Synthesis of Macromolecules by Chain Growth Polymerization

3

Polymerization reactions can proceed by various mechanisms, as mentioned earlier, and can be catalyzed by initiators of different kinds. For chain growth (addition) polymerization of single compounds, initiation of chains may occur via radical, cationic, anionic, or so-called coordinative-acting initiators, but some monomers will not polymerize by more than one mechanism. Both thermodynamic and kinetic factors can be important, depending on the structure of the monomer and its electronic and steric situation. The initial step generates active centers that generally cause the reaction to propagate very rapidly via macroradicals or macroions; chain termination yields inactive macromolecules. It is important to note that in classical uncontrolled chain growth mechanism the molar mass of the formed polymers increases fast in the first reaction period but reaches a plateau value even at relatively low monomer conversion which leads to the fact that monomer as well as terminated final polymer chains are present in the reaction system. The most important initiators are summarized in Table 3.1.

3.1 Radical Homopolymerization

Radical polymerization is induced by an initiation step in which radicals are formed. Radicals can be generated thermally from the monomer, although such a mechanism of initiation has only been completely verified in the case of styrene (see Example 3.1). Radicals are usually generated by decomposition of an initiator (frequently also called the catalyst). The radicals so formed then react successively with the monomer molecules in the propagation step leading to growing radicals (macroradicals) which are finally deactivated by chain transfer or termination. Termination usually occurs by combination or disproportionation of two macroradicals; the radicals generated by the decomposition of the initiator are incorporated into the macromolecules as end groups, giving two such end groups per macromolecule for termination by combination, but only one for termination by disproportionation.

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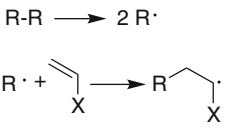
Table 3.1 Initiators for chain growth (addition) polymerizations

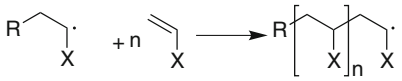
Radical	Cationic	Anionic	Coordinative
Inorganic and organic peroxo compounds, e.g., peroxodisulfates, peroxides, hydroperoxides, peresters	Protic acids	Proton acceptors	Organometallic compounds
Aliphatic azo compounds	Lewis acids with or without co-initiators	Lewis bases	Mixed catalysts (Ziegler-Natta catalysts)
Substituted ethanes, e.g., benzpinacol	Carbonium ions	Organometallic compounds	p-Complexes with transition metals, e.g., metallocenes
Redox systems with inorganic and organic components	Iodonium ions	Electron-transfer agents, e.g., alkali metals, alkali-aromatic complexes, alkali metal ketyls	Activated transition metal oxides
Controlled radical polymerization: stable nitroxy radicals, R–X/Cu(I)/ligand, thiocarbamates (transferters)			
Heat	Ionizing radiation		
UV radiation, high energy radiation			

In transfer reactions the growth of a chain is ended, for example, by transfer of a hydrogen atom from the molecule ZH, but at the same time a new polymer chain is started by the radical $Z^{\bullet}$ that is formed simultaneously. Thus, several macromolecules result from one primary radical; therefore, the kinetic chain length, i.e., the total number of monomer molecules induced to be polymerized by one primary radical, is much larger than the degree of polymerization of the macromolecules formed. A general scheme is as follows:

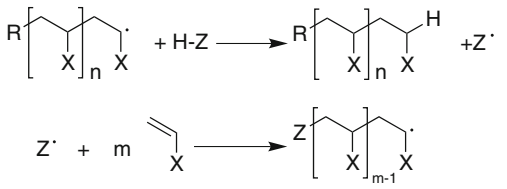
Start:



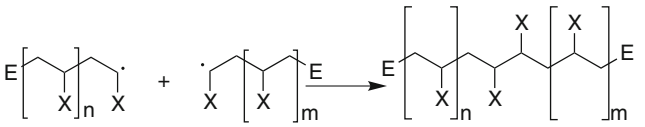
Propagation:



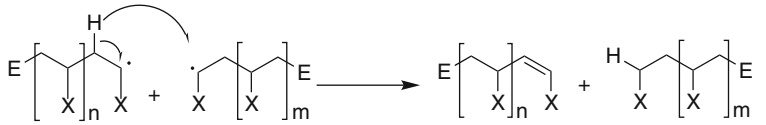
Chain transfer:



Chain termination by combination:



Chain termination by disproportionation:



Let us for the moment disregard chain transfer reactions. Radical polymerization then consists of three component reactions: initiation, propagation of the polymer chains, and termination of chain growth. The rate of primary radical formation, v_i by decomposition of the initiator I, may be written:

$$v_i = k_i \cdot [I] \tag{3.1}$$

The rate constant k_i contains a factor that allows for the efficiency of initiation; not all the radicals generated by the initiator are capable of starting polymer chains, some are lost by combination or other reactions. The initiator efficiency is defined as the ratio of the number of initiator molecules that start polymer chains to the number of initiator molecules decomposed under the given conditions of the polymerization. With most radical initiators the efficiency lies between 0.6 and 0.9; it also depends on the nature of the monomer.

The rate of propagation v_p is given by:

$$v_p = \frac{-d[M]}{dt} = k_p \cdot [M] \cdot [R^{\bullet}] \tag{3.2}$$

Here it is assumed that k_p is independent of the number of monomer molecules already added; $[R]$ denotes the concentration of radicals in the system.

The rate of the termination reaction v_t is given by:

$$v_t = \frac{-d[R^\bullet]}{dt} = k_t \cdot [R^\bullet]^2 \tag{3.3}$$

According to Bodenstein, for a chain reaction in the steady state, the number of radicals formed and disappearing in a given time must be the same. This applies to most addition polymerizations, at least in the region of low conversion. Under these conditions v_i and v_t may be equated:

$$v_i = v_t \text{ or } k_i[I] = k_t \cdot [R^\bullet]^2 \tag{3.4}$$

Therefore:

$$[R^\bullet] = \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} \cdot [I]^{\frac{1}{2}} \tag{3.5}$$

Inserting this value in Eq. 3.2 yields:

$$v_p = \frac{-d[M]}{dt} = k_p \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} \cdot [M] \cdot [I]^{\frac{1}{2}} \tag{3.6}$$

where v_p is identical with the overall rate of polymerization R_p, since at sufficiently large chain length it determines the consumption of the monomer M almost completely. Hence the rate of polymerization is proportional to the monomer concentration and the square root of the initiator concentration. At high initiator concentrations or with stable radicals formed, termination of this primary radicals can occur and the reaction kinetics change.

For initiation of polymerizations by light or high energy radiation, the initiator concentration $[I]$ is replaced by the radiation intensity in the above kinetic equations.

Raising the temperature of a radical chain reaction causes an increase in the overall rate of polymerization since the main effect is an increase in the rate of decomposition of the initiator and hence the number of primary radicals generated per unit time. At the same time the degree of polymerization falls since, according to Eq. 3.3, the rate of the termination reaction depends on the concentration of radicals (see Example 3.2). Higher temperatures also favor side reactions such as chain transfer and branching, and in the polymerization of dienes the reaction temperature can affect the relative proportions of the different types of CRUs in the chains.

Although the above derivations involve certain simplifications, they nevertheless represent correctly the kinetics of many addition polymerization reactions. However, the behavior is different when the polymerization is conducted under heterogeneous conditions, e.g., in suspension or in emulsion (see literature cited in Sect. 2.2.4).

For radical polymerizations of some monomers in bulk a specific effect can appear when the conversion exceeds a certain value. In these cases the viscosity of the reaction mixture increases to such an extent as a result of the formation of macromolecules that the mobility of the growing macroradicals becomes severely restricted. Bimolecular termination, but not the propagation reaction, is then hindered, so that both the degree of polymerization and the reaction rate increase; the system is no longer in a steady state and the radical concentration rises continuously. The increasing reaction rate, coupled with the more difficult heat exchange in the very viscous medium, leads to a rise in temperature as a consequence of the heat evolution, and hence to an auto-acceleration of the reaction, which can become explosive in nature. This phenomenon is called the gel effect or Trommsdorff-Norrish effect, but does not occur to the same extent in all monomers. It is especially noticeable with methyl methacrylate (see Example 3.8). Basically, the gel effect is based on restrained diffusion since it can be also observed if the polymerization is run strictly isothermal. Somewhat similar behavior is observed in the polymerization of some monomers in poor solvents in which the resulting macromolecules are more tightly coiled than in good solvents, where the polymer chains are more strongly solvated and more mobile. The interplay of radical formation, propagation, and termination of the growing chains determines the overall rate and degree of polymerization, provided there are no chain transfer reactions. When a growing polymer chain undergoes chain transfer its growth is terminated, but at the same time a new polymer chain is started; the kinetic chain is therefore uninterrupted.

