibrium reactions, governed by the law of mass action. For example, in the case of polyesterification, if 1 mol of hydroxy groups (1/2 mol of diol) reacts with 1 mol of carboxylic acid groups (1/2 mol of dicarboxylic acid), this takes the form (according to Flory and Schulz):

$$K = \frac{p \cdot n_w}{(1-p)^2} \tag{4.5}$$

As before, p is the fraction of functional groups that have already reacted (see Eq. 4.1), i.e., the mols of ester groups formed (N_0 and N are the numbers of functional groups present at the start and a given time of the reaction, respectively), $(1-p)$ the molar quantity of unreacted hydroxy and carboxy groups, and n_w is the mole fraction of water present in the reaction mixture. Solving Eq. 4.5 for p we obtain the upper limit of conversion as a function of the ratio $\beta = K/n_w$:

$$p = \frac{1}{2\beta}\left(1 + 2\beta - \sqrt{1 + 4\beta}\right) \tag{4.6}$$

Since the number-average degree of polymerization P_n is reciprocally proportional to the free functional groups $1-p$ still present (see Eq. 4.2), the upper limit of the degree of polymerization, when governed by the condensation equilibrium, is given by Eq. 4.7:

$$P_n = \frac{2\beta}{\sqrt{1 + 4\beta} - 1} \tag{4.7}$$

Since, in practically all cases, one aims at as high a conversion as possible, i.e., a value of p tending towards unity, Eqs. 4.6 and 4.7 may be simplified to obtain:

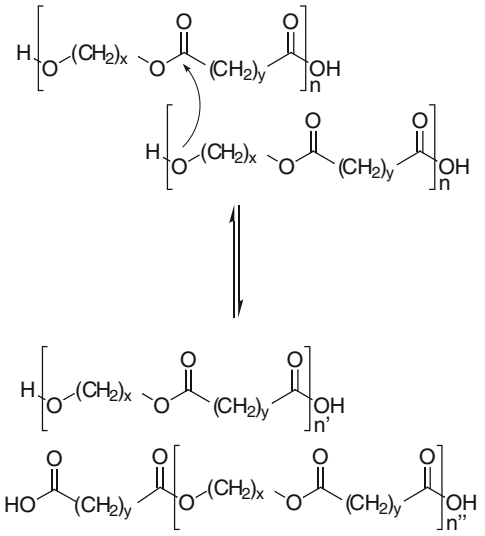
$$p \approx 1 - \sqrt{\frac{1}{\beta}} \tag{4.8}$$

and

$$P_n \approx \sqrt{\beta} = \sqrt{\frac{K}{n_w}} \tag{4.9}$$

If the equilibrium constant K has a value between 1 and 10, less than a thousandth of the total amount of water formed in the reaction mixture is sufficient to prevent the formation of really high-molecular-weight condensation polymers. Hence it follows that it is extremely important to remove as completely as possible the low-molecular-weight reaction products, for example, water, eliminated during a polycondensation. In principle, these equilibriums are also known in stepwise addition polymerizations (polyaddition) like the back-reactions of urethane groups. Since they mostly occur at higher temperatures only, they can be neglected.

The second factor that additionally effects polycondensations are *exchange reactions* which can occur between free end groups and junction points in the chain, for example, between OH end groups and ester groups of a polyester (transesterification):



Neither the number of free functional groups, nor the number of molecules, nor the number-average degree of polymerization, is thereby altered. Thus, two equal-sized macromolecules could react with one another to give one very large and one very small macromolecule; conversely a very large and a very small macromolecule can be converted into two macromolecules of similar size. Independent of the initial distribution these exchange reactions will in each case lead to a state of dynamic equilibrium in which the rates of formation and consumption of molecules of a given degree of polymerization are equal. This results in an equilibrium distribution of molecular weights which is formally the same as that obtained by purely random polycondensation. Therefore, in normal polycondensations the exchange reactions will not affect the molecular-weight distribution. On the other hand by mixing a low molecular weight and a high-molecular-weight polyester in the melt, especially if a catalyst is still present, the molecular-weight distribution very soon adjusts to an equilibrium distribution with a single maximum, instead of the two in the original mixture. Such exchange reactions between the end groups and the junction positions are known for polyesters, polyamides, polysiloxanes, and polyanhydrides.

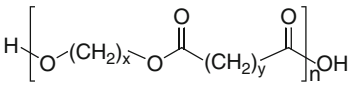
Finally, it has to be considered that also the formation of macrocyclic oligomers and polymers cannot be fully neglected. For example, by use of mass spectrometry, the existence of ring-shaped polycondensates is definitely elucidated in all types of polycondensates.

Although the procedures for the preparation of condensation polymers are analogous in many respects to those for the condensation reactions of monofunctional compounds, some additional factors must be taken into account if one wishes to attain high molecular weights in polycondensations. These are essentially consequences of Eqs. 4.1, 4.2, 4.3, 4.4, 4.5, 4.8, and 4.9. Firstly, the condensation reaction must be specific and proceed with the highest possible yield,

otherwise only mixtures of oligomers will be obtained. Furthermore, for polycondensation reactions in which two or more components may participate, care must be taken to ensure strict equivalence in the proportions of the reacting groups through-out the reaction. The equilibrium position of the reaction must be displaced as far as possible towards condensation. By analogy with the condensation of monofunctional compounds this may be achieved by removing the low-molecular-weight reaction product, e.g., water, as completely as possible from the reaction mixture. This can be done by distillation under high vacuum or by azeotropic distillation. It is advantageous to pass very dry inert gas through the well-stirred reaction mixture in order to facilitate the diffusion of the eliminated component from the viscous solution formed during polycondensation. High demands are placed on the purity of the starting materials. They must be especially free from monofunctional compounds since these block the end groups of the resulting macromolecules and so prevent further condensation. Only bifunctional compounds can be used for the preparation of linear condensation polymers, since polyfunctional compounds give rise to branching, hyperbranching, and crosslinking. Finally, polycondensation reactions should be carried out under exclusion of oxygen, since oxidative decomposition can easily occur at the high reaction temperatures that are frequently needed.

4.1.1 Polyesters

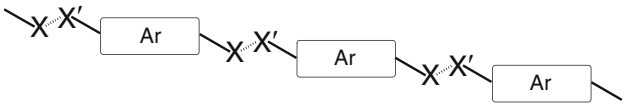
Polyesters are macromolecules whose monomeric units are linked with an ester group:



Their properties depend markedly on their chemical composition. Pure aliphatic polyesters are generally crystalline and have melting points below 100°C (with the melting point increasing with the number of methylene groups between the ester groups). At room temperature they are soluble in formic acid, methylene chloride, and dichlorobenzene, and they are easily hydrolyzed. In contrast, polyesters made from aromatic or cycloaliphatic dicarboxylic acids and diols, like polyesters made from terephthalic acid and ethylene glycol, or terephthalic acid and 1,4-cyclohexylenedimethanol, have different properties. They also crystallize but have significantly higher melting points. At room temperature, they are insoluble and hard to hydrolyze. Additionally, they have good mechanical properties, which make them suitable for the preparation of fibers, films, and moldable plastics.

Unusual properties of fully aromatic polyesters are observed if they have at least partially a rigid planar chain structure. In particular, they can form thermotropic liquid crystalline states (see Example 4.5). As already discussed in Sect. 1.2.4 an important structural prerequisite for LCPs of Type A in order to attain the liquid

crystalline state of aromatic polyesters (and aromatic polyamides, see Example 4.14), is a rigid main chain according to the following construction principle:



The flat-structured aromatic units (Ar) are responsible for the formation of the liquid crystalline domains. The two-atom linking group –X–X′– should be stabilized by additional π-bonds that can contribute to the rigidity of the chain. Suitable are azo, azomethine, ethenyl, ester, and amide groups. For polyaramides, processed from solution, a strong *para*-linkage is favorable (see Example 4.14). In contrast to this, an all *para*-linkage in thermotropic polyesters leads to high melting points and high melt viscosities, so that a thermoplastic processing is mostly impossible. Depression of the melting point by maintaining the possibility to form liquid crystalline states is mainly achieved by the following two concepts:

– Insertion of appropriate side groups,
– Insertion of discontinuity in the main chain.

The effect of the incorporation of side groups into aromatic polyester is demonstrated in Example 4.5.

Discontinuities in the main chain can be obtained by different means. Example 4.6 describes the incorporation of flexible aliphatic segments. Of special interest is the overall orientation of incorporated mesogens by mechanically or electrically applied external forces.

From a practical point of view, the deviation from main-chain continuity is the most interesting one. Especially the concept of the so-called parallel offset of the main chain is favorized. It is realized in a commercial product made from 4-hydroxybenzoic acid and 2,6-hydroxynaphthalenecarboxylic acid. The incorporation of small amounts of 2,6-hydroxynaphthalenecarboxylic acid causes a discontinuity in the main chain but only in form of a parallel offset of some chain segments. Thus, the ability to form liquid crystalline states is largely maintained as well as the anisotropic properties of the molten and solid polyester. Instead, the melting point is significantly reduced, as desired.

The preparation of fully aromatic polyesters is mostly performed by melt condensation. Complex phase equilibriums and states of aggregation are formed in this manner. This is in most cases not easy to control under laboratory conditions. Example 4.5 describes a polyester that is easy to prepare under laboratory conditions and allows the observation of typical properties of some thermotropic liquid crystalline polymers.

From an industrial point of view, not only the high-molecular-weight linear polyesters are of interest. Also, a series of low-molecular-weight linear or branched polyesters (Example 4.1) find application in surface coating systems (alkyd resins), as coreactants in unsaturated polyester resins (Example 4.8), or in polyurethane foams (Examples 5.26 and 5.27).

Polyesters are prepared by the following methods:
- Polycondensation of hydroxycarboxylic acids,
- Polycondensation of diols with dicarboxylic acids,
- Polycondensation of diols with derivatives of dicarboxylic acids (e.g., cyclic dicarboxylic acid anhydrides, dicarboxylic acid chlorides, or dicarboxylic acid esters),
- Polycondensation of dicarboxylic acids with derivatives of diols (e.g., acetates of bisphenols), or
- Ring-opening polymerization of lactones (see Sect. 3.2.3.3)

The establishment of the equilibrium is often accelerated by acidic or basic catalysts, for example, by strong acids (*p*-toluenesulfonic acid), metal oxides (antimony trioxide), Lewis acids (titanium tetrabutoxide, tin acetates or tin octoates), weak acid salts of alkali metals or alkaline earth metals (acetates, benzoates), or by alcoholates.

4.1.1.1 Polyesters from Hydroxycarboxylic Acids

The synthesis of polyesters from hydroxycarboxylic acids belongs to the polycondensation of the AB type. Both reacting groups are part of the same monomer. Polycondensation of aliphatic hydroxycarboxylic acids, such as glycolic acid, lactic acid, or 12-hydroxy-9-octadecenoic acid (ricinoleic acid), are mostly carried out in the melt and yield high-molecular-weight polymers. However, these reactions often result in the formation of cyclic esters (lactones). The tendency towards ring formation depends on the number of methylene groups between the hydroxy and carboxylic acid groups; it is greatest for γ-hydroxybutyric acid, δ-hydroxyvaleric acid, and ε-hydroxycaproic acid. The polycondensation of aromatic hydroxycarboxylic acids, e.g., 4-hydroxybenzoic acid and 2,6-hydroxynaphthalenecarboxylic acid, which are very useful components in the synthesis of thermotropic liquid-crystalline polyesters, has gained importance in recent years.

4.1.1.2 Polyesters from Diols and Dicarboxylic Acids

Polycondensation of diols with dicarboxylic acids is often performed in the melt. However, it does not always lead to high-molecular-weight polyesters. Sometimes, the starting materials or the resulting polyester are thermally unstable at the high condensation temperatures. If the reactants and the polyester are well soluble, one can carry out the polycondensation in solution (see Example 4.2). The elimination of water from diols and dicarboxylic acids frequently occurs rather slowly. In such cases suitable functional derivatives of the diols and dicarboxylic acids (esters or anhydrides) can be used instead of the direct condensation, as described in Sect. 4.1.1.3.

Example 4.1 Preparation of a Low-Molecular-Weight Branched Polyester from a Diol, a Triol and a Dicarboxylic Acid by Melt Condensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

(a) *Preparation of a Slightly Branched Polyester*

A 250 ml three-necked flask is fitted with a nitrogen inlet, a stirrer, a thermometer that reaches deep into the flask, a fractionating column of about 20-cm length packed with Raschig rings, at the upper end the another thermometer, and a condenser for distillation, with vacuum adapter and graduated receiver. 73 g (0.5 mol) of adipic acid, 55.3 g (0.52 mol) of anhydrous bis(2-hydroxyethyl) ether, (diglycol), and 4.5 g (0.0335 mol) of anhydrous 1,1,1-tris-(hydroxymethyl) propane are weighed in, some antibump granules added, and the air is displaced by evacuation and filling with nitrogen. The flask is then heated slowly under a gentle stream of nitrogen; when the contents become fluid between 80°C and 110°C, the stirrer is switched on. Polyesterification sets in at 130–140°C as evidenced by the formation of water. The internal temperature is now raised to 200°C at such a rate that the temperature at the head of the column does not exceed 100°C. During this period (normal pressure phase) most of the water (18 g) is eliminated; it is important not to interrupt the stirring because of the danger of bumping.

As soon as the temperature at the head of the column drops much below 100°C, after the internal temperature has reached 200°C, the vacuum pump is attached and the pressure reduced to 12–14 Torr. At this stage of the experiment (vacuum phase), distillation of the diglycol must be completely avoided; if necessary one must evacuate more slowly. The reaction is now allowed to continue at 12–14 Torr and 200°C, samples being taken at intervals of 5 h in order to determine the acid number (see below). In order to take the samples, the apparatus is momentarily filled with nitrogen and then evacuated again. When the acid number is smaller than 2 (total time about 35–40 h) the experiment is terminated. Addition of a catalyst, e.g., 5 ppm $SnCl_2$ before the vacuum phase reduces the reaction time about 25–30%. The slightly branched polyester remains, after cooling under nitrogen, as a viscous, pale yellow mass. It has an OH number of about 60 and can be directly processed and converted to an elastic polyurethane foam (see Example 5.26).

(b) *Preparation of a Highly Branched Polyester*

8.45 g (0.06 mol) of adipic acid, 21.3 g (0.075 mol) of oleic acid, 22 g (0.15 mol) of phthalic anhydride, and 52.5 g (0.39 mol) of anhydrous 1,1,1-tris-(hydroxymethyl)propane are placed into the apparatus as described under (a) and the air is displaced by evacuation and filling with nitrogen. The mixture is slowly heated under a stream of nitrogen; at 120°C the contents of the flask have melted and the stirrer can be started. The internal temperature is raised to 190°C over a period of 2 h; as soon as the temperature at the top of the column drops below 70°C, the pump is attached and the apparatus slowly evacuated to 40 Torr over the course of 2 h. At this pressure and an internal temperature of 190°C, the mixture is stirred for a further 8 h. The pump is then switched off and the product allowed cooling under nitrogen. The highly branched polyester, which remains as a viscous liquid, has an acid number of 2 and an OH number of 350; it can be used directly for the preparation of a rigid polyurethane foam (see Example 5.27). Addition of 5 ppm $SnCl_2$ as catalyst reduces the reaction time by 10%.

(c) *Determination of the Acid Number*

1–2 g of the polyester are dissolved by warming with 50 ml of acetone and, after cooling, are titrated as quickly as possible with 0.1 M alcoholic potassium

hydroxide using phenolphthalein as indicator, until the red color remains for a second. The alkali requirement of the solvent is determined in a blank experiment. The acid number is given by the weight of KOH in mg, required to neutralize 1 g of substance:

$$\text{acid number} = 5.61 \cdot f \cdot (A - B)/E$$

where
A = titer for the sample in ml
B = titer for the blank in ml
E = weight of sample in g
f = concentration of the alcoholic KOH in mol/l

(d) *Determination of the Hydroxy Number*

To acetylate the free hydroxy groups of a polyester, a solution of 15 g of freshly distilled acetic anhydride (bp 140°C) in 35 g of freshly distilled dry pyridine is prepared. The solution, which turns slightly yellow with time, is stored in a dark bottle.

To determine the hydroxy number, about 2.5 g of polyester are weighed to the nearest 10 mg into each of three conical flasks with ground joints. The samples are each dissolved with gentle warming in 10 ml of pyridine. After cooling, 10 ml of the acetylating solution are added with a pipette to each of the flasks. 10 ml of pyridine and 10 ml of acetylating solution are placed in each of two conical flasks with ground joints, for the determination of the blank value. All five flasks are closed with stoppers fastened with adhesive tape. They are then placed in an oven at 110°C for 70 min. (Caution when removing: Use safety goggles and safety gloves!). After cooling, a few drops of 0.1% aqueous Nile blue chloride solution are added to each of the samples which are then titrated with 1 M NaOH solution until the color changes suddenly to violetred. The hydroxy number indicates how many mg KOH are equivalent to the free hydroxy groups present in 1 g of substance.

$$\text{OH number} = 56.1 \cdot f \cdot (B - A)/E$$

where
A = titer for the sample in ml
B = titer for the blank in ml
E = weight of sample in g
f = concentration of the NaOH in mol/l.

The average value is taken of those values which do not differ by more than ±2 from each other.

Example 4.2 Preparation of a High-Molecular-Weight Linear Polyester from a Diol and a Dicarboxylic Acid by Condensation in Solution

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

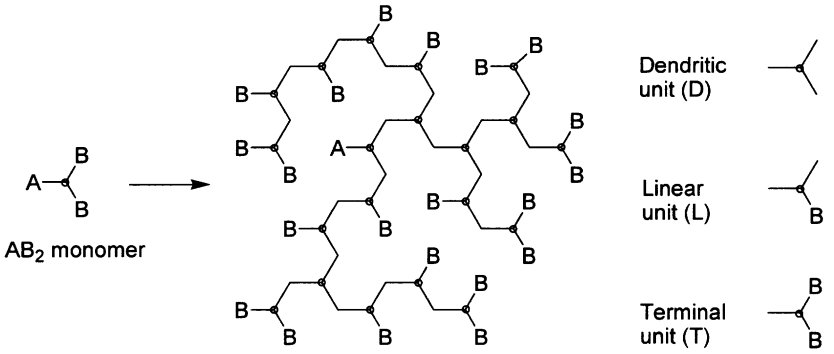
The recycling apparatus shown in Fig. 2.4 is charged with 29.55 g (0.25 mol) of 1,6-hexanediol (purified by vacuum distillation), 29.55 g (0.25 mol) of recrystallized succinic acid, 100 ml of dry toluene, and 0.75 g of pure *p*-toluenesulfonic acid; at the same time, the siphon is also filled with toluene so that the circulation of the solvent can begin immediately. After adding some antibump granules the solution is heated on an oil or air bath to boiling; the toluene should flow quickly through the drying tube filled with soda-lime back into the flask. After some hours, when about three-quarters of the theoretical amount of water has collected in the separator, the soda-lime is renewed for the first time; it is renewed again after another 10 h.

The viscosity of the solution gradually increases and so does the temperature in the flask. In order to maintain a quick rate of distillation (and therefore polycondensation), each time the internal temperature reaches 130°C about 25 ml of pure toluene are added. After about 25 h the flask is cooled to room temperature and the solution is added drop-wise to a tenfold amount of methanol; the polymer is filtered off and dried to constant weight in vacuum at 40°C. Yield: about 90%.

The linear polyester so obtained is of higher molecular weight than that produced by melt polycondensation. It is soluble in toluene, chloroform, and formic acid, and readily hydrolyzable (see Example 5.1); the melting point is about 100°C. The increase of molecular weight during polycondensation can be followed by taking samples from time to time (initially at short intervals) and determining the limiting viscosity numbers of the precipitated and dried samples; the carboxyl and hydroxy end groups can also be quantitatively determined (see Example 4.1).

Hyperbranched Polymers

Hyperbranched polymers are a relatively new type of highly branched materials, which in contrast with dendrimers, often can be prepared in a one-step synthesis of AB_x ($x \geq 2$) monomers. The growth proceeds in an uncontrolled fashion and the development of the structure is statistic, as for linear polymerizations. The resulting macromolecules, as dendrimers, have a high density of functional groups. The number of these groups can be directly connected with the degree of polymerization (DP): if the reaction is performed with an AB_2 monomer, each molecule will have exactly one functional group more than the number of repetition units (number of B groups: DP + 1). Dendritic, linear, and terminal units can be identified, depending on the number of reacted functional groups: in a dendritic unit both B groups have been involved in the reaction; while in linear and terminal units, only one, and none of the B groups respectively, have been employed, and can therefore still be used for successive modifications. The impossibility of forming "entanglements" and the highly compact structure are most certainly responsible for their lower solution viscosities and the better solubilities, compared to the linear analogues. Furthermore, most hyperbranched polymers are amorphous and, therefore, no crystallite melting point T_m can be detected.



Schematic representation of hyperbranched polymer (A = focal unit)

By modifying the functional groups they can be used, for example, as crosslinkers in high solid or powder coatings and in thermosets. Because of their good miscibility and low melt viscosity, they find applications as melt modifiers and as blend components. Modified hyperbranched polymers, like alkyl chain substituted poly(ether)s and poly(ester)s sometimes exhibit amphiphilic behavior. They can, therefore, be used as carriers for smaller molecules, for example, dyestuffs into polypropylene.

Example 4.3 Preparation of a Hyperbranched Polyester by Polycondensation of 4,4-bis(4′-hydroxyphenyl)Valeric Acid

Safety precautions: Before the experiment is carried out, Sect. 2.2.5 must be read as well as the material safety sheets (MSDS) for all chemicals and products used. Due to the high temperature of the oil bath needed in this experiment, special care has to be taken and one has to work in a closed hood. In addition, a safety shield is required when working under high vacuum.

4,4-Bis(4′-hydroxyphenyl)valeric acid (15.1 g, 52.7 mmol) is a commercial monomer but has to be used in high purity (not colored). If the purity of the chemical as received is not sufficient it has to be purified by column chromatography.

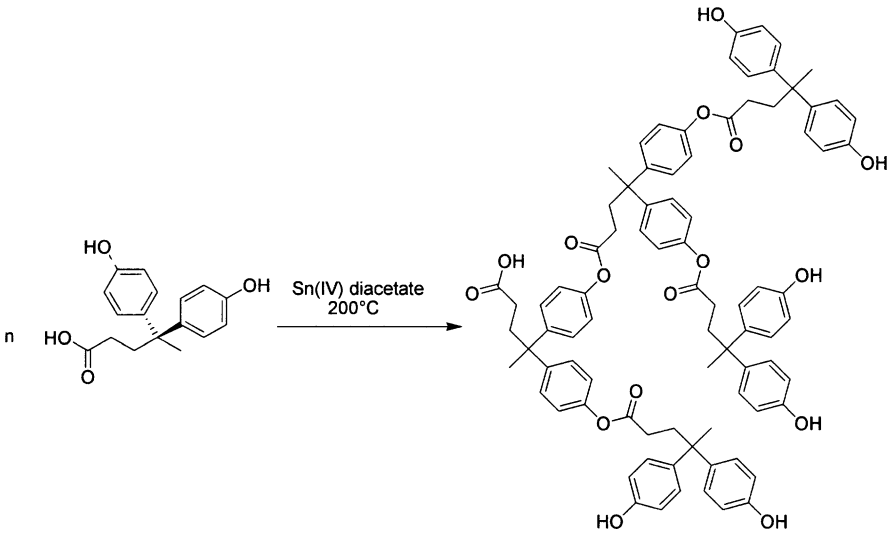
4,4-Bis(4′-hydroxyphenyl)valeric acid and 3 drops of dibutyl tin diacetate are placed in a dry standard apparatus with mechanical stirrer connected to a vacuum line. The polycondensation is carried out in two steps in order to obtain high conversion and high molar mass: First, the monomer is stirred in a nitrogen stream for 70 min at 200°C; during this time period an increase in viscosity of the melt should be observed. After that, vacuum is applied at 225°C for 3 h with stirring and then for 1 h without stirring until a final vacuum of 0.010 mbar is reached. The crude product is dissolved twice in approximately 100–150 ml THF and precipitated into 500 ml water. After filtration the product is dried over phosphorus pentaoxide for several days.

The molar mass of the products is very dependent on the final conversion achieved and thus, on the final quality of the vacuum. Under the described

conditions number average molar masses as determined by GPC in DMAc/LiCl (3 g/l)/water (2 vol%) will reach values between 2,000–5,000 g/mol.

The polymers are easily soluble in polar solvents like THF, DMAc, and DMSO, indicating that the solubility is enhanced by the large number of polar end groups and the branched structure. It is fully amorphous with a glass transition temperature between 90°C and 110°C, depending on molar mass.

The degree of branching is determined by NMR analysis of the product in DMSO-d6. The different structural isomers (linear l, dendritic d, terminal t units) can be identified best by analyzing the quarternary carbon found at about 148 ppm (up to 6 signals for this carbon for a sample containing oligomers). However, quantitative analysis of the ^{13}C NMR requires special conditions. Similarly, the proton NMR gives three signals for the methyl group corresponding to the different structural units at about 1.5 ppm which can be quantified (d = 1.63 ppm, l = 1.58 ppm, t = 1.53 ppm). The degree of branching is calculated by $(I_t + I_d)/(I_t + I_d + I_l)$ and should be close to 0.5 (I = intensity of the proton NMR signal).



4.1.1.3 Polyesters from Diols and Dicarboxylic Acid Derivatives

The polycondensation of a diol and the diester of a dicarboxylic acid (e.g., the dimethyl ester) can be carried out in the melt at a considerably lower temperature than for the corresponding reaction of the free acid. Under the influence of acidic or basic catalysts a transesterification occurs with the elimination of the readily volatile alcohol (see Example 4.3). Instead of diesters of carboxylic acids one can also use their dicarboxylic acid chlorides, for example, in the synthesis of high-melting aromatic polyesters from terephthaloyl dichloride and bisphenols. The commercially very important polycarbonates are obtained from bisphenols and phosgene, although the use of diphenyl carbonate as an alternative component is of increasing interest (see Example 4.4). Instead of free acids, cyclic carboxylic

acid anhydrides (e.g., maleic anhydride or phthalic acid anhydride) are suitable for the synthesis of polyesters. Unsaturated polyester resins, which are synthesized from diols and maleic anhydride (together with other dicarboxylic acid anhydrides) possess great importance. The maleic ester units, which are incorporated into the polyester chain (or fumaric ester units which are formed by thermal rearrangement) can be crosslinked with styrene by radical copolymerization (see Example 4.8).

Example 4.4 Preparation of Polyester from Ethylene Glycol and Dimethyl Terephthalate by Melt Condensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Pure ethylene glycol is dried by refluxing for 1 h in the presence of 2 wt% metallic sodium and is then distilled. Dimethyl terephthalate is recrystallized from methanol and carefully dried in vacuum (mp 141–142°C). 9.7 g (0.05 mol) of dimethyl terephthalate, 7.1 g (0.115 mol) of ethylene glycol, 0.015 g of pure anhydrous calcium acetate, and 0.04 g of pure antimony trioxide are weighed into a 50 ml round-bottomed flask. The flask is then fitted with a Claisen stillhead, an air-cooled condenser, a vacuum adapter, and a graduated receiver (or a measuring cylinder). The air is removed by evacuating and filling with nitrogen, and the components melted on an oil or metal bath at 170°C. The Claisen head is now immediately fitted with a capillary tube (attached to a ground joint) that reaches to the bottom of the flask and a slow stream of nitrogen is passed through. The transesterification sets in almost at once; the progress of reaction is followed by the amount of methanol that has distilled over into the graduated receiver. When the methanol production decreases (after about 1 h) the temperature is raised to 200°C for 2 h, whereby the remainder of the methanol distills over. Finally, the excess ethylene glycol is distilled over during 15 min at 220°C, the temperature then being raised to 280°C. After 15 min the graduated receiver is replaced by a simple round-bottomed flask and the apparatus gradually evacuated while keeping the temperature steady at <0.5 Torr. After another 3 h the polycondensation is complete. The flask is allowed to cool under nitrogen and then broken carefully with a hammer to remove the poly(ethylene terephthalate). The polyester is soluble in *m*-cresol and can be reprecipitated in ether or methanol. The limiting viscosity number is determined in *m*-cresol or in a mixture of equal parts of phenol and tetrachloroethane (see Sect. 2.3.3.3); the softening range is also determined. Fibers can be spun from the melt or pulled out from the melt by means of a glass rod.

Example 4.5 Preparation of a Polycarbonate from 4,4-Isopropylidenediphenol (Bisphenol A) and Diphenyl Carbonate by Transesterification in the Melt

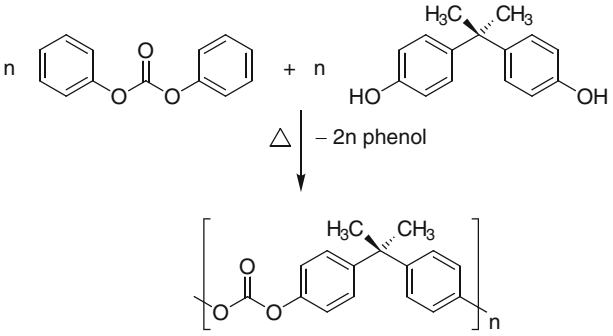
Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

The reaction between diols and phosgene is especially useful for the preparation of polycarbonates. The commercially very important polycarbonates are obtained from aromatic dihydroxy compounds (bisphenols). In contrast to the products of the reaction of aliphatic diols and phosgene they show considerable resistance to water but they are degraded by strong alkali, ammonia, and amines. Due to their angled chain structure with relatively low mobility, the aromatic colorless polycarbonates exhibit high glass transition temperatures, and they are often amorphous and highly transparent. Furthermore, they have good mechanical and optical properties.

The reaction between a dihydroxy compound (bisphenol) and phosgene, which is performed on an industrial scale, proceeds even at room temperature. The reaction is generally carried out in a biphasic medium consisting of methylene chloride (with dissolved phosgene) and aqueous sodium hydroxide (with dissolved bisphenol sodium salt) and a phase transfer catalyst (e.g. triethylamine). The procedure is termed interfacial polycondensation (see Sect. 4.1.2.3 and Examples 4.5, 4.12, and 4.13).

Another useful method is the transesterification of diphenyl carbonate with bisphenols under elimination of phenol. However, the major disadvantages are that the process requires high temperature and vacuum. The polycondensation reaction is carried out stepwise, i.e., the temperature and vacuum are raised slowly, in order to avoid diphenyl carbonate loss by sublimation at the beginning of the reaction. However, an excess of diphenyl carbonate is necessary in order to obtain high molecular weight.

This method of transesterification is of high technical interest. Particularly the reaction of bisphenol A with diphenyl carbonate is a preferred phosgene-free process because biphenyl carbonate can be obtained directly from phenol and dimethyl carbonate. The latter is an industrial product made from CO and methanol.



The following example illustrates this synthetic method.

Experimental Procedure

This reaction should be carried out in a hood behind a protective shield. Bisphenol A powder is particularly irritating to the eyes. All contact with this substance is, therefore, to be avoided.

A 250-ml three-necked flask is fitted with metal stirrer, nitrogen inlet, Vigreux column (30 cm), and condenser for distillation with a vacuum adapter and round flask as receiver. The high-vacuum pump must be connected over a cold trap with the vacuum adapter.

9.12 g (0.04 mol) bisphenol A (4,4′-isopropylidenediphenol), 9.42 g (0.044 mol) diphenyl carbonate, and 1.6 mg sodium methoxide are placed in the reaction flask under a stream of nitrogen. The flask is then evacuated to about 30 Torr and placed in a preheated (150°C) metal bath (Woods metal), whereby the components melt. The mixture is now vigorously stirred and gradually (about 1°C/min) heated to 220°C under reduced pressure. After the larger part of segregated phenol is distilled off, the pressure is reduced to 7 Torr, and the mixture heated to 235°C over a period of 1 h. Subsequently, the temperature is increased to about 280–300°C under higher vacuum (<0.1 Torr) during a period of 2 h. It is held at this temperature until the reaction mixture becomes very viscous. The vacuum is then released and the molten mass poured into a porcelain dish.

The solidified polycarbonate is a colorless, glassy material, which is soluble in methylene chloride, chloroform, pyridine, 1,4-dioxane, and tetrahydrofuran.

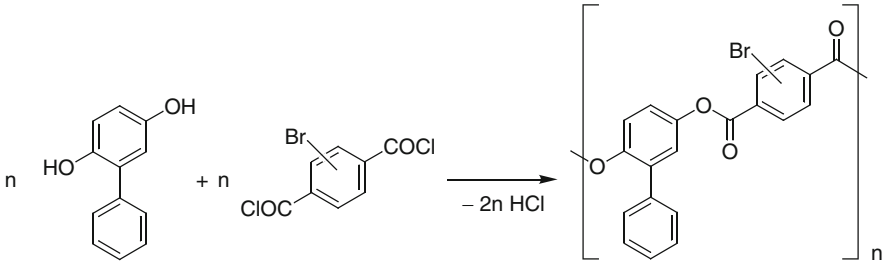
For characterization, the polymer is dissolved in methylene chloride, precipitated again in methanol and dried at 50°C in vacuum. The limiting viscosity number is determined in tetrahydrofuran at 20°C and the molecular weight calculated (see Sect. 2.3.3.3). Additional information can be obtained by infrared spectroscopy. There should be no absorption of the OH-group at ~3,400 cm^{-1}.

Polycarbonates find use as amorphous thermoplasts in nonbreakable windshields, housings for electric and electronic equipment, and as substrate in optical storage devices (CD, DVD).

Example 4.6 Preparation of a Liquid Crystalline (LC), Aromatic Main-Chain Polyester by Polycondensation in the Melt

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

This example describes the lowering of the melting point by introduction of side groups.



The highest purity of monomers and exact control of the reaction conditions are necessary for the synthesis of aromatic polyesters.

Purification of the Monomers

Phenylhydroquinone: 20 g of phenylhydroquinone are purified by fractional vacuum distillation ($p < 0.01$ Torr) and stored under dry nitrogen.

Bromoterephthaloyl chloride: A mixture of 10 g bromoterephthalic acid, 20 g freshly distilled thionyl chloride, and 1 ml of DMF is refluxed under a stream of nitrogen for 3 h. Next, the excess thionyl chloride is removed by vacuum distillation (about 10 Torr). The remaining bromoterephthalic dichloride is converted to bromoterephthalic acid dimethyl ester by adding the fourfold amount of anhydrous methanol. The excess of methanol is taken off on a rotary evaporator or by distillation and the pure bromoterephthalic acid dimethyl ester can be isolated by fractional distillation ($p < 0.01$ Torr) over a short column. The purity of bromoterephthalic acid dimethyl ester can be checked by gas chromatography. The pure bromoterephthalic acid dimethyl ester is converted to the acid by saponification with the fourfold amount of sodium hydroxide in boiling methanol. The bromoterephthalic acid is precipitated by addition of half-concentrated hydrochloric acid. It is filtered after cooling and washed with demineralized water and dried. Pure bromoterephthalic acid is placed in an exactly weighed reaction flask (the polycondensation reaction is carried out in the same flask), then freshly distilled thionyl chloride and 1 ml of DMF are added and treated as described above. After the reaction is complete, the excess of thionyl chloride is distilled off by vacuum distillation. Now the air is removed from the apparatus by repeated evacuation and filling with nitrogen.

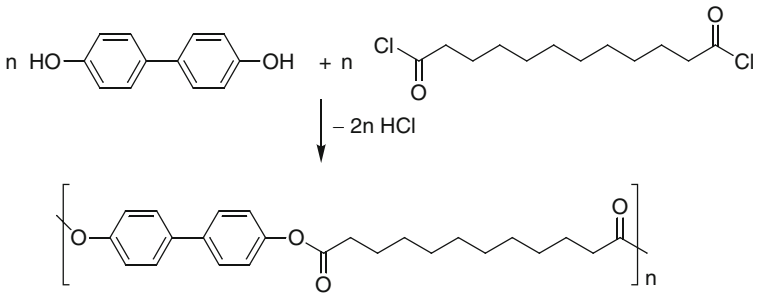
Preparation of Polyester by Melt Condensation

The exact amount of bromoterephthaloyl chloride is calculated by subtracting the weight of the empty flask from that of the reaction flask. Under a stream of nitrogen an equimolar amount of phenylhydroquinone is added. The further conversion has to be carried out according to a precise temperature program. The mixture is heated under a slow stream of nitrogen (important for the removal of hydrochloric acid; the pH is checked using moist pH paper) with stirring (with a sealed stirrer) for 2 h at 120°C, then 2 h at 180°C, 1 h at 200°C, 1 h at 220°C, and finally 2 h at 240°C. After cooling, the solid residue is ground, dissolved in a mixture of 1,1,2,2-tetrachloroethane (the dissolution takes place more rapidly with slight warming), and precipitated in methanol.

Characterization of the polyester can be done by infrared spectroscopy and inherent viscosity measurement ($c = 5$ g/l at 25°C) in a mixture of 1,1,2,2-tetrachloroethane/phenol (1:1). The inherent viscosity should be at least 0.1 l/g.

Example 4.7 Preparation of a Thermotropic, Main-Chain Liquid Crystalline (LC) Polyester by Interfacial Polycondensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.



In a 500 ml flat-bottomed three-necked flask, equipped with a powerful stirrer, dropping funnel, nitrogen inlet, and bubble counter are placed successively 0.93 g (5 mmol) of bisphenol A, 1.0 g of tetrabutylammonium bromide (phase transfer catalyst), and 2.5 g of KOH, suspended in 50 ml of water. A stream of nitrogen is now passed into the carefully stirred mixture at such a rate that the bubbles can be individually distinguished. The mixture is stirred until the initially cloudy reaction mixture becomes clear. A solution of 1.34 g (5 mmol) of dodecanedioic acid chloride in 50 ml of dry dichloromethane is introduced quickly through the dropping funnel. After the addition is complete, stirring is continued for a further 10 min and during this time the stirring rate should be adjusted to give good mixing. The polymer is precipitated from the white emulsion by pouring it dropwise into 400 ml of methanol. The polymer is separated by centrifugation, the upper organic layer decanted off, the polymer washed by slurrying several times with methanol, then with acetone, and dried under reduced pressure (water pump).

The liquid crystalline phases in polymeric materials can often be identified by polarized light microscopy and DSC measurements. The DSC diagram shows endothermic signals during heating because the molecular order of the polymer changes. The order of the above LC polymer is lost in two steps, therefore two peaks appear in the DSC curve. At the melting point (about 200°C) the transition of the crystalline, highly ordered structure to the smectic LC phase takes place, in which the rigid parts of molecules are arranged in layers, parallel to each other. The centers of gravity of the molecules possess a direction-dependent mobility. At the clearance point (about 260°C) this order is lost and the polymer chains are transformed into the fully irregular isotropic phase.

With polarizing microscopy the birefringence of a thin polymer film (between two glass plates) can be observed between two crossed polarizers provided that the polymer shows ordered regions in the same order of dimension as the wavelength of the light. A further characteristic of main-chain LC polymers is their low melt viscosity. Therefore, the glass plates can easily be moved against each other above the melting point.

Another class of crosslinkable polyesters is the so-called alkyd resins. Alkyd resins are defined as branched or crosslinked polyesters obtained, for example, by polycondensation of a dicarboxylic acid with a polyfunctional alcohol. Branching and crosslinking occur consecutively in a controllable manner. Thus, in the

polycondensation of glycerol with phthalic acid anhydride, there is first formed a branched polyester that remains soluble and fusible as long as the polycondensation is interrupted before more than about 75 mol% of the hydroxy or carboxyl groups have reacted. If this degree of condensation is exceeded the branched polyester transforms by further polycondensation (self-crosslinking) into completely insoluble products. Since one is dealing with crosslinking by polycondensation here, a temperature of about 200°C is generally required (baking varnishes). Of course, if carboxylic acids containing double bonds are incorporated into the alkyd resins they can be crosslinked by the action of atmospheric oxygen at lower temperatures. However, the crosslinking then proceeds by a different mechanism.

The dicarboxylic acids normally employed are phthalic acid or its anhydride, or mixtures of them with, for example, adipic acid or unsaturated acids. The polyhydroxy compounds generally used are glycerol, trimethylolpropane, or pentaerythritol. In the preparation and crosslinking of alkyd resins (with the exception of some unsaturated alkyd resins) the reaction is practically always carried out in the melt, taking the precautions discussed in Sect. 4.1.

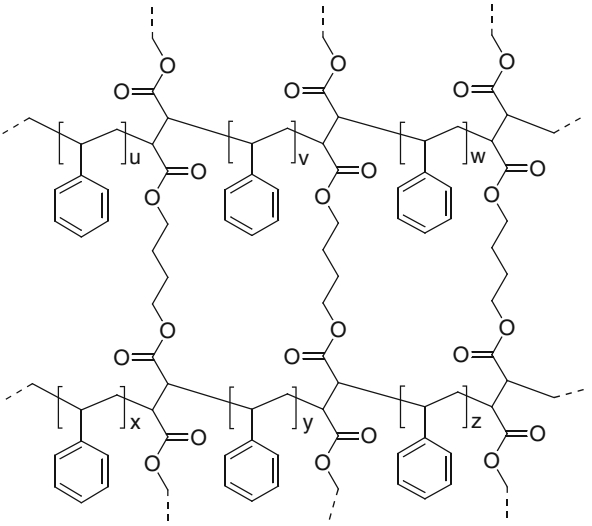
Example 4.8 Preparation of Unsaturated Polyesters

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Polycondensation of a diol with a dicarboxylic acid, either of which may contain a double bond, results in an unsaturated polyester. For this purpose suitable starting compounds are maleic anhydride and 2-butylene-1,4-diol. These can also be used mixed with saturated dicarboxylic acids or diols (copolycondensation) in order to vary the number of double bonds per macromolecule and thereby the properties of the polyester. Unsaturated polyesters are generally prepared by melt condensation. The resulting products are often viscous or waxy substances of relatively low molecular weight.

The incorporation of double bonds into polyesters provides the possibility for subsequent reactions. Of particular interest in this context are reactions that lead to crosslinking.

One of the best examples of ionic crosslinking is the addition of polyhydroxy compounds to double bonds, which sometimes takes place during the actual preparation of the unsaturated polyester. However, radically induced crosslinking reactions are much more important. They may be brought about by the action of oxygen and light, especially in the presence of suitable catalysts such as cobalt(II) compounds ("air drying"). The possibilities are considerably widened if one carries out a crosslinking copolymerization: the unsaturated polyester is dissolved in a radically polymerizable monomer, e.g., styrene and the polymerization then initiated by addition of a radical-forming system. Their structure can be represented schematically as follows:



The temperature required depends on the initiator used. With peroxides such as dibenzoyl peroxide, cyclohexanone peroxide, or cumyl hydroperoxide the reaction is carried out at 70–100°C ("hot curing"); with redox systems it can be done at room temperature ("cold curing"). Suitable redox systems consist of a combination of peroxides with reducing agents that are soluble in organic media, for example, metal salts (cobalt- or copper-naphthenoates or -octanoates) and tertiary amines (*N*,*N*-dimethylaniline). The most commonly used monomer for this crosslinking graft copolymerization is styrene; allyl compounds such as diallyl phthalate can also be employed. In all cases transparent, insoluble, three-dimensionally crosslinked products are formed that exhibit good heat stability and, especially when mixed with glass fibers, good mechanical properties.

The crosslinking graft copolymerization (curing) is generally carried out by first dissolving the unsaturated polyester (about 70 parts) by stirring in the monomer to be grafted (about 30 parts). High temperatures (up to 130°C) must often be used for this purpose. In order to prevent premature polymerization it is best to add some inhibitor (0.1–0.5 wt% hydroquinone or 4-*tert*-butylpyrocatechol). As soon as a homogeneous solution is obtained, it is cooled to the desired polymerization temperature and the initiator (about 1–3 wt% with respect to the total solution) is stirred in. The onset of polymerization is evidenced by gelation of the reaction mixture; the initially added inhibitor does not upset the catalyzed polymerization. The fully polymerized mass (allow a reaction time of up to 24 h according to the reaction conditions) often contains a low proportion of soluble material (homopolymer of the vinyl compound) that can be determined quantitatively by extraction of a well-ground sample using a suitable solvent (e.g., toluene when the monomer is styrene) for a period of 30 min. In this way one obtains an indication of the relative proportions of grafting and crosslinking.

The crosslinking copolymerization of unsaturated polyesters with styrene is utilized industrially for the production of surface coatings. More extensive are applications in fiber-reinforced plastics where the unsaturated polyesters are used as a matrix for inorganic and organic fibers (see Example 5.20). Areas of application are (large) parts in boats, vehicles, and sport equipment construction.

(a) *Preparation of the Unsaturated Polyester*

In a 500 ml three-necked flask, fitted with stirrer, nitrogen inlet, thermometer, and condenser for distillation with vacuum adapter, are placed 40 g (0.5 mol + excess of 5 mol%) of propane-1,2-diol, 24.5 g (0.25 mol) of maleic anhydride, 37 g (0.25 mol) of phthalic acid anhydride, and 20 mg (0.01%) of hydroquinone (as polymerization inhibitor). The air is removed from the apparatus by evacuating and filling with nitrogen. The mixture is then heated under a slow stream of nitrogen; melting occurs at 80–90°C so that the stirrer can be set in motion. Esterification begins at 180–190°C as indicated by distillation of water. This temperature is maintained until the acid number of the polyester has fallen to 50; this takes about 5–6 h. The melt is now cooled to 140°C and 100 g of monomeric styrene (to which 0.02% hydroquinone has been added after distillation) are introduced with stirring over a period of 1 min. The mixture is cooled immediately to room temperature with a water bath in order to prevent premature polymerization. One thus obtains a viscous, colorless to pale-yellow solution of the unsaturated polyester in styrene.

Determination of the Acid Number

1–2 g of the polyester (without styrene) are dissolved by warming with 50 ml acetone and, after cooling, are titrated as quickly as possible with 0.1-N alcoholic potassium hydroxide using phenolphthalein as indicator, until the red color remains for a few seconds.

The alkali consumption of the solvent is determined in a blank experiment. The acid number is given by the weight of KOH in mg, required to neutralize 1 g of substance.

(b) *Crosslinking (Curing) of the Unsaturated Polyester with Styrene*

Cold curing: To crosslink the polyester at room temperature (cold curing), 10 g of the polyester solution prepared in (a) are placed in a small beaker or flat tin can and the components of a suitable redox system stirred in one after the other (on no account at the same time!), for example:

1. 0.06 ml of a 10% solution of cobalt(II) naphthenoate (or octanoate) in styrene and
2. 0.2 ml of cyclohexanone peroxide or 2-butanone peroxide (e.g., as 50% solution in dibutyl phthalate);

or

1. 200 mg of dibenzoyl peroxide and
2. 0.05 ml of pure dimethylaniline.

After 30–40 min the mixture warms up and gels, indicating that the crosslinking graft copolymerization has begun. After 1 h, the mixture has become almost solid, most of the styrene having polymerized.

Hot curing: To carry out the crosslinking at higher temperatures (hot curing), 0.1 g of dibenzoyl peroxide is dissolved in 10 g of the polyester solution prepared in (a) and heated to 80°C. The polymerization sets in after a few minutes (gelation) and is essentially complete after 15 min.

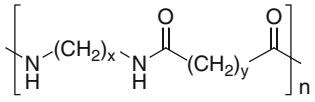
After curing: The sample obtained by cold or hot curing is not yet fully polymerized and to obtain optimum rigidity, an after-curing treatment is necessary. If it is performed at room temperature it takes 2–3 weeks, at 30–40°C a few days are sufficient and at 70–80°C some hours are adequate.

1 g each of the well-ground samples (see Sect. 2.5.1) obtained by cold, hot, and after curing is boiled with 10 ml of toluene for 30 min, filtered after cooling, and washed with toluene. The samples are thoroughly dried in vacuum at 60°C and the weight loss is determined. The toluene solutions are dropped into methanol and any extracted polystyrene is precipitated. The swellability of all samples is determined in an organic solvent.

Glass-fiber-reinforced plates can also be made in the above manner. For this purpose a mat of glass fibers is impregnated with the polyester solution already containing the radical initiator and cured at the appropriate temperature (see Example 5.20).

4.1.2 Polyamides

Polyamides are macromolecules whose constitutional repeating units are joined by amide groups, for example:



It has become the custom to name linear aliphatic polyamides according to the number of carbon atoms of the diamine component (first named) and of the dicarboxylic acid. Thus, the condensation polymer from hexamethylenediamine and adipic acid is called polyamide-6,6 (or Nylon-6,6), while the corresponding polymer from hexamethylenediamine and sebacoic acid is called polyamide-6,10 (Nylon-6,10). Polyamides resulting from the polycondensation of an aminocarboxylic acid or from ring-opening polymerization of lactams are indicated by a single number; thus polyamide-6 (Nylon-6) is the polymer from *e*-aminocaproic acid or from ε-caprolactam.

Many properties of polyamides are attributable to the formation of hydrogen bonds between the NH and CO groups of neighboring macromolecules. This is evidenced by

their solubility in special solvents (sulfuric acid, formic acid, *m*-cresol), their high melting points (even when made from aliphatic components), and their resistance to hydrolysis. In addition, polyamides with a regular chain structure crystallize very readily.

The melting points of *aliphatic polyamides* depend on the chain length of the starting materials: the melting point falls with increasing distance between the amide groups in the macromolecule, but polyamides made from components with an even number of carbon atoms melt at a higher temperature than the neighboring odd-numbered members of the series. Alkyl side chains (on carbon or nitrogen) lower the melting point, but at the same time improve the solubility.

Aliphatic polyamides are used as fibers and as engineering thermoplasts in automotive, electrical, and consumer product applications.

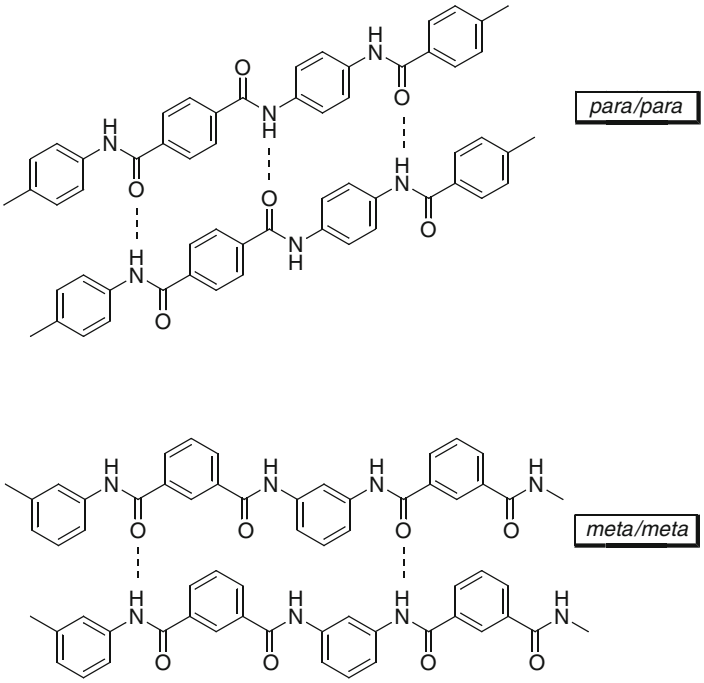
Aromatic polyamides (polyaramides) melt at considerably higher temperatures, often above their decomposition temperature so that they are mostly not thermoplastically processable. But they can be spun from solution to fibers of high technical value. Polyaramide fibers from *m*-phenylene diamine and isophthaloyl dichloride are nonflammable and find use in fire-protecting clothing and upholstery. The para-linked polyaramides, due to their linear and stiff main chain are able to form liquid crystalline phases in solution. Fibers spun from these solutions exhibit extraordinary high values of Young's modulus and strength.

The special properties and differences between all-*meta* linked and all-*para* linked polyaramides have three reasons:

- Microlinearity of the chain as a result of all-*para* linkage,
- Stiffness and planarity of the chain because of the partial double bond characteristics of the amide groups, and
- Stability of the conformation in the solid state by intermolecular hydrogen bonds.

As a consequence of this almost perfect alignment of molecule structures, such polyamides are able to orientate in solution and to form liquid crystalline phases (see Sect. 1.3.4). Out of these solutions one obtains fibers of poly(*p*-phenylene terephthalamide) (PPTA) having 5–10-fold higher values for stiffness and strength as the all-*meta* linked polymers. In addition, PPTA crystallizes, whereupon the fibers achieve an extraordinary temperature resistance: in a nitrogen atmosphere they decompose at temperatures above 550°C without melting.

These facts can be explained by a simple comparison of the stretched conformations of poly(*p*-phenylene terephthalamide) and poly(*m*-phenylene *iso*-phthalamide). Whereas the all-*para* linked polyamide can build up many hydrogen bonds to the neighboring molecules, this is less possible for the all-*meta* linked polymer:



The extreme insolubility of PPTA in common organic solvents is a serious disadvantage for the production and processing of this type of polymer. The solubility in strong polar solvents, e.g., *N*-methylpyrrolidone is improved by complexation of the polar amide groups with alkali halides or alkaline earth halides. The solubility still amounts to merely 3% and is, therefore, not sufficient for a spinning process. However, concentrated polyamide solutions can be obtained in concentrated sulfuric acid without additional complexing agent. In both cases the intermolecular polymer–polymer hydrogen bonds are broken. Furthermore, an electrostatic repulsion of the complexed (i.e., charged) amide groups within the polymer chain causes an additional stretching and stiffening of the macromolecules. This is evidenced by an α-value larger than 1 in the Mark-Houwink equation.

If one follows the solution viscosity in concentrated sulfuric acid with increasing polymer concentration, then one observes first a rise, afterwards, however, an abrupt decrease (about 5–15%, depending on the type of polymers and the experimental conditions). This transition is identical with the transformation of an optical isotropic to an optical anisotropic liquid crystalline solution with nematic behavior. Such solutions in the state of rest are weakly clouded and become opalescent when they are stirred; they show birefringence, i.e., they depolarize linear polarized light. The two phases, formed at the critical concentration, can be separated by centrifugation to an isotropic and an anisotropic phase. A high amount of anisotropic phase

is desirable for the fiber properties. This can be obtained by variation of the molecular weight, the solvent, the temperature, and the polymer concentration.

Sufficiently concentrated polyamide solutions as needed for physical measurements (e.g., viscosimetry, optical tests) must be prepared in two steps: At first, synthesis of the polyamide by use of precipitation polymerization and secondly, dissolving the carefully washed and dried polymer in concentrated sulfuric acid.

Fully aromatic polyamides are synthesized by interfacial polycondensation of diamines and dicarboxylic acid dichlorides or by solution condensation at low temperature. For the synthesis of poly(*p*-benzamide)s the low-temperature polycondensation of 4-aminobenzoyl chloride hydrochloride is applicable in a mixture of *N*-methylpyrrolidone and calcium chloride as solvent. The rate of the reaction and molecular weight are influenced by many factors, like the purity of monomers and solvents, the mode of monomer addition, temperature, stirring velocity, and chain terminators. Also, the type and amount of the neutralization agents, which react with the hydrochloric acid from the condensation reaction, play an important role. Suitable are, e.g., calcium hydroxide or calcium oxide.

The following are the main reactions employed for the preparation of polyamides:

- Polycondensation of ω-aminocarboxylic acids,
- Polycondensation of diamines with dicarboxylic acids,
- Polycondensation of diamines with derivatives of dicarboxylic acids (e.g., acid chlorides), and
- Ring-opening polymerization of lactams (see Sect. 3.2.3.4).

In principle, the attainment of chemical equilibrium can be accelerated by catalysts; however, in contrast to polyester formation, catalysts are not absolutely essential in the above-mentioned polycondensations. The first two types of reactions are generally carried out in the melt; solution polycondensations at higher temperature, e.g., in xylenol or 4-*tert*-butylphenol are of significance only in a few cases on account of the poor solubility of polyamides. On the other hand, polycondensation of diamines with dicarboxylic acid chlorides can be carried out either in solution at low temperature or as interfacial condensation (see Sect. 4.1.2.3).

4.1.2.1 Polyamides from ω-Aminocarboxylic Acids

The formation of polyamides by elimination of water from aminocarboxylic acids at high temperature (see Example 4.10) is generally only possible with acids having more than four methylene groups between the amino and carboxyl groups; under these conditions α- or *β*-aminocarboxylic acids undergo preferential ring closure (e.g., glycine/2,5-dioxopiperazine; *γ*-aminobutyric acid/*γ*-butyrolactam).

Example 4.9 Preparation of an Aliphatic Polyamide by Polycondensation of ε-Aminocaproic Acid in the Melt

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

The polycondensation can be performed in the apparatus described in Example 4.3. For the preparation of small amounts of Nylon-6 the following procedure is especially suitable, and at the same time permits a quantitative determination of the water eliminated.

5 g of ε-aminocaproic acid are weighed into a thick-walled tube of about 20 ml capacity, carrying a ground joint. The tube is fitted with as small a distillation adapter as possible and connected via a short tube to a weighed U-tube filled with anhydrous granular calcium chloride. The adapter and attached tube are wrapped with aluminum foil. A slow stream of nitrogen is passed through the distillation head which serves both to carry away the eliminated water and to provide a buffer against atmospheric oxygen, the presence of which leads to strongly colored products.

The tube is now immersed nearly up to its neck in an oil or metal bath and the ε-amino-caproic acid melted at a bath temperature of 220°C. Then it is heated quickly to 260°C and held at this temperature under a continuous stream of nitrogen for 15 min. Should any water condense on the wall of the connecting tube leading to the calcium chloride tube, it can be removed by warming with a hot-air blower before the heating bath is taken away and the melt allowed to cool under nitrogen. Finally, the tube is broken and the solid polyamide removed. The calcium chloride tube is weighed again to determine the amount of water eliminated. The experiment is repeated twice more, extending the reaction times to 30 and 60 min, respectively. The limiting viscosity numbers of the three samples are determined in concentrated sulfuric acid at 30°C ($c = 10$ g/l) using an Ostwald viscometer (capillary diameter 0.6 mm). The increase of the η_{sp}/c values with reaction time is a measure of the progress of the polycondensation.

The resulting Nylon-6 has a melting point of 215°C; fibers can be drawn from the melt. The product still contains small amounts of cyclic and linear polyamides that can be extracted from the finely ground product with methanol in a Soxhlet apparatus (12 h). The extract contains ε-caprolactam as well as cyclic and linear oligomers up to the pentamer; these can be quantitatively determined by evaporating of the methanol in vacuum. The ε-caprolactam is then dissolved out by digestion with anhydrous ether. The residue is taken up in methanol (1% solution) and passed through a column filled with a strongly acidic cation exchange resin (elute with the same volume of methanol). The linear oligomers are retained on the column, while the cyclic oligomers are quantitatively determined by evaporating the eluate to dryness. They can be separated by chromatography (e.g., HPLC).

4.1.2.2 Polyamides from Diamines and Dicarboxylic Acids

The polycondensation of diamines with dicarboxylic acids can be carried out simply by melting together the highly purified components under nitrogen at 180–300°C. However, considerable amounts of diamine can be carried over with the water that distills off, especially towards the end of the reaction when vacuum is applied. The equivalence of the reaction partners, which is a prerequisite for the attainment of a high molecular weight, is thereby disturbed. Therefore, it is

advantageous to start with an excess of diamine; the optimum excess must be determined for each individual case. Accordingly, the technical synthesis of polyamides from diamines and dicarboxylic acids is carried out in autoclaves.

An elegant variation of this procedure is to carry out the polycondensation with the salt of a diamine and a dicarboxylic acid (see Example 4.10). In this case, the formation of salt (which is also the first step in the direct polycondensation of a diamine and a dicarboxylic acid) and the polycondensation are carried out as two separate steps. The salts can be obtained in good crystalline form most simply by mixing equimolar amounts of diamine and dicarboxylic acid in a solvent in which the salt formed is insoluble (e.g., ethanol). In order to attain high molecular weights by such polycondensations the salts should be as neutral as possible (exactly equivalent amounts of diamine and dicarboxylic acid) and very pure (recrystallize, for example, from mixtures of ethanol/water).

Example 4.10 Preparation of Polyamide-6,6 from Hexamethylenediammonium Adipate (AH Salt) by Condensation in the Melt

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Preparation of the AH Salt

12 g (0.082 mol) of pure adipic acid (mp 152°C) are dissolved in 100 ml of 95% ethanol and 9.7 g (0.082 mol) of pure hexamethylenediamine are dissolved in a mixture of 27 ml of ethanol and 10 ml of water. Both solutions are filtered if they are not perfectly clear.

The adipic acid solution is now placed in a 250 ml beaker and the diamine solution added dropwise with stirring over a period of 8 min, during which the solution warms up to 40–45°C. After stirring for a further 30 min and allowing to cool, the crystallized AH salt is filtered off with suction, washed twice with 95% ethanol and dried in vacuum. Yield: 90–95%; mp 183°C (with loss of water); pH value of 9.5% aqueous solution: 7.62. Impure AH salt can be recrystallized from ethanol/water mixtures (volume ratio 3:1).

Polycondensation of the AH Salt

A 50 ml pear-shaped flask, fitted with distillation head, air condenser, vacuum adapter, and receiver is three-quarters filled with AH salt and the air removed by evacuation and filling with nitrogen. It is then heated under nitrogen for 1 h on a silicone oil bath at 220°C, and for further 3 h at 260–270°C. After cooling, the flask is broken carefully with a hammer. The polyamide from adipic acid and hexamethylenediamine melts at 265°C. It can be spun from the melt into threads which can be cold drawn. The viscosity number is determined in concentrated sulfuric acid or in 2 M KCl in 90% formic acid (see Sect. 2.3.3.3).

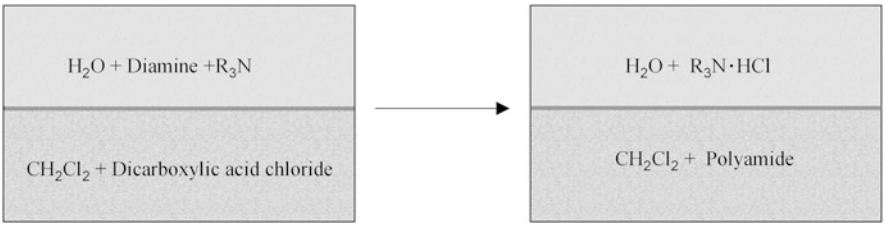


Fig. 4.1 Interfacial polycondensation of dicarboxylic acid and diamine

4.1.2.3 Polyamides from Diamines and Dicarboxylic Acid Derivatives

As in the preparation of polyesters, also in the preparation of polyamides, the reaction temperature can be considerably reduced by using derivatives of dicarboxylic acids instead of the free acids. Especially advantageous in this connection are the dicarboxylic acid chlorides which react with diamines at room temperature by the Schotten-Baumann reaction; this polycondensation can be carried out in solution as well as by a special procedure known as interfacial polycondensation (see Examples 4.11 and 4.12).

The solution polycondensation usually works at room temperature in approximately 10% solution in toluene, methylene chloride, *N*-methylpyrrolidone (NMP), or dry tetrahydrofuran (THF). Tertiary amines (triethylamine) or dispersed calcium hydroxide are added as acid acceptor. This procedure has the following advantages: The polycondensation is carried out at low temperature (0–40°C); it is nevertheless very fast, the reaction usually being over in a few minutes. At low temperatures practically no side reactions occur. Disadvantages are the following: relatively large amounts of solvent must be purified and handled; and large amounts of salts are formed as by-products. Condensation in solution at low temperature is, therefore, above all a laboratory method, in which these disadvantages are not so important. It is to be particularly recommended in that it yields a high-molecular-weight condensation polymer in a short time with simple equipment.

In interfacial polycondensation, the two components are separately dissolved in two immiscible solvents. The polycondensation can now take place only at the interface of the two liquids, whereby the practically instantaneously formed thin polyamide film prevents further diffusion of the two reactants. The polycondensation can only continue when this film is pulled carefully away from the interface; the process can thus be run continuously in a simple way (Fig. 4.1).

Interfacial polycondensation can be also performed in dispersion (Example 4.13): For this purpose the solution of acid dichloride is dispersed in the aqueous solution of diamine by vigorous stirring (if necessary in the presence of a water-soluble dispersion stabilizer). The polycondensation then takes place at the surface of the droplets. Water is especially suitable as solvent for the diamine component, while aliphatic chlorinated hydrocarbons are best for the dicarboxylic acid dichlorides.

Interfacial polycondensation can be carried out not only with aliphatic but also with aromatic dicarboxylic acid dichlorides (with disulfonic acid dichlorides the

corresponding polymeric sulfonamides are formed). An exact equivalence of the two reactants is not absolutely necessary. If, however, very high molecular weights are the goal, the optimum conditions must be found by varying the concentrations of the reactants. A major advantage of interfacial polycondensation is the high reaction rate; in many cases the reaction is finished in a few minutes even at low temperature. Thus, side reactions, such as transamidation, as well as oxidative and thermal decomposition are avoided; these almost always occur during melt condensation. In addition, the experimental equipment is very simple.

In this way one can prepare successfully even high-molecular-weight, very high-melting polyamides that are obtainable by the usual methods only in low molecular weights, if at all. Furthermore, reactants can be used that still carry reactive groups (for example, hydroxy groups, C/C double or triple bonds). An advantage over solution condensation at low temperature is that the eliminated hydrogen chloride does not precipitate as a salt that needs to be separated later, but remains in solution as amine hydrochloride. The molecular weights attainable by interfacial polycondensation are at least as high as those obtained by melt condensation (10,000–30,000), and are often much higher.

Example 4.11 Preparation of Polyamide-6,10 from Hexamethylenediamine and Sebacoyl Dichloride in Solution and by Interfacial Polycondensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

(a) *By Polycondensation in Solution at Low Temperature (Precipitation Polycondensation)*

The alcohol-free chloroform required for this experiment is first prepared by running 70 ml of chloroform through a column filled with basic aluminum oxide.

Sebacoyl dichloride is obtained as follows: 20 g of sebacoic acid and 50 g of thionyl chloride are refluxed on a water bath for 2 h. The excess thionyl chloride is then distilled off and the sebacoyl dichloride fractionated in vacuum (bp 142°C/2 Torr).

1.77 g (16.7 mmol) of hexamethylenediamine and 5.1 ml of triethylamine are dissolved in 33 ml of alcohol-free chloroform in a 250 ml three-necked flask fitted with stirrer and reflux condenser. With vigorous stirring, 3.57 ml (16.7 mmol) of sebacoyl dichloride in 13.5 ml of alcohol-free chloroform are then added as quickly as possible (in about 10 s) at room temperature, stirring being continued for another 5 min. The polycondensation occurs instantaneously with considerable heat evolution and precipitation of the condensation polymer. The reaction mixture is cooled and filtered, the product being washed successively with chloroform, petroleum ether, 1 N hydrochloric acid, water, and 50% acetone and is finally dried in vacuum at 50°C. Yield: about 70%; a further low-molecular-weight fraction can be isolated from the filtrate by shaking with petroleum ether.

(b) *By Interfacial Polycondensation*

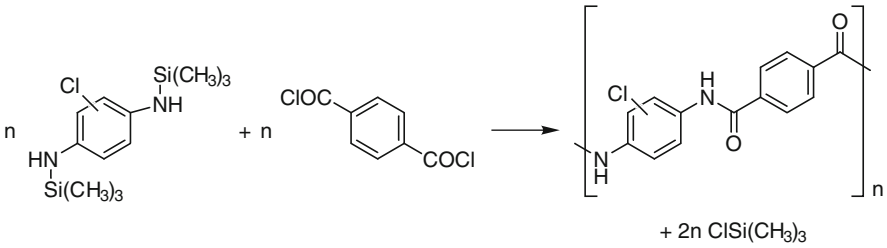
A solution of 3 ml (14 mmol) of freshly distilled sebacoyl dichloride (for preparation see above) in 100 ml of carbon tetrachloride is placed in a 250 ml beaker. A solution of 4.4 g (38 mmol) of hexamethylenediamine in 50 ml of water is carefully run on to the top of this solution, using a pipette. (The aqueous solution can be made more readily visible by coloring it with a few drops of phenolphthalein solution.) A polyamide film is immediately formed at the interface and can be pulled out from the center with tweezers or clamps and laid over some glass rods; it can now be pulled out continuously in the form of a hollow thread and wound up on to a spool driven by a slow-running motor. The polycondensation comes rapidly to a standstill if the motor is stopped, but immediately recommences, even after some hours, when the motor is restarted.

The drawn-off polyamide thread is thoroughly washed in 50% ethanol or in acetone, then with water and dried in vacuum at 30°C. The Nylon-6,10 so obtained has the same physical properties as that obtained by condensation in solution (see under above) or by melt condensation. It melts at 228°C and can be spun from the melt by pulling with a glass rod; the threads can be cold drawn.

Example 4.12 Synthesis of a Lyotropic Liquid Crystalline Aromatic Polyamide from Terephthalic Acid Dichloride and Silylated 2-chloro-1,4-Phenylenediamine by Polycondensation in Solution

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

In order to activate the aromatic amino groups, the synthesis is carried out with trimethylsilyl-substituted diamines:



Purification of the Monomers

During the synthesis of aromatic polyamides special attention must be paid to the purity of the monomers and an exact control of the reaction conditions.

2-Chloro-1,4-phenylenediamine sulfate is dissolved in water and the pH value adjusted to 10 by addition of a 50% potassium hydroxide solution. After evaporation at reduced pressure, the diamine is recovered by repeated extraction with ether. The ether layer is dried with Na_2SO_4, the ether is removed and the diamine sublimated in vacuum at 80°C, whereby a colorless product results which decomposes above 135°C. Melting point: 64–65°C.

Terephthaloyl dichloride is distilled in vacuum, Melting point: 82–83°C.
LiCl is dried in vacuum at 150°C for 24 h.

Polycondensation

In a 250 ml three-necked flask fitted with stirrer and internal thermometer 11.04 g (0.078 mol) of 2-chloro-1,4-phenylenediamine are dissolved in 150 ml dry *N*,*N*-dimethylacetamide (containing 2 wt% LiCl). 29.5 ml (0.233 mol) of highly pure trimethylchlorosilane (>99%) are dropped into the solution under stirring at 20°C. Then 15.71 g (0.078 mol) of terephthaloyl dichloride are added, whereupon the temperature and the solution viscosity increase immediately. After 2 h opaque, lytropic liquid crystalline solution is obtained. This solution is poured into a beaker and water is slowly added to the solution, whereupon the polyamide precipitates. It is washed with water to remove the salt-containing solvent. Finally, the product is purified by extraction with propane-2-ol. The polymer is dried in a vacuum oven at 100°C. The polyamide is characterized by determination of the solution viscosity at 20°C (1.25 g of polymer in 50 ml *N*-methylpyrrolidone with 2 wt% of LiCl).

Example 4.13 Microencapsulation of a Dyestuff by Interfacial Polycondensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Microencapsulation means the envelopment of liquid droplets or solid particles with natural or synthetic polymers. The encapsulation of a substance with a polymer membrane is undertaken for various reasons, for example, as protection against moisture, or to obtain delayed dissolution of fertilizers, herbicides, or drugs by microencapsulation with semipermeable membranes.

Various techniques have been developed for the preparation of microcapsules with diameters of 1–5,000 μm; one of these involves the method of interfacial polycondensation. The following example describes the microencapsulation of a dyestuff, which has practical application in the manufacture of carbon-free copy paper.

(a) *Preparation of Dye-Containing Microcapsules*

The following ingredients are prepared in parallel:

1. *Dispersion system*: 1 g of low-molecular-weight poly(vinyl alcohol) which serves both as dispersing agent and protective colloid, is dissolved in about 150 ml of distilled water in a narrow 600 ml beaker. It is stirred with a paddle stirrer at room temperature for about 2 h until dissolved. The polymer used should be a partially (88%) hydrolyzed poly(vinyl acetate), a 4% aqueous solution of which has a viscosity of 4 cP.
2. *Acid chloride solution*: 7.7 g (0.04 mol) of terephthaloyl dichloride are finely powdered in a mortar and dissolved in 40 g of dibutyl phthalate by stirring at 70°C, taking care to exclude moisture. Dissolution takes about 30 min; any insoluble material is filtered off.

3. *Dyestuff solution*: 1 g of crystal violet lactone [3,3-bis(*p*-dimethylaminophenyl)-6-dimethylaminophthalide] is dissolved in 10 g of dibutyl phthalate by stirring at 90°C for 15 min. The solution is brown/red.
4. *Amine solution*: 3 g (0.03 mol) of diethylenetriamine and 3.2 g of NaOH pellets are dissolved in 20 ml of distilled water with cooling; time required: 15 min. (*Caution*: use hood and avoid all contact of the amine with the skin or clothes!)

The paddle stirrer in the dispersion system [vessel (1)] is now replaced by a high-speed disperser with a strong shearing action. To minimize the formation of foam the contents are stirred at about 2,000 rpm, solutions (2) and (3) are then mixed together with gentle stirring (magnetic stirrer). This water-insoluble mixture is run dropwise into the dispersion vessel over a period of 30 s, the stirrer speed having been raised to about 7,000 rpm as the first drops enter. After a further 30 s the emulsion drop size has adjusted to about 6–10 μm. The particle size can be checked by examination of a sample under a transmission microscope (magnification about 500) with a built-in measuring scale.

The amine solution (4) is now immediately run in dropwise over a period of 30 s and the stirrer speed reduced to 2,000 rpm After 2–3 min the high-speed stirrer is replaced by a normal paddle stirrer and the dispersion stirred (500 rpm) for a further 30 min at room temperature to complete the interfacial polycondensation between terephthaloyl dichloride and diethylenetriamine.

(b) *Testing the Microcapsules*

The microcapsules can be seen under the microscope as individual spherical particles or as small agglomerates.

The use of the microcapsules to make carbon-free copy paper can be demonstrated in principle. The dispersion is painted on to a sheet of typing paper with a fine paint brush. To prevent the paper from curling up it is fixed to a glass plate with adhesive tape. After drying the paper with a hot air drier, the coated side is laid on a silica gel plate. The other side is then written on with gentle pressure. This breaks down the microcapsules, causing the colorless color-forming solution to flow out onto the underlying silica gel plate, developing a blue-colored imprint; thus a blue copy of the writing appears on the silica gel plate, e.g., a plate for thin layer chromatography. One must take care that the painted paper is completely dry, otherwise no copy appears. The resulting blue coloration on the silica gel plate can be removed reversibly by moistening.

4.1.3 Phenol-Formaldehyde Resins

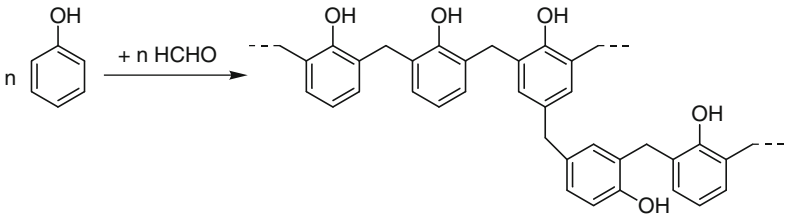
The high-molecular-weight products formed by the condensation of phenols with carbonyl compounds (especially with formaldehyde) are known as phenolic resins. They are mixtures of structurally nonuniform compounds that are initially soluble and fusible but which can become crosslinked (cured) by subsequent reactions. One distinguishes between acid- and base-catalyzed condensations, since they lead to different end products; the properties of the condensation polymer are also affected by the mole ratio of phenol to formaldehyde.

Condensation in acid medium gives soluble, fusible phenolic resins, with an average molecular weight between 600 and 1,500, and a structure consisting essentially of phenol residues linked by methylene groups in the *ortho*- and *para*-positions; they are called Novolaks. No further condensation occurs on heating this product for longer periods; but it can be crosslinked by reaction with suitable polyfunctional components, e.g., with additional formaldehyde. On the other hand, in basic medium one obtains soluble, fusible hydroxymethylphenols, with a molecular weight between 300 and 700, containing one or more benzene nuclei; they are called Resols. In contrast to the Novolaks, the Resols undergo crosslinking through their reactive groups on heating, giving insoluble, infusible products (Resites).

By far the most important phenolic resins are those made from phenol and formaldehyde. They exhibit high hardness, good electrical and mechanical properties, and chemical stability. Very often they are used in combination with (reactive) fillers like sawdust, chalk, pigments etc.

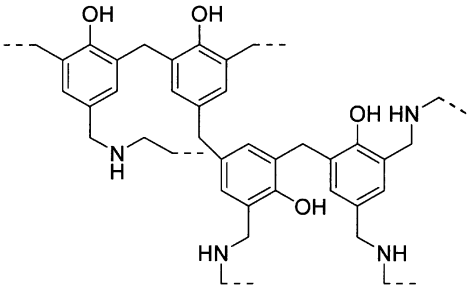
4.1.3.1 Acid-Catalyzed Phenol-Formaldehyde Condensation (Novolaks)

The condensation of phenol with formaldehyde in acid medium is an exothermic reaction (97 kJ/mol) yielding soluble phenolic resins. The melting point(between 100°C and 140°C) is depending on the molecular weight of resulting resin (600–1,500 g/mol). The structure of the Novolaks can only be indicated schematically, since the coupling of the phenolic nuclei through methylene groups can occur in both *ortho*- and *para*-positions; coupling also occurs through oxymethylene groups so that there are a multitude of possibilities:



This polycondensation is practically always carried out in aqueous solution, either by dropwise adding an approximately 30% solution of formaldehyde at 80–100°C slowly into an acidified phenol solution, or by mixing the components at room temperature and then heating. In order to avoid premature crosslinking, the molar ratio of phenol/formaldehyde should not be higher than 1:0.8. After all the formaldehyde has been added, the mixture is allowed to react until the formaldehyde has disappeared. The aqueous layer is separated off and the product washed with hot water to remove the acid as completely as possible. The residual water and the unconverted phenol are then removed under vacuum at higher temperature. The resins so obtained are generally soluble in alcohols, lower esters, ketones, and dilute alkali. As catalyst one should choose an acid that is easy to remove from the final product by washing or distillation. Hydrochloric acid, oxalic acid, or mixtures of the two are very suitable. Oxalic acid can be removed both by washing and by heating to 180°C.

Since Novolaks have no reactive groups that can lead to self-crosslinking, they must be subsequently crosslinked (cured) by addition of suitable di- or polyfunctional compounds that react with phenols. Amongst these are formaldehyde, hydroxymethyl compounds, aminobenzyl alcohols, hydroxy- and aminobenzylamines, and bis(hydroxybenzyl) ether. The most commonly used crosslinking agent is hexamethylenetetramine (urotropine). Crosslinking is effected by mixing the components and heating for a short time (a few minutes) to 150–220°C. The structure of the crosslinked phenolformaldehyde resin is very complex. If crosslinking is carried out with hexamethylenetetramine the crosslinks consist mainly of dibenzylamine and tertiary amine bridges:



Example 4.14 Acid-Catalyzed Phenol-Formaldehyde Condensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

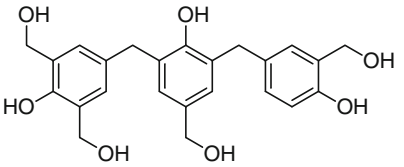
Caution: Because of the formation of gaseous formaldehyde all reactions must be carried out in a closed hood.

32.5 g (0.345 mol) of phenol, 23 g of a 37% aqueous formaldehyde solution (0.285 mol), 3.75 ml of water, and 0.5 g of oxalic acid dihydrate are placed in a 250 ml three-necked flask, fitted with stirrer and reflux condenser, and heated under reflux on an oil bath for 1.5 h. 75 ml of water are then added, stirred briefly, and allowed to cool, whereby the condensation polymer settles out. The aqueous layer is separated and the residual water distilled off at 50–100 Torr while slowly raising the temperature to 150°C. This temperature is maintained (at most for 1 h) until test samples solidify on cooling. The resin is poured out while still warm and solidifies to a colorless, brittle mass, soluble in alcohol.

The Novolak obtained is used to fabricate a molding by mixing with sawdust and hexamethylenetetramine as follows: 12.5 g of finely ground Novolak, 12.5 g of dry sawdust, 1.75 g of hexamethylenetetramine, 0.5 g of magnesium oxide (to trap residual acid from the condensation), and 0.25 g of calcium stearate (as lubricant) are thoroughly mixed (best in a ball mill or analytical mill) and then heated in a mold at 140 bar for 5 min at 160°C. The resulting molding is infusible and insoluble.

4.1.3.2 Base-Catalyzed Phenol-Formaldehyde Condensation (Resols)

Condensation of phenols with an excess of formaldehyde in basic medium yields phenolic resins (Resols), with an average molecular weight of 300–700, which are generally soluble in water or alcohol. Like Novolaks they consist essentially of phenol nuclei linked to one another through methylene groups; they differ, however, especially in their content of hydroxymethyl groups. The latter makes a number of reactions accessible (e.g., esterification and ether formation). The coupling of the phenol residues and the incorporation of hydroxymethyl groups again occurs in the *ortho*- and *para*-positions. The structure of Resols may be indicated schematically as follows:

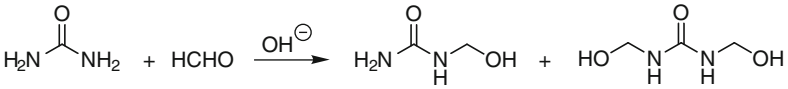


Resols are prepared by heating an aqueous phenol solution with a 1.1–1.5-fold excess of formaldehyde in basic medium. Suitable catalysts are the hydroxides of the alkali and alkaline earth metals, also primary and secondary amines, and especially ammonia; the use of amines can lead to their incorporation in the phenolic resin. The reaction temperature should be kept below 70°C if possible; otherwise the water solubility of the resulting Resol is reduced. Reaction times of 2–5 h are generally required. In contrast to the Novolaks, Resols can be transformed into insoluble, infusible products by self-crosslinking under mild conditions; water is eliminated from the hydroxymethyl groups, forming dimethylene ether bridges. Crosslinking, accompanied by structural transformations (formaldehyde elimination) and rearrangements, occurs on heating to 150–200°C; depending on the chemical composition and structure of the Resol, this requires a few minutes to several hours to achieve complete hardening.

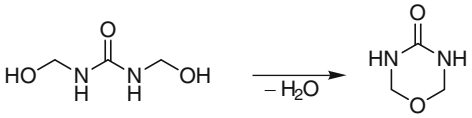
4.1.4 Urea- and Melamine-Formaldehyde Condensation Products

4.1.4.1 Urea-Formaldehyde Resins

Condensation of urea with formaldehyde leads to products of various structures and properties according to the experimental conditions (pH, temperature, reaction time, molar ratio of components). The condensation is generally carried out in basic medium, resulting essentially in the formation of hydroxymethyl compounds; some oxymethylene groups are also formed, particularly on heating. Mono-, di-, and trihydroxymethylurea have been proved to be primary products of this condensation; whether tetrahydroxymethylurea is also formed is as yet uncertain:



4-Oxo-perhydro-1,3,5-oxadiazine (urone) is also formed by intramolecular condensation:



These "pre-condensates" are soluble in water and alcohol; they are transformed by further condensation with elimination of water, first into high-molecular-weight, poorly soluble materials and finally into crosslinked insoluble products. The structure of the crosslinked (hardened) urea-formaldehyde resins is not yet entirely understood.

The soluble hydroxymethyl compounds can be chemically modified, before crosslinking, by reaction with monofunctional compounds (e.g., by esterification or ether formation). The properties of the starting materials as well as the crosslinked end products can thereby be substantially altered. For example, by partial etherification with butanol the hydroxymethyl compounds, originally soluble only in polar solvents, become soluble also in nonpolar solvents (toluene), without losing their ability to undergo self-crosslinking.

Urea-formaldehyde resins are generally prepared by condensation in aqueous basic medium. Depending on the intended application, a 50–100% excess of formaldehyde is used. All bases are suitable as catalysts provided they are partially soluble in water. The most commonly used catalysts are the alkali hydroxides. The pH value of the alkaline solution should not exceed 8–9, on account of the possible Cannizzaro reaction of formaldehyde. Since the alkalinity of the solution drops in the course of the reaction, it is necessary either to use a buffer solution or to keep the pH constant by repeated additions of aqueous alkali hydroxide. Under these conditions the reaction time is about 10–20 min at 50–60°C. The course of the condensation can be monitored by titration of the unused formaldehyde with sodium hydrogen sulfite or hydroxylamine hydrochloride. These determinations must, however, be carried out quickly and at as low temperature as possible (10–15°C), otherwise elimination of formaldehyde from the hydroxymethyl compounds already formed can falsify the analysis. The isolation of the soluble condensation products is not possible without special precautions, on account of the facile back-reaction; it can be done by pumping off the water in vacuum below 60°C under weakly alkaline conditions, or better by careful freeze-drying. However, the further condensation to crosslinked products is nearly always performed with the original aqueous solution. This can be done either by heating the neutral solution to 120–140°C (10–60 min) or catalytically in the presence of acids at low temperatures. The catalytic crosslinking (acid hardening) can be carried out not

only with free acids (e.g., phosphoric acid), but also with compounds that become acidic on heating (latent hardeners). The latter include sodium salts of halogenated carboxylic acids, esters of phosphoric acid, ammonium chloride, and pyridine hydrochloride. Addition of large amounts, for example, of phosphoric acid (pH $\approx$ 2), causes crosslinking even at room temperature (cold glue). All crosslinking reactions of urea-formaldehyde resins occur by further condensation of hydroxymethyl compounds with expulsion of water. This water can, during the curing of large moldings, lead to inhomogeneity and fissures; however, these difficulties can be overcome by addition of water-absorbing fillers such as cellulose or other polyhydric alcohols (Example 4.17).

Example 4.15 Urea-Formaldehyde Condensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Caution: Because of the formation of gaseous formaldehyde all reactions must be carried out in a closed hood.

Preparation of a Urea-Formaldehyde Resin

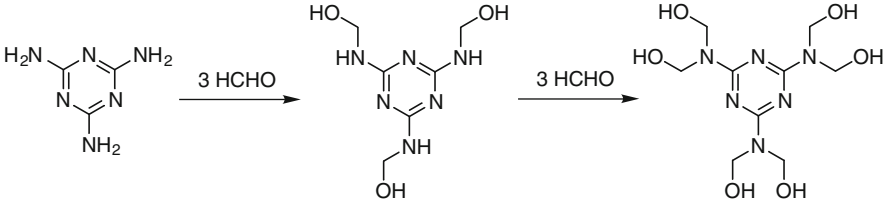
30 g (0.5 mol) of urea are dissolved in 61 g of a 37% aqueous formaldehyde solution (0.75 mol) heated to 50°C (use a well ventilated hood) in a 250 ml three-necked flask fitted with thermometer, stirrer, and reflux condenser. 2.5 ml of concentrated ammonia solution are then added and the temperature is raised to 85°C. After about 20 min the solution becomes cloudy and the viscosity increases; at the same time the pH value falls to about 5. After a total period of 1 h the heating is removed and a small sample is tested to see if the condensation product is still soluble in water.

Cellulose powder is now stirred into the cooled solution until the mass can still just be stirred. The contents of the flask are then transferred to a large beaker and more cellulose powder is kneaded in by hand (wear rubber gloves!) until a total of 35 g has been added. The crumbled mixture is dried for 24 h at 50°C in the vacuum oven. Finally, the dried product is finely ground in a mortar, mixed with 1% of ammonium chloride and 1% of zinc stearate (as lubricant) and crosslinked (cured) by heating to about 160°C for 10 min in a simple press at 300–400 bar. A thin transparent plate is obtained that is no longer soluble in or attacked by water; this is more convincing if a small piece is allowed to stand overnight in a beaker of water.

If a heatable press is not available, one may proceed as follows: Two flat iron plates of about 2-cm thickness are heated in an oven to 240°C and then taken out. One of these plates is laid on the lower jaw of a horizontally mounted vice. It is allowed to cool until a crumb of the filled condensation product no longer decomposes (colors) when placed on the plate. A few grams of the mixture are then quickly put on the plate, the second plate placed on top and the whole tightened in the vice.

4.1.4.2 Melamine-Formaldehyde Resins

Formaldehyde resins with better water- and temperature-stabilities are obtained if the urea is partly or wholly replaced by melamine (aminoplasts). These condensations are likewise carried out mainly in alkaline medium, again yielding soluble "pre-condensates" consisting essentially of *N*-[tris- and hexakis-(hydroxymethyl)] compounds of melamine.



These pre-condensates are most stable at pH 8–9; they are transformed by further condensation (essentially by elimination of water from hydroxymethyl groups and free NH groups) into poorly soluble and finally insoluble, crosslinked products. Chemical modification of the soluble pre-condensate, for example, by esterification or ether formation, is again possible.

The practical preparation of melamine-formaldehyde resins is done under the same conditions as for urea-formaldehyde resins. Melamine is at first insoluble in the aqueous reaction mixture but dissolves completely as the condensation proceeds. Because of the greater stability of the *N*-hydroxymethylmel-amines compared with the corresponding urea compounds the reaction can easily be followed by titration of the unconverted formaldehyde with sodium hydrogen sulfite (see Sect. 4.1.4.1).

Crosslinking (hardening) of these pre-condensates can be carried out exactly as for the urea-formaldehyde resins, best at a pH value of 3.5–5. Melamine-formaldehyde condensates crosslink most quickly if prepared using a 2.8–3-fold excess of formaldehyde.

Urea- and melamine-formaldehyde resins are used as moldings, lacquers, and adhesives (for wood), also as textile additives (increased crease resistance) and paper additives (improved wet strength).

Example 4.16 Melamine-Formaldehyde Condensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Caution: Because of the formation of gaseous formaldehyde all reactions must be carried out in a closed hood.

Preparation of the Polymer

The experimental arrangement consists of a 250 ml three-necked flask equipped with stirrer, double-necked head with reflux condenser and thermometer, and a rubber stopper through which passes a glass rod. 63 g (0.5 mol) of melamine

and 150 g of a 40% aqueous formaldehyde solution (2.0 mol) are placed in the flask; the aqueous suspension is stirred and adjusted to pH 8.5 by adding a few drops of 20% NaOH. The mixture is heated on a water bath to 80°C within 5–10 min, with continuous stirring. Complete solution is reached at 70°C to 80°C. During this warm-up period the decrease of pH of the solution must be continually compensated by dropwise addition of 20% NaOH. The stirred solution is now heated to 80°C at constant pH of 8.5 until the precipitation ratio (see below) reaches 2:2. The solution is cooled and filtered from small amounts of insoluble material.

Melamine dissolves in aqueous formaldehyde solution on warming, with the formation of *N*-hydroxymethyl compounds. The latter are crystalline substances that dissolve in hot water but are only slightly soluble in cold water. If a sample of the reaction mixture is cooled immediately after the melamine has been completely taken into solution, the poorly soluble *N*-hydroxymethyl compounds precipitate.

With further heating, condensation polymers are obtained that at first are completely miscible with water. However, they still contain a relatively large number of low-molecular-weight *N*-hydroxymethyl compounds so that the solutions quickly become cloudy on cooling. With longer heating times the aqueous solutions of the resins remain clear. At this stage of condensation, however, the solutions are clear only if a limited amount of water is present; they precipitate on dilution. With increasing condensation time the compatibility with water is diminished further until finally the melamine-formaldehyde condensation polymer separates out from the reaction solution.

Determination of the Precipitation Ratio

After about 50–60 min condensation time a small sample of the reaction mixture is dropped into iced water and the cloudiness observed. From this moment on, samples of exactly 2 ml are taken at regular intervals of 10 min and, after allowing cooling to 20°C, distilled water at 20°C is added dropwise with stirring. The condensation experiment is stopped when the sample becomes slightly cloudy after the addition of 2 ml of water.

Impregnation of Paper

The resin solution prepared above is transferred to a porcelain dish and in it are immersed about 10–20 circular filter papers (diameter 9 cm). After about 1–2 min the filter papers are lifted out with tweezers and the excess solution allowed to drip off. The impregnated filter papers are fastened with clips to a line and allowed to dry overnight.

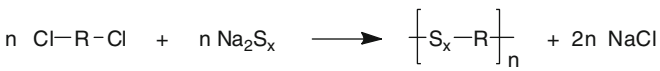
Fabrication of a Laminated Molding

Ten of the resin-impregnated papers are stacked on top of each other. This stack is laid between two aluminum foils (15 × 15 cm) and pressed in a hydraulic press at 135°C and a pressure of 40–100 bar for 15 min. After releasing the pressure the sample is removed while it is still hot.

The fabrication of laminated plastics with good transparency requires pressures of the magnitude indicated. All heatable, hydraulic, laboratory or commercial presses are suitable for this work. It is also possible to use two nickel-plated iron plates, 2 cm thick, heated to about 140°C in an oven, and clamped in a horizontally mounted vice (see Sect. 2.5.2.1). The resistance of the hardened melamine-formaldehyde laminated plastic is tested against solvents and chemicals.

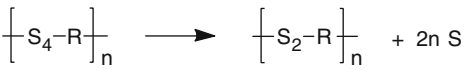
4.1.5 Poly(Alkylene Sulfide)s

The reaction of suitable aliphatic dihalogen compounds with alkali or alkaline earth polysulfides results in the formation of linear, rubbery or resinous, poly(alkylene sulfide)s:



The most widely used dihalide is 1,2-dichloroethane. The use of polyhalides (e.g., 2% 1,2,3-trichloropropane) results in the formation of branched or crosslinked products. Sodium tetrasulfide (Na_2S_4) is generally used as the polysulfide since it contains scarcely any of the monosulfide which reacts with dihalides to form cyclic by-products with unpleasant odors.

Sulfur can be removed from the poly(alkylene sulfide) with the aid of sulfur-binding agents; for example, by treatment of an aqueous dispersion with Na_2S, NaOH, or Na_2SO_3 at 30–100°C, the sulfur content can be reduced to two atoms per constitutional repeating unit of the macromolecule:



Further desulfurization results in degradation of the poly(alkene sulfide)s to low-molecular-weight products. Vulcanization of the linear poly(alkene sulfide)s yields crosslinked elastic materials which are commercially important because of their solvent and oil resistance. They are also less sensitive to oxygen and light than most synthetic rubbers. The technical properties can be modified especially by changing the sulfur content, as well as by admixture of fillers. Poly(alkene sulfide)s are used as solvent-resistant rubbers, sealing compounds, and adhesives. Aromatic polysulfides [poly(arylene sulfide)s, PPS] possess substantially higher glass transition temperatures. Hence these polymers can be used as temperature-stable thermoplastics (see Sect. 4.1.6.2).

Poly(alkene sulfide)s are prepared by allowing the dihalide to drip slowly under vigorous stirring into a moderately concentrated aqueous polysulfide solution (generally in 10–20% excess). Temperature and reaction time depend mainly on the dihalide being used: for 1,2-dichloroethane, temperatures between 50°C and 80°C, and reaction times of about 5 h suffice; on the other hand, long-chain dihalides

Table 4.3 Different poly(arylene ether)s and their properties

X	Y	Chemical name	Properties
–O–	–O–	Poly(arylene ether)s	amorphous
–S–	–S–	Poly(arylene sulfide)s	crystalline
–O–	$–SO_2–$	Poly(arylene ether sulfone)s	amorphous
–O–	–CO–	Poly(arylene ether ketone)s	crystalline
–O–	Imide	Poly(arylene ether imide)s	amorphous

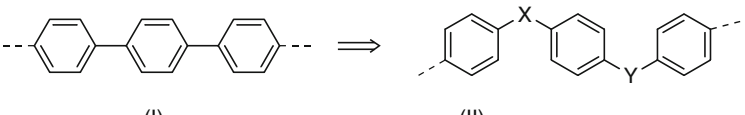
require 20–30 h at 100°C. Since the poly(alkene sulfide)s are insoluble in water and very easily agglomerate into lumps, thereby making further reaction and subsequent washing very difficult, it is expedient to carry out the polycondensation in the presence of a dispersing agent (for example, 2–5% magnesium hydroxide). Emulsifiers are not recommended since they make the work-up difficult. When the reaction has finished, the mixture is freed from sodium chloride and unreacted sodium polysulfide by slurrying several times with water. It is then acidified with concentrated hydrochloric acid in order to coagulate the poly(alkene sulfide). The resulting yellow-white spongy cake has an unpleasant smell. It is dried in a vacuum desiccator over P_2O_5. The dry product is partially soluble in carbon disulfide. Poly (alkene sulfide)s can also be prepared by ring-opening polymerization of episulfides.

4.1.6 Poly(Arylene Ether)s

According to investigations on oligomeric model compounds, macromolecules consisting of C–C linked, unsubstituted aromatic rings (polyphenylenes (I)) should be thermally and chemically very stable due to their low-energy crystal structures and their high melting points ($T_m > 500°C$). However, unsubstituted polyphenylenes are neither soluble nor meltable without decomposition and thus cannot be processed.

When groups are inserted into the main chain, its regularity is disturbed and chain mobility increases (reduction of the enthalpy of melting as well as increase of the entropy of melting). Thus, polymers are formed that can be further processed from solution or in bulk.

In cases where carbonyl or sulfonyl groups are inserted between the aromatic rings in addition to oxygen or sulfur, the resulting type of polymers is commonly classified as poly(arylene ether)s (II).



(I) (II)

X, Y = O, S, CO, SO_2

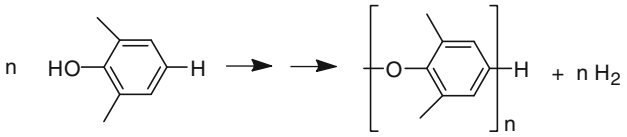
The five classes of poly(arylene ether)s of technical interest are shown in Table 4.3.

Poly(arylene ether)s generally exhibit high glass transition temperatures, resistance to hydrolysis, as well as an excellent thermo-oxidative stability.

4.1.6.1 Poly(Phenylene Ether)s

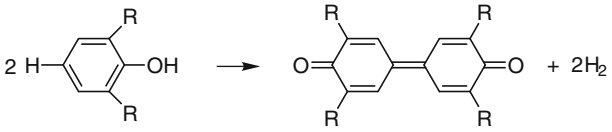
Dehydrogenation of aromatic compounds is a general method for the synthesis of poly(phenylene ether)s. This type of reaction, in which monomers are joined together to form macromolecules by loss of hydrogen, is formally to be classified as polycondensation reaction; here too, polymers are formed from monomers by continuous elimination of a low-molecular-weight compound (hydrogen), while the polymer retains its activity towards the growth reaction. The first step is the elimination of one electron (oxidation) from the highest-occupied molecular orbital (HOMO) of the phenolate molecule whereby a neutral radical is formed. This step of reaction is catalyzed by copper(I) ions (redox catalyst). Further steps of the oxidative polycondensation are abstraction of a hydrogen atom, combination of radicals with increase of the molecular weight and reoxidation of the electron-rich π-system.

To this type of reaction belongs the synthesis of poly(phenylene ether)s from substituted phenols, for example, poly(2,6-dimethylphenylene ether), PPE, from 2,6-dimethylphenol in the presence of pyridine and copper(I) chloride:



For the synthesis of polymers by dehydrogenation of phenols, the monomer structure and the reaction conditions must conform to certain requirements:

- The substitution of hydrogen atoms must occur in the 2-, 4-, or 6-position relative to the OH group.
- To obtain linear polymers, the phenolic nucleus must be substituted in the 2- and 6-positions.
- Halogen atoms can be present; they decrease the rate of the reaction and may be eliminated during the polymerization with the formation of branching points.
- The phenol must be relatively easily oxidizable; substituents that raise the oxidation potential lead to an inhibition of the dehydrogenation reaction (2,6-dichlorophenol gives only a low-molecular-weight polymer and 2,6-dinitrophenol does not react at all).
- The substituents in the 2- and 6-positions must not exceed a certain geometrical size. Otherwise, instead of regular –O–C– coupling leading to the poly (phenylene ether)s, there is simply a –C–C– coupling of the monomers to form diphenylquinones. This reaction is favored by higher temperatures. The pale-yellow coloration of poly(-2,6-dimethyl-1,4-phenylene ether) may be caused by the presence of quinones.



Suitable catalysts are copper(I) salts [e.g., Cu(I) chloride, bromide, and sulfate] in combination with amines to form oxidation sensitive phenolates. The amine/copper salt ratio must be made as large as possible, to minimize the formation of diphenylquinone and to give a high molecular weight.

Example 4.17 Preparation of Poly(2,6-Dimethylphenylene Ether)

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Poly(2,6-dimethylphenylene ether) can be prepared by dehydrogenation of 2,6-dimethylphenol with oxygen in the presence of copper(I) chloride/pyridine as catalyst at room temperature. It is known that the mechanism involves a stepwise reaction, probably proceeding via a copper phenolate complex that is then dehydrogenated.

0.4 g of copper(I) chloride are slurried in a mixture of 100 ml of chloroform and 20 ml of pyridine contained in a 500 ml three-necked flask fitted with stirrer, gas inlet, and thermometer. Oxygen is passed through the flask under vigorous stirring. After 10–20 min a clear, dark-green solution is formed. 10 g (0.082 mol) of pure 2,6-dimethylphenol are added to this solution and more oxygen is passed through under vigorous stirring. The temperature of the solution rises slowly to about 40°C and the color of the solution becomes yellow-brown. After the temperature has reached its maximum (about 30 min), the viscous solution is poured into 1 l of methanol containing 10 ml of concentrated hydrochloric acid to destroy the copper complex. The polymer is washed with methanol and precipitated again from chloroform (100 ml) into 1 l of methanol containing 10 ml of HCl. Yield: quantitative.

When working with larger quantities, the temperature can be kept constant by external cooling. A temperature of 30°C is advantageous for the formation of a high-molecular-weight product. The higher the 2,6-dimethylphenol concentration, the higher is the molecular weight of the polymer formed.

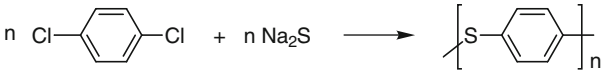
Poly(2,6-dimethylphenylene ether) is amorphous and has a glass transition temperature of about 170°C. It is soluble in chlorinated hydrocarbons such as chloroform, carbon tetrachloride, as well as tetrachloroethane, and also in nitrobenzene and toluene. It is mainly used as a homogeneous blend with polystyrene (see Sect. 5.5).

To make a film, 2 g of the polymer is pressed for 5 min between two metal plates heated to 320°C (see Sect. 2.5.2.1). After chilling the metal plates with water, the film can be peeled off.

4.1.6.2 Aromatic Polysulfides [Poly(Arylene Sulfide)s]

The technically most important polysulfide is polythiophenylene or poly(*p*-phenylene sulfide), PPS. It is obtained by reacting sodium sulfide and *p*-dichlorobenzene in a polar solvent, for example, 1-methyl-2-pyrrolidone at about 280°C under pressure. The mechanism of the reaction is very complex and cannot be described by a simple aromatic substitution. This synthesis requires special autoclaves and is therefore not suitable for a laboratory course (for an experimental procedure see Table 2.3).

Because of the limited solubility of PPS – even at high temperature – the attainable molecular weights are relatively low (M_n = 1,000–20,000).

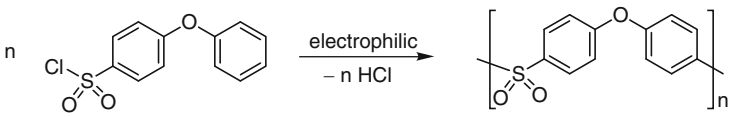


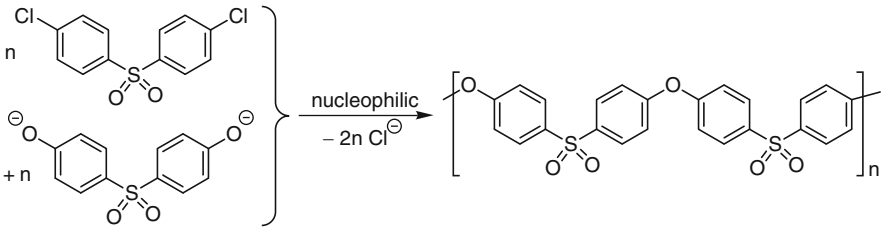
Nevertheless, PPS has an interesting property profile even at these molecular weights. To a large extent it is linear and crystalline with a glass transition temperature of 85°C and a crystallite melting point of 280°C. Due to its high chemical resistance – PPS is practically insoluble in common organic solvents – and inherent non-flammability, it has found applications in harsh environments. In addition, PPS can be filled with minerals or glass fibers at concentrations of up to 70 wt%. Hence, it can replace metals in many areas (machines, apparatus constructions, and electronics).

4.1.6.3 Poly(Arylene Ether Sulfone)s

The incorporation of SO_2 groups into the main chain of poly(phenylene ether)s leads to poly(phenylene ether sulfone)s. The preferential synthetic routes are:

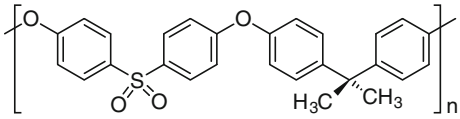
– Electrophilic aromatic substitution, using Friedel-Crafts catalysts and
– Nucleophilic aromatic substitution, according to an addition-elimination mechanism.





The nucleophilic polycondensation has the advantage that the chemical structure and thus the properties of the poly(ether sulfone)s can be varied in a relatively simple way through the selection of the bisphenol components.

The technically most important poly(arylene ether sulfone) is obtained from bisphenol A and 4,4′-dichlorodiphenyl sulfone by nucleophilic aromatic polysubstitution.



The reaction is carried out in dimethyl sulfoxide at 130–160°C under an inert atmosphere. High purity of the starting materials is of prime importance in order to obtain high molecular weights. The water, which results from the neutralization of the bisphenols, can be removed via an azeotropic distillation with toluene.

Because of the angled structure of poly(arylene ether sulfone)s, they generally do not crystallize. They are thus amorphous and optically transparent with glass transition temperatures between 150–200°C. They are soluble in some polar solvents, hydrolysis resistant, and inherently flame resistant. Fields of application for these materials are found particularly in the area of electronics and membrane technology.

The chemical modification of poly(arylene ether sulfone)s has already been described in numerous papers. They relate to sulfonation, fluorination, and halomethylation. These derivatives are particularly suitable for the preparation of hydrolysis- and temperature-resistant separation membranes. They are used already for sea water desalination, and also for the separation of gas mixtures.

Example 4.18 Synthesis of Poly(Arylene Ether Sulfone) from Bisphenol A and 4,4′-Dichlorodiphenyl Sulfone

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

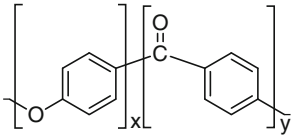
In a 500 ml three-necked flask, fitted with stirrer, thermometer, and water trap, 5.71 g (25 mmol) of bisphenol A are dissolved in a mixture of 60 ml dry dimethyl sulfoxide and 30 ml dry toluene. After thorough flushing with nitrogen, 7.0 g (50 mmol) potassium carbonate are added. The mixture is then heated under stirring at 170°C for 4 h, in order to remove the water by azeotropic distillation with toluene. Then 7.18 g (25 mmol) of 4,4′-dichlorodiphenyl sulfone are added to this suspension. After further 10 h at 170°C, the reaction mixture is cooled, diluted with 100 ml of THF followed by careful addition of 80 ml of concentrated hydrochloric acid. The aqueous phase is extracted repeatedly with THF. Phase separation is induced by addition of small amounts of methyl *tert*-butyl ether. The organic phases are collected and concentrated. This viscous solution is slowly dropped into 3 l of distilled water with intensive stirring, whereupon the polymer precipitates. After

further 20 h stirring the suspension is filtered, and the product washed with distilled water. For purification, the polysulfone is dissolved in 80 ml of THF, precipitated again in 2 l of ethanol, and dried for 3 days at 80°C in vacuum.

The synthesis of poly(arylene ether sulfone)s with other bisphenols, e.g., 4,4-bis (4-hydroxyphenyl)pentanoic acid, can be carried out in a similar way.

4.1.6.4 Poly(Arylene Ether Ketone)s

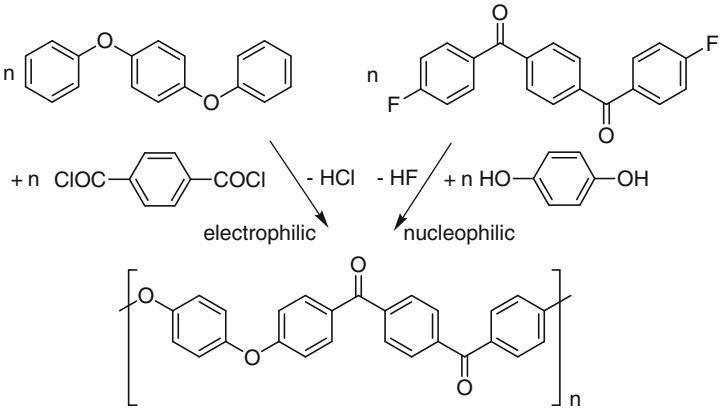
Poly(arylene ether ketone)s have the following general structure:



Depending on the number of ether and keto groups in the constitutional repeating units one distinguishes between poly(ether ketone)s (PEK, x = y = 1), poly (ether ether ketone)s (PEEK, x = 2, y = 1), poly(ether ketone ketone)s (PEKK, x = 1, y = 2), and poly(ether ether ketone ketone)s (PEEKK, x = y = 2).

In analogy to poly(arylene ether sulfone)s, there are two different polycondensation methods for the technical synthesis of poly(arylene ether ketone)s:

– Electrophilic aromatic substitution using Friedel-Crafts catalysts and
– Nucleophilic aromatic substitution according to an addition-elimination mechanism.



poly(ether ether ketone ketone) (PEEKK)

Depending on the type of the monomers, a large number of crystallizable poly (arylene ether ketone)s with different contents of keto and ether groups can be synthesized by employing one of the two procedures. The ratio of keto to ether groups determines essentially the thermal properties of the linear unsubstituted poly

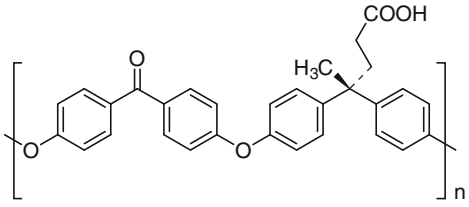
(arylene ether ketone)s. In addition to glass transition temperatures ranging from 120–190°C, crystallite melting points between 270°C and 400°C can be achieved. Unsubstituted poly(arylene ether ketone)s are generally poorly soluble. Often they can only be dissolved in concentrated sulfuric acid at room temperature, whereas in the proximity of their melting points only few organic solvents with high boiling points (e.g., diphenyl sulfone) can be used. Therefore, the synthesis of these polymers on an industrial scale is not an easy matter. The nucleophilic polycondensation is achieved in diphenyl sulfone as solvent and at temperatures above 320°C. It is experimentally not simple to separate the formed salt and the solidified solvent at room temperature from the rigid, stone-hard reaction mixture. Therefore, the synthesis of a substituted and thus substantially more easily soluble poly(arylene ether ketone) is described in Example 4.22. It can be performed in standard laboratory equipment. Because of the lower electron-withdrawing activity of the keto group in comparison to the sulfone group the more reactive aryl-difluoride must be used.

In addition to the excellent thermostability, which is due to their high crystallite melting points, poly(arylene ether ketone)s exhibit a very good chemical resistance because of their low solubility.

They display a high non-flammability, and for a partly crystalline material, an unusually high impact strength. The high stability of the melt permits one to process the material using conventional methods (injection molding, extrusion). Accordingly, poly(arylene ether ketone)s are used in the automobile, electrical, and electronic industry.

Example 4.19 Preparation of a Substituted Poly(Ether Ether Ketone) from 4,4-bis(4-hydoxyphenyl)Pentanoic Acid and 4,4′-Difluorobenzophenone

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.



In a 250 ml three-necked flask, fitted with internal thermometer, stirrer, and water trap 7.16 g (25 mmol) of 4,4-bis(4-hydoxyphenyl)pentanoic acid are dissolved in a mixture of 60 ml of dry DMSO and 30 ml of dry toluene. After thoroughly flushing with inert gas, 7.0 g (50 mmol) of potassium carbonate are added. This mixture is heated under stirring to 170°C for 4 h to remove the water by azeotropic distillation with toluene. Then 5.45 g (25 mmol) of 4,4′-difluorobenzophenone are added to this suspension. After further 10 h at 170°C, the mixture is cooled, whereby a phase separation occurs. The upper phase is discarded, whereas the lower phase is diluted with a mixture of THF and concentrated hydrochloric

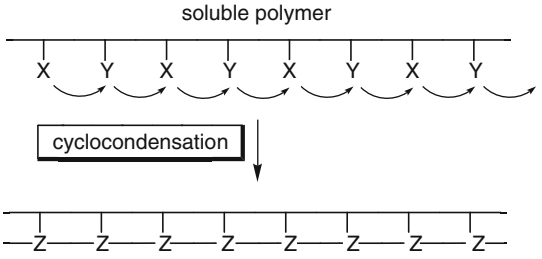
acid (200 ml, 3:1 vol. ratio). The crude product is obtained by slowly dropping this viscous solution into 3 l of distilled water, followed by intensive stirring for further 20 h. The polymer is filtered and washed with distilled water. The resulting solid is dissolved in 80 ml of THF, precipitated again in 1.2 l of ethanol, and dried for 3 days at 80°C in vacuum.

Due to the side chains this polymer is amorphous with a glass transition temperature of 185°C. In contrast, unsubstituted poly(arylene ether ketone)s are crystalline and high melting ($T_m > 300$°C). The IR spectrum shows absorption bands at 3,300 cm^{-1} and 1,710–1,730 cm^{-1} for the acid group in the side chain and at 1,650 cm^{-1} for the keto group.

4.1.7 Polymers with Heterocyclic Rings in the Main Chain

In general, polymers with heterocyclic rings as structural element show a high chemical and thermal stability. On the other hand, they are insoluble and infusible, so that they could not initially be used for practical applications in this form.

It was not until the synthesis was accomplished in two steps that it became possible to process these polymers from solution. In the first reaction step, two tetrafunctional monomers form a linear and soluble macromolecule by a polyreaction of two of the functional groups of each molecule. Subsequently, cyclocondensations take place in a second step, in which the heterocyclic rings are formed. This side reaction occurs intramolecularly. Therefore, it does not lead to a further molecular enlargement. The resulting polymers have heterocyclic units in their main chain; they are mostly insoluble and infusible:



insoluble polymers with heterocyclic units in the main chain

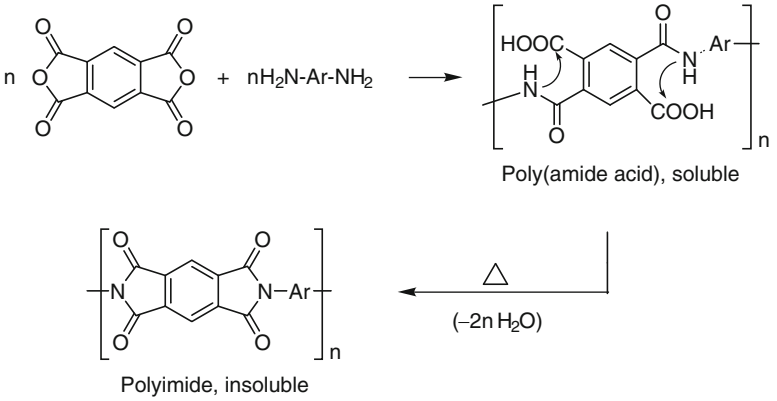
Stepwise addition polymerizations (polyaddition) or condensation polymerizations (polycondensation) are possible polyreactions for the first step. The two latter combinations attained interest in the technical synthesis of polyimides and polybenzimidazoles.

There are two possibilities for practical implementation. If the polymers with the heterocyclic groups are to be isolated in powder form, the polycyclocondensation can be achieved in the same reaction mixture, i.e., in solution. However, if the polymer is to be isolated in the form of fibers, foils, coatings, or adhesives, the following procedure is appropriate: The soluble, still reactive polymers of the first

reaction step are poured out, e.g., as a film, or spun into a fiber. Then the solvent is evaporated and afterwards the polycyclocondensation is carried out by heating the finished article in the solid state.

4.1.7.1 Polyimides

Polyimides are obtained by a two-step synthesis, i.e., a combination of stepwise polyaddition followed by a polycyclocondensation. The first reaction consists of the addition of an aromatic diamine to a dianhydride of a tetracarboxylic acid and occurs rapidly at 20–40°C in a strongly polar solvent (*N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, *N*-methylpyrrolidone). The resulting poly(amide acid) is soluble. The highly viscous solution of the poly(amide acid) so produced, is cast in a thin layer and heated to 150–300°C; the solvent evaporates and the second reaction occurs at the same time, resulting in ring closure with intramolecular elimination of water to give the polyimide. The commercial polyimides are obtained from pyromellitic- or 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and phenylenediamine or dianiline derivatives (which are linked by methylene groups or a heteroatom).



Among other properties, polyimides exhibit very good electrical characteristics. They are very resistant to chemicals and temperature. Thus, foils or coatings made of polyimides are applied in the electric and microelectronic industry (cable insulation, flexible printed circuit boards) or in membrane technology. By using a special sintering technology, plates and rods can be produced from polyimide powder, and from these, finished parts for mechanical engineering (valves, bearings, seals) can be made by metal cutting.

Example 4.20 Preparation of a Polyimide from Pyromellitic Dianhydride and 4,4′-Oxydianiline by Polycyclocondensation

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

First Reaction (Stepwise Addition Polymerization): Preparation of the Poly(Amide Acid)

4.0 g (0.02 mol) of 4,4′-oxydianiline (recrystallized from toluene and dried in vacuum for 8 h at 50°C) are dissolved in 30 ml of pure dimethylformamide in a dry 100 ml round-bottomed flask, fitted with a drying tube and magnetic stirrer. 4.36 g (0.02 mol) of pyromellitic dianhydride (sublimed in high vacuum) are added in portions over a period of a few minutes, with continuous stirring. The stepwise addition polymerization begins immediately and is completed by stirring the viscous solution for a further hour at 15°C.

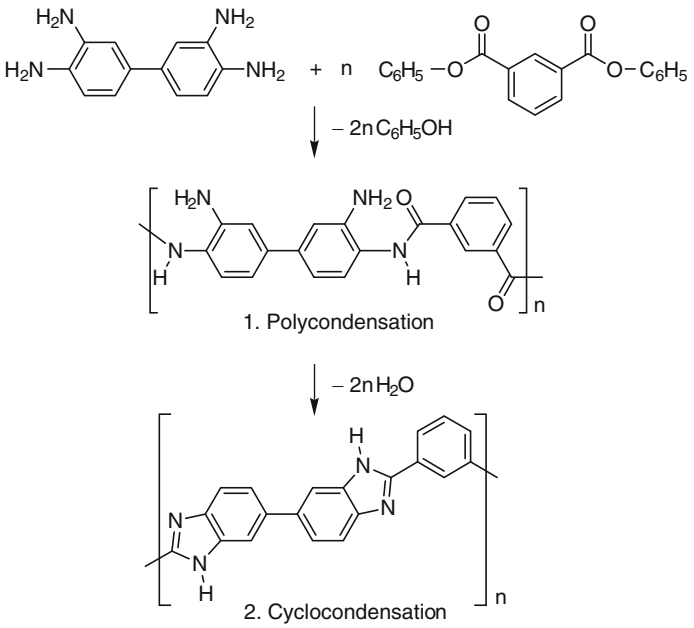
About 20 ml of the poly(amide acid) solution are then dropped into 300 ml of water with vigorous stirring. The precipitated colorless polymer is filtered with suction, washed several times with water, and dried in vacuum at 100°C for 20 min. The limiting viscosity number is determined in dimethylformamide at 25°C (Ostwald viscometer, capillary diameter 0.4 mm).

Second Reaction (Polycyclocondensation): Preparation of the Polyimide

The polyimide is formed by the thermal polycyclocondensation of the poly(amide acid). For this purpose, 5 ml of poly(amide acid) solution are placed on a watch glass (diameter 10 cm) and kept in a vacuum oven at 50°C for 24 h. The solvent evaporates and at the same time cyclization to the polyimide takes place; the resulting film is insoluble in dimethylformamide. The formation of the polyimide can be followed by IR spectroscopy: the NH-band at 3,250 cm^{-1} disappears while imide bands appear at 1,775 and 720 cm^{-1}. Once the initial drying process has raised the solid content to 65–75%, the polyimide formation can be accelerated by heating the poly(amide acid) film to 300°C in a vacuum oven for about 45 min. The polyimide made from pyromellitic dianhydride and 4,4′-oxydianiline exhibits long-term stability in air above 200°C.

4.1.7.2 Poly(Benzimidazole)s

The technical production of poly(benzimidazole) (PBI) is also carried out in two steps. In the first step an aromatic tetramine is condensed with the diphenyl ester of an aromatic dicarboxylic acid at 220–260°C, yielding a poly(amino amid) with elimination of phenol. Ring closure with elimination of water occurs in the second step (solid-phase polycyclocondensation), conducted at 400°C and yielding the polybenzimidazole (experimental procedure, see Table 2.3).

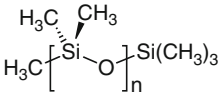


The resulting polybenzimidazole is amorphous and shows a very high glass transition temperature of 425°C. It is highly flame resistant. Therefore, PBI fibers that are spun from solution, are used for the production of fireproof protection clothes and also for fabrics of airplane seats.

By the use of a special sintering technology, moldings (semifinished materials) can be made from PBI powder. By mechanical processing, articles with exceptional properties can be produced. Due to the high pressure resistance PBI is suitable for bearings and also sealing rings for thermal and mechanical highly stressed parts.

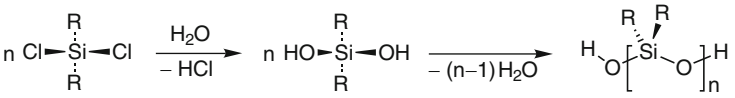
4.1.8 Polysiloxanes

Polysiloxanes are macromolecules which have a backbone of alternating silicon and oxygen atoms, with the two remaining valencies of the silicon atoms linked to organic side groups, e.g., methyl groups. Polysiloxanes have the tendency to form helical conformations, in which the methyl groups are located at the outer side of the helix, thus causing a "shielding-effect" for the –Si–O–bonds. This explains the unusual combination of properties of these macromolecules, e.g., high temperature stability and resistance to weathering due to the strength of the –Si–O–bond, flexibility at low temperatures, low surface tension, and hydrophobicity, although their main chain is relatively polar. As a result, polysiloxanes either unfilled or filled with minerals, have found a multitude of quite different applications, like temperature-stable oils, greases, sealing materials, lacquers, and elastomers.



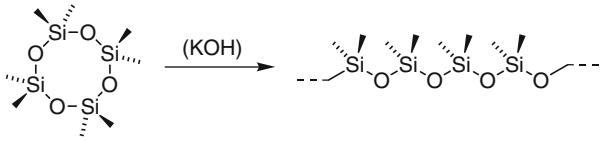
In their properties, polysiloxanes are intermediate between purely organic polymers and inorganic silicates; the structure may be varied in numerous ways to shift the pattern of properties of silicones either in one direction or the other. Commercial polysiloxanes generally contain methyl substituents. Whereas in the scientific literature the name polysiloxanes is used, the name silicones (silicone oil, silicone grease, silicone rubber) is preferred in the technical literature.

Various functional silanes (e.g., R_2SiCl_2 or $RSiCl_3$) can be used as starting materials for the preparation of polysiloxanes. The silanes are first hydrolyzed to the corresponding silanols, which are very unstable and easily undergo polycondensation with the elimination of water and the formation of –Si–O–Si– linkages:



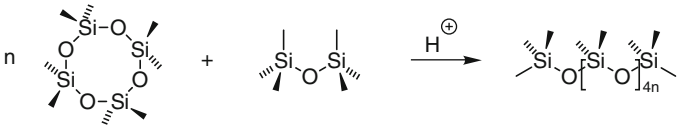
Linear polysiloxanes obtained by the hydrolysis of dichlorosilanes are of relatively low molecular weight; they can, however, be condensed further through the terminal OH groups by thermal after-treatment.

The siloxanes have a great tendency towards ring formation so that in the hydrolysis products of dichlorosilanes one finds not only linear polysiloxanes, but also cyclic oligosiloxanes with 3 to 9 Si–O units in the ring; under the right reaction conditions these ring compounds can even be the main product (see Example 4.24). Cyclic siloxanes can be polymerized by ring-opening both cationically (e.g., with Lewis acids) and anionically (e.g., with alkali hydroxides); trimers and tetramers of dimethylsiloxane are especially suitable as monomers (see Example 4.21):



The polysiloxanes obtained by anionic initiation have considerably higher molecular weights than those obtained by cationic initiation.

Ring-opening polymerization of cyclic siloxanes with cationic initiators allows the possibility of introducing stable end groups by the use of suitable chain transfer agents. Thus, polysiloxanes with trimethylsilyl end groups are formed when the cationic polymerization of octamethylcyclotetrasiloxane is carried out in the presence of hexamethyldisiloxane as transfer agent:



The acid-catalyzed degradation of a high-molecular-weight polysiloxane, containing OH end groups, when carried out in the presence of hexamethyldisiloxane, also leads to low-molecular-weight polysiloxanes with trimethylsilyl end groups (see Example 4.21). This reaction is also named "equilibration". Polysiloxanes that do not possess OH end groups cannot condense further on heating; the molecular weight and therefore the viscosity of this product remains constant on heating, which is a very important property of silicone oils.

Low-molecular-weight polysiloxanes are oily or waxy substances (silicone oils). High-molecular-weight polysiloxanes on the other hand are elastomeric; they can be converted to silicone rubbers by crosslinking. Depending on the nature of the organic side group this crosslinking can occur by condensation, by metal-catalyzed addition or with peroxides. Crosslinking by means of peroxides (see Example 4.21) probably occurs by abstraction of hydrogen atoms from methyl groups yielding carbon radicals on the polysiloxane molecules. Combination of carbon radicals of different macromolecules then causes crosslinking by the formation of C–C bonds.

Example 4.21 Ring-Opening Polymerization of a Cyclic Oligosiloxane to a Linear, High-Molecular-Weight Polysiloxane with Hydroxy End Groups; Curing of the Polymer

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

(a) *Preparation of Octamethylcyclotetrasiloxane*

200 g of dimethyldichlorosilane are dripped slowly from a dropping funnel (protected from moisture by a $CaCl_2$ tube) into 600 ml of water with vigorous stirring at room temperature. The organic phase is then taken up in about 200 ml of ether, separated from water, and washed twice with distilled water; the ethereal solution is dried over magnesium sulfate. The ether is taken off on a rotary evaporator or by distillation; the resulting oil consists essentially of cyclic oligosiloxanes that can be separated by distillation. A small amount (about 0.5%) of hexamethylcyclotrisiloxane comes over first (bp 134°C/760 Torr, mp 64°C), followed by the main product octamethylcyclotetrasiloxane (bp 175°C/760 Torr, bp 74°C/20 Torr, mp 17.5°C); yield: about 40%. Finally, a few percent of pentamer (bp 101°C/20 Torr) and hexamer (bp 128°C/20 Torr) distill over at temperatures around and above 200°C.

The residue from distillation is a viscous oil consisting of high-molecular-weight compounds. Further cyclic oligomers, especially trimer and tetramer, can be obtained by heating this oil to about 400°C. To do this, a new receiver is fitted to the distillation apparatus and the flask heated to 400–450°C. The more volatile products are carried over in a slow stream of nitrogen and the distillate is then fractionated as before.

(b) *Polymerization of an Oligosiloxane*

60 g of distilled octamethylcyclotetrasiloxane are mixed with 0.1 g of very finely powdered potassium hydroxide and 0.5 ml DMSO as solubilizer in a 250 ml conical flask, which is then placed in an oil bath at 140°C. The increase in viscosity of the mixture can easily be observed by occasional swirling. After 20–30 min, the liquid has reached the consistency of thin honey. Half the product is taken out and cooled [further work-up under (c) and (d)]. The residue is heated again until, after 2–3 h, a plastic, putty-like mass is produced. It is allowed to cool, whereby a rubbery polymer is obtained. Yield: 90–95%.

(c) *Hot Curing of the Polysiloxane*

The polysiloxane from experiment (b) is soluble in toluene. It can be converted by hot vulcanization into an insoluble silicone rubber. Using a small blender, 10 g of the polymer are kneaded with 10 g of quartz powder or 7.5 g of ground kieselguhr, and 0.6 g of dibenzoyl peroxide paste (50% in silicone oil). To work the additives into the silicone rubber without a mechanical blender is very tedious and difficult to achieve completely.

The mixture is then heated for 10 min in the oven at 110°C to bring about crosslinking. The solubilities of the mixture and the resulting silicone rubber are tested in toluene.

(d) *Cold Curing of the Polysiloxane at Room Temperature*

10 g of the honey-like polysiloxane from experiment (b) are mixed with 5 g of quartz powder or ground kieselguhr in a mortar. The viscous syrup is poured into a beaker and 0.3 g of tetraethyl silicate (crosslinking agent) are stirred in, together with 0.3 g of dibutyltin dilaurate as vulcanization accelerator. The mass solidifies in 1–2 h to an elastic silicone rubber. Such a silicone rubber retains its elasticity over an unusually large temperature range (−90–300°C); it is also very resistant towards harsh atmospheric conditions.

Example 4.22 Equilibration of a Silicone Elastomer to a Silicone Oil with Trimethylsilyl End Groups

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

10 g of the rubbery silicone with hydroxy end groups, made in Example 4.21 (b) are taken up in 20 g of toluene. 0.5 g of 96% sulfuric acid and 0.2 g of hexamethyldisiloxane are added to the very viscous solution, with stirring or shaking until the high-molecular-weight material has disappeared. 0.3 ml of water are then added and stirring is continued for 2 h. The solution is next washed with water in a separating funnel until the washings have a neutral reaction. The toluene is distilled off, leaving a clear, mobile silicone oil (viscosity 200–500 Pa·s). Yield: 70%.

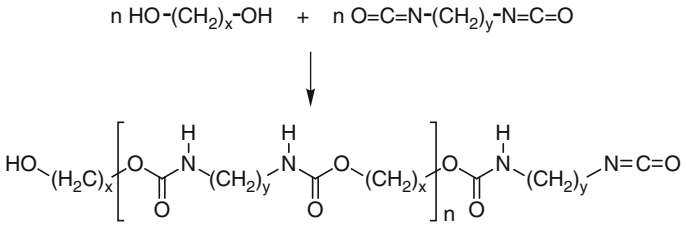
4.2 Stepwise Addition Polymerization (Polyaddition)

The addition polymerizations described here involve a stepwise reaction of at least two bifunctional compounds, leading to the formation of macromolecules. In contrast to condensation polymerization, no low-molecular-weight compounds

are eliminated; the coupling of the monomer units is, instead, a consequence of the migration of a hydrogen atom (cf. the equation for the formation of a polyurethane from a diol and a diisocyanate, Sect. 4.2.1). Like condensation polymerization, this kind of addition polymerization is also a stepwise reaction, consisting of a sequence of independent individual reactions, so that here, too, the average molecular weight of the resulting polymer steadily increases during the course of the reaction. The oligomeric and polymeric products formed in the individual steps possess the same functional end groups and the same reactivity as the starting materials; they can be isolated without losing their reactivity, in contrast to the products of addition polymerization. As stepwise reactions, they are governed by kinetic laws similar to those for condensation polymerization (see Eqs. 4.1–4.4 in Sect. 4.1). The experimental techniques are also similar.

4.2.1 Polyurethanes

Polyurethanes are macromolecules in which the constitutional repeating units (CRUs) are coupled with one another through urethane (oxycarbonylamino) groups. They are prepared almost exclusively by stepwise addition polymerization reactions of di- or polyfunctional hydroxy compounds with di- or polyfunctional isocyanates:



This addition reaction proceeds readily and quantitatively. Side reactions can give amide, urea, biuret, allophanate, and isocyanurate groupings, so that the structure of the product can deviate from that above; such side reactions are sometimes desired (see Sect. 4.2.1.2).

Linear polyurethanes made from short-chain diols and diisocyanates are high melting, crystalline, thermoplastic substances whose properties are comparable with those of the polyamides because of the similarity in chain structure. However, they generally melt at somewhat lower temperatures and have better solubility, for example, in chlorinated hydrocarbons. The thermal stability is lower than for polyamides: depending on the structure of the polymer the reverse reaction of the urethane groups begins at temperatures as low as 150–200°C with regeneration of functional groups; the cleavage of the allophanate groups begins at the still lower temperature of 100°C. Basically, polyurethanes are predominantly biphasic multiblock copolymers consisting of a sequence of more flexible elastomeric chain segments [e.g., $-(-CH_2-)_x-$ in the above formula] separated by

corresponding hard domains formed by the diurethane groups with intermolecular hydrogen bonds (see Sects. 4.2.1.2 and 5.6).

A key factor in the preparation of polyurethanes is the reactivity of the isocyanates. Aromatic diisocyanates are more reactive than aliphatic diisocyanates, and primary isocyanates react faster than secondary or tertiary isocyanates. The most important and commercially most readily accessible diisocyanates are aliphatic and colorless hexamethylene-1,6-diisocyanate (HDI), isophorone diisocyanate (IPDI), and aromatic, brownish colored diphenylmethane-4,4′-diisocyanate (MDI), 1,5-naphthalenediisocyanate, and a 4:1 mixture of 2,4- and 2,6-toluenediisocyanates (TDI).

As already mentioned, polyurethanes decompose on heating into isocyanates and hydroxy compounds, the decomposition temperature depending on the structure of the urethane. Use is made of this fact when reacting polyhydroxy compounds with so-called "capped isocyanates" or "isocyanate splitters". One may use, for example, diurethanes of aromatic diisocyanates and phenols that revert to the original components at 150–180°C. Such diurethanes can be mixed with polyhydroxy compounds at room temperature and stored without change; on heating, the diisocyanate is split off and reacts with the free hydroxy groups forming urethane groups of greater stability, while the phenol distills away.

The addition of isocyanates to hydroxy compounds is inhibited by acid compounds (e.g., hydrogen chloride or *p*-toluenesulfonic acid); on the other hand, it can be accelerated by basic compounds (e.g., tertiary amines like triethylamine, *N*,*N*-dimethylbenzylamine, and especially 1,4-diazabicyclo[2.2.2]octane) and by certain metal salts or organometallic compounds (e.g., dibutyltin dilaurate, bismuth nitrate). These catalysts are often effective in amounts of much less than 1 wt%.

Polyurethanes are used for the fabrication of fibers, while crosslinked polyurethanes are employed as lacquers and adhesives, as coatings for textiles and paper, and as elastomers and foams.

4.2.1.1 Linear Polyurethanes

The addition polymerization reaction of dihydroxy compounds with diisocyanates sets in on mixing the two components and gentle warming. Under proper conditions, linear polyurethanes with molecular weights up to about 15,000 can be obtained. As in the case of polyamides and polyesters, the softening point of the aliphatic polyurethanes depends on the number of carbon atoms between the urethane groups.

The polymerization in bulk requires relatively high temperatures, and, in addition, the polyurethane formed is exposed to the action of the diisocyanate throughout the duration of the reaction, so that secondary reactions can easily take place (see Sect. 4.2.1). For the preparation of polyurethanes with a high molecular weight and with as linear a structure as possible, polymerization in solution is, therefore to be preferred. Suitable inert solvents are toluene, xylene, chlorobenzene, and 1,2-dichlorobenzene. The diisocyanate is normally dripped into the solution of the dihydroxy compound at the desired temperature, which may conveniently be the boiling point of the solvent. The resulting polyurethane often separates from

the reaction mixture and is so much less vulnerable to secondary reactions than when the polymerization is carried out in bulk.

Example 4.23 Preparation of a Linear Polyurethane from 1,4-Butanediol and Hexamethylene Diisocyanate in Solution

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

22.5 g (0.25 mol) of pure 1,4-butanediol, 42 g (0.25 mol) of pure hexamethylene diisocyanate, and 125 ml of anhydrous chlorobenzene are placed in a dry 500 ml three-necked flask fitted with stirrer, thermometer, reflux condenser with attached drying tube, and nitrogen inlet; the air is removed by evacuation and the flask filled with nitrogen. The mixture is then heated carefully in an oil bath under a slow stream of nitrogen. At about 95°C the initially cloudy reaction mixture suddenly becomes clear; the temperature now climbs rather rapidly and under some circumstances may exceed the prevailing oil bath temperature. About 15 min after the solution has come to boiling (132°C), a faint cloudiness appears (recognizable as a blue rim at the vessel wall) which visibly strengthens. Finally, the high-molecular-weight polyurethane settles out in the form of sand. The reaction is completed by heating for a further 15 min. After cooling, the polyurethane powder is filtered off with suction. [If the mixture is filtered hot (100°C), about 1–3% of the low-molecular-weight portion remains in solution and can be isolated by precipitation with methanol]. The residual absorbed chlorobenzene is best removed by steam distillation. In this way, one obtains 62 g (96%) of a white powder that melts at 181–183°C and is soluble in *m*-cresol and formamide.

4.2.1.2 Branched and Crosslinked Polyurethanes

Essentially two methods can be used for the preparation of branched and crosslinked polyurethanes.

(a) The reactions of diisocyanates with compounds that possess more than two hydroxy groups per molecule.

The degree of crosslinking here depends essentially on the structure and functionality of the polyhydroxy compound so that the properties of the polyurethane can be altered by variation of this component. This procedure is applied mainly to the preparation of lacquers (reactions with diisocyanates at low temperature in anhydrous solvents such as butyl acetate) or moldings (usually with "capped" diisocyanates at higher temperatures).

(b) The reaction of linear oligourethanes, which possess either hydroxy or isocyanate end groups, with suitable reactive compounds, followed by crosslinking through one of the mechanisms described below.

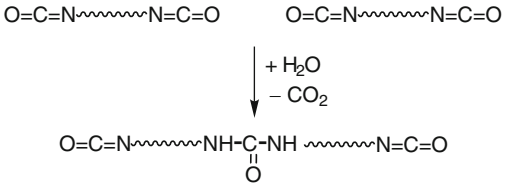
According to O. Bayer, the latter procedure, which is used especially for the preparation of elastomeric polyurethanes, is carried out in two separate stages. First, a carefully dried, relatively low-molecular-weight, aliphatic polyester or polyether with hydroxy end groups is reacted with an excess of diisocyanate. A "chain extension" reaction occurs in which two to three linear diol molecules are coupled

with diisocyanate, so as to yield a linear polymer with some in-chain urethane groups and with isocyanate end groups.

Suitable starting compounds are polyesters from poly(ethylene oxide) and adipic acid, also poly(propylene oxide) or poly(oxytetramethylene) with molecular weights around 2,000, whose hydroxy end groups can be reacted with very reactive diisocyanates such as 1,5-naphthalene diisocyanate, 1,4-phenylene diisocyanate, and diphenylmethane-4,4′-diisocyanate.

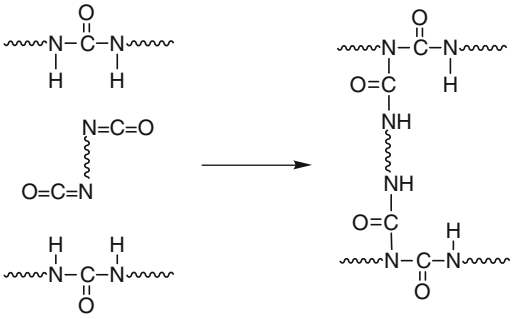
The chain-extended, linear poly(ester urethanes) so obtained can now be crosslinked in a second stage, involving reaction with – water – or glycols – or diamines.

In crosslinking with water, pairs of isocyanate end groups in the chain-extended polymer OCN–X–NCO first react with a molecule of water; this results in a linear coupling through urea groupings, with simultaneous elimination of CO_2:



(1)

The subsequent crosslinking probably occurs by reaction of the hydrogen atoms of the resulting urea groups with isocyanate groups still present in the starting polymer or the chain-extended polymer, with the formation of biuret groups:



(2)

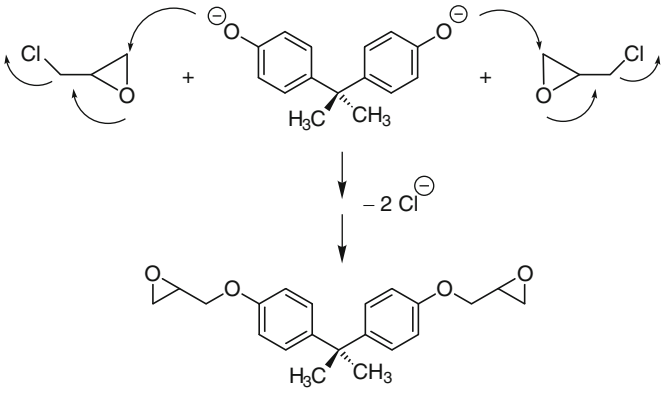
Crosslinking with glycols or diamines proceeds according to a similar scheme (but without elimination of CO_2). The first reaction is again a linear chain-extension reaction. With glycols, this occurs with the formation of urethane groups, which can then react with residual isocyanate end groups to give crosslinking with formation of allophanate groups. With diamines the linear coupling occurs through urea groups and the crosslinking reaction then proceeds as formulated in structure (2).

Crosslinking with glycols and diamines plays a major role in the preparation of polyurethane elastomers. The properties of the resulting products can be widely varied by choice of starting components and the number of crosslinks (“mesh width”).

Crosslinking with water is mainly used in the preparation of polyurethane foams (see Sect. 5.6).

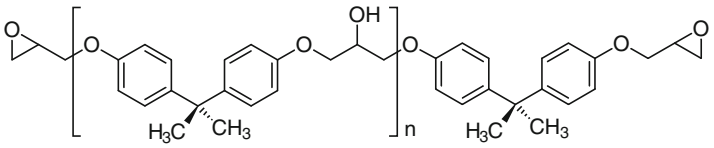
4.2.2 Epoxy Resins

Epoxy resins are usually understood to be products of reaction of polyfunctional hydroxy compounds with 1-chloro-2,3-epoxypropane (epichlorohydrin) in basic medium. In the simplest case two mol of epichlorohydrin react, for example, with one mol of bisphenol A, according to the following scheme:



(I)

Higher-molecular-weight products II result from coupling of epoxide I with further bisphenol:



(II)

However, side reactions can also occur. Thus, bisphenol may add only one epoxy group and some of the very reactive epoxy groups may be hydrolyzed during the preparation so that the number of hydroxy groups will deviate from that shown in structure (II).

Depending on the conditions, reactions (I) and (II) can be carried out either concurrently or consecutively. If one works from the outset in alkaline medium, for example, by dropping the desired amount of epichlorohydrin into the mixture of hydroxy compound and the equivalent amount of aqueous alkali hydroxide at 50–100°C, then the addition reaction and the HCl elimination occur side by side (Example 4.24). On the other hand, if the hydroxy compound and epichlorohydrin are allowed to react in nonaqueous medium in the presence of acid catalysts, the corresponding chlorohydrin is first formed; this can then be transformed into the epoxy compound in a second step by reaction with an equivalent amount of alkali hydroxide.

The structure and molecular weight of the resulting epoxy resin are strongly influenced by the reaction conditions: A large excess of epichlorohydrin (about 5 mol per mol phenolic hydroxy groups) favors the formation of terminal epoxy groups; however, the molecular weight (and hence the softening point) of the product decreases with increasing amount of epichlorohydrin. The reaction temperature is also important: high temperatures promote secondary reactions such as hydrolytic cleavage of epoxy groups, leading to the formation of additional hydroxy groups.

The commercially most important epoxy resins are those prepared from 4,4′-isopropylidenediphenol (bisphenol A) and epichlorohydrin. They have molecular weights between 450 and 4,000 [n in formula (II) between 1 and 12] and softening points between 30°C and 155°C. Such epoxy resins are still soluble, but become insoluble and infusible through subsequent crosslinking reactions.

In principle, crosslinking (curing) can be brought about with any di- or polyfunctional compound that adds to epoxy groups (e.g., amines, aminoamides, thiols). Moreover, self-crosslinking can also be achieved by addition of catalytic amounts of a tertiary amine or acid compound, such as a sulfonic acid or a Friedel-Crafts catalyst (generally in the form of their adducts with ether or alcohols); this reaction often occurs even at low temperature, but does not proceed uniformly. Crosslinking of epoxy resins is an exothermic reaction, liberating 22–26 kcal per mol epoxy groups. In most cases, the amount of crosslinking agent used is equivalent to the analytically determined content of epoxy groups. Crosslinking is carried out always after application or molding. The crosslinking is generally carried out in bulk (casting resin), but sometimes in solution (lacquers, adhesives). A variant of crosslinking in solution is to use reactive thinners: These are substances which, on the one hand, lower the viscosity of the epoxy resin, but at the same time act as crosslinking agents (e.g., low-viscosity mono- and diepoxides or allyl glycidyl ether). Most crosslinking reactions only set in at higher temperatures so that the epoxy resin and crosslinker can be mixed and stored at room temperature. In practice, polybasic carboxylic acids, acid anhydrides, and amines are generally used as curing agents. In contrast to carboxylic acids, which only react sufficiently fast at high temperatures (above 180°C), carboxylic acid anhydrides (e.g., phthalic acid anhydride) allow crosslinking to be achieved at 100°C, especially in the presence of catalytic amounts of a tertiary amine. Optimum crosslinking is obtained with about 0.5 mol anhydride per mol epoxy groups.

Crosslinking with amines can be carried out either catalytically with tertiary amines (e.g., with *N*,*N*-dimethylbenzylamine), or especially by equimolar conversion with primary or secondary oligoamines at higher temperatures. This reaction is catalyzed by compounds that are capable of forming hydrogen bonds (water, alcohols, phenols, carboxylic acids, etc.). The most favorable ratio of amine/epoxide is not necessarily the stoichiometric ratio and therefore must be determined empirically in each case.

In the crosslinked state, epoxy resins are highly resistant to chemicals, temperature, and solvents and are also endowed with good electrical properties. They are therefore employed, for example, as casting resins in electro- and electronic

industry as well as resistant lacquers and coatings. Moreover, they possess excellent adhesive power for many plastics, wood, and metals ("reaction adhesives"; "two-component adhesives").

Example 4.24 Preparation of Epoxy Resins from Bisphenol A and Epichlorohydrin

Safety precautions: Before this experiment is carried out, Sect. 2.2.5 must be read as well as the material safety data sheets (MSDS) for all chemicals and products used.

Epichlorohydrin, epoxy resins, and their curing agents are considered to be primary skin irritants. Some aromatic amines used as curing agents may be carcinogenic and should be handled with great care. Moreover, by prolonged action on the skin, epichlorohydrin is absorbed by the body and causes poisoning. All contact with these substances is, therefore, to be avoided; if necessary, wash off with plenty of water. Wear safety goggles and rubber gloves!

(a) *Preparation of an Epoxy Resin with a Molecular Weight of 900*

22.8 g (0.1 mol) of pure bisphenol A (recrystallized from dilute acetic acid) are mixed, under a hood, with a solution of 7.5 g (0.188 mol) of NaOH in 75 ml water contained in a 250 ml three-necked flask, fitted with thermometer, reflux condenser, and a powerful stirrer (good stirring is essential since the reaction mixture becomes heterogeneous). The contents of the flask is vigorously stirred and heated on an oil bath to 50°C within 10 min; 14.5 g (0.157 mol) of freshly distilled epichlorohydrin are then added in one batch. (The molar ratio epichlorohydrin/bisphenol A is thus 1.57). The temperature is now raised to 95°C within 20 min and held steady for 40 min. The temperature should not be allowed to exceed 95°C since high temperature favors side reactions. The reflux condenser is now removed and the stirrer switched off so that the resin formed can settle out. The clear aqueous upper layer is carefully siphoned off and the resin washed by vigorously stirring with hot distilled water at 80–95°C. It is allowed to settle again and the wash water removed. This washing procedure is repeated several times until 50 ml of the wash water is equivalent to less than 0.075 ml of 0.1 N HCl (indicator: methyl red). In order to remove the trapped water the washed resin is heated to 150°C with moderate stirring for 30 min, until it becomes clear. Finally, it is poured into a porcelain dish where it solidifies on cooling. The solid epoxy resin has a softening point of about 70°C and a molecular weight of approximately 900 [n = 2 in formula (II)]. The epoxy value (see below) is about 0.2, corresponding to 1.8 epoxy groups per molecule of resin (equivalent weight 500). It is soluble in aromatic hydrocarbons, tetrahydrofuran, and chloroform.

(b) *Preparation of an Epoxy Resin with a Molecular Weight of 1,400*

Under similar conditions to those used in (a), 22.8 g (0.1 mol) of bisphenol A, 5.55 g (0.14 mol) of NaOH (dissolved in 56 ml water), and 11.3 g (0.123 mol) of epichlorohydrin are allowed to react with one another. Because of the smaller molar ratio of epichlorohydrin to bisphenol A (1.22) the resulting epoxy resin is of higher molecular weight than that produced in (a). The epoxy value is approximately 0.1, corresponding to 1.44 epoxy groups per molecule of resin (equivalent weight

approximately 970). The molecular weight of the resin, softening at 97–103°C, is found to be about 1,400 [n = 3.7 in formula (II)].

Determination of the Epoxy Value

This method of determination depends on the addition of hydrogen halide to epoxy groups (1 mol of hydrogen halide is equivalent to 1 mol of epoxy groups) and is carried out as follows: 0.5–1.0 g of epoxy resin are refluxed with an excess (50 ml) of pyridine hydrochloride solution (16 ml pure concentrated hydrochloric acid are made up to 1 l with pure pyridine) for 20 min and, after cooling, are back-titrated with 0.1 N NaOH, using phenolphthalein as indicator. The epoxy number represents the gram equivalents of epoxide-oxygen per 100 g resin:

$$\text{Epoxy number} = \frac{(\text{B} - \text{A}) \cdot \text{N}}{10\text{E}} \left[\frac{\text{Epoxide equivalent}}{100\text{g}}\right]$$

where A = titer for the sample (back titration), in ml; B = titer of the pyridine hydrochloride solution, in ml; N = concentration of sodium hydroxide used for titration, in mol/l, E = weight of resin, in g.

The equivalent weight is the amount of resin that contains one equivalent of epoxide; this is equal to 100/epoxy value.

(c) *Crosslinking (Curing) of Epoxy Resins*

With an amine: After determining the epoxy value and equivalent weight of the resin prepared according to (b), a small sample is melted in the oven at 150°C with the equivalent amount (0.25 mol per mol epoxy groups) of finely powdered 4,4′-methylenedianiline and the mixture well stirred for 30 s. After heating for 1 h at 150°C, the sample is taken out; it has now become insoluble and infusible.

With a carboxylic acid anhydride: 5 g of the resin prepared according to (a) are melted in a beaker at 120°C and 1.5 g of phthalic acid anhydride (0.6–0.8 equivalents per equivalent of epoxy groups) are stirred into the melt. The mixture is held at 120°C for 1 h (after this time the resin is still soluble in acetone or chloroform) and then cured at 170–180°C for 1–2 h.

Crosslinking of epoxy resins with carboxylic acid anhydrides is catalyzed by tertiary amines; thus, if 50 mg *N*,*N*-dimethyl aniline are added to the initial mixture in the above example, the curing process is already complete after 1 h at 120°C.

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