The kinetic chain length is given by the number of monomer molecules consumed per initiation step. Since the efficiency of most initiators is not known quantitatively it is necessary to compare the rate of the propagation reaction with either the rate of initiation or the rate of termination. If there is no chain transfer, the kinetic chain length ν for termination by disproportionation is equal to the number-average degree of polymerization:

$$P_n = \nu = \frac{v_p}{v_i} = \frac{v_p}{v_t} \tag{3.7}$$

On the other hand, for termination by combination the degree of polymerization is equal to twice the kinetic chain length:

$$P_n = 2 \cdot \nu = 2 \cdot \frac{v_p}{v_i} = 2 \cdot \frac{v_p}{v_t} \tag{3.8}$$

If chain transfer does take place the rate v_f of the chain transfer reaction ($R^{\bullet} + ZH \rightarrow RH + Z^{\bullet}$) must be taken into account:

$$P_n = \frac{v_p}{v_i + v_f} \tag{3.9}$$

and for termination by combination:

$$P_n = \frac{v_p}{\frac{1}{2}v_i + v_f} \tag{3.10}$$

Taking the reciprocal of P_n and inserting the expressions for v_p, v_i, and v_f from Eqs. 3.4, 3.5 and 3.6, one obtains:

$$\frac{1}{P_n} = \frac{v_i}{\alpha \cdot v_p} + \frac{v_f}{v_p} = \frac{k_i \cdot [I]}{\alpha \cdot k_p \cdot \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} \cdot [I]^{\frac{1}{2}} \cdot [M]} + \frac{k_f \cdot [R^\bullet] \cdot [ZH]}{k_p \cdot [R^\bullet] \cdot [M]} \tag{3.11}$$

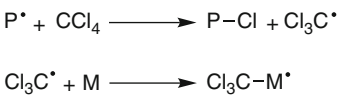
where $\alpha = 1$ for termination by disproportionation and $\alpha = 2$ for termination by combination.

Since the chain carrier ZH may be the monomer, the initiator, the solvent (S), an added transfer agent (regulator), or the polymer already formed, a more general form of Eq. 3.11 is:

$$\frac{1}{P_{n,0}} = K \cdot \frac{[I]^{\frac{1}{2}}}{[M]} + C_M + C_I \cdot \frac{[I]}{[M]} + C_S \cdot \frac{[S]}{[M]} + C_{ZH} \cdot \frac{[ZH]}{[M]} + \ldots \tag{3.12}$$

where C_x denotes the chain transfer constant k_f/k_p, appropriate to the chain transfer agent X (see Example 3.8). Since the chain transfer constant C_I for most initiators is approximately zero, Eq. 3.12 shows that at moderate conversion the reciprocal of the degree of polymerization is a linear function of the square root of the initiator concentration. Since in turn $[I]^{1/2}$ is proportional to the overall rate of polymerization R_p, Eq. 3.6, the degree of polymerization is lower, the faster the polymerization occurs.

Transfer reactions with solvent and with those compounds termed regulators are especially important because of their marked effect on the molecular weight of the polymer being formed. While the transfer constants for most solvents are not very big (e.g., for benzene reacting with the growing polystyrene radical at 60°C, C_S is of the order of 10^{-5}), there are some with relatively high transfer constants, so that the polymer formed has a relatively short chain length. A particularly well-investigated case is that of the polymerization of styrene in carbon tetrachloride, where the transfer constant is about 10^{-2}. The resulting polystyrene is of very low molecular weight and consists of a mixture of oligomers.



Such a process is called telomerization. The polymer thus contains chloro and trichloromethyl end groups. More important, however, is the ability to control the

reduction of molecular weight by the use of regulators. The molecular weight of a polymer can only be controlled to a limited extent by adjustment of the monomer concentration, initiator concentration, and temperature. Hence, in industry it is common practice to add transfer agents. For this purpose one may use various thiols which, because of their high transfer constants (e.g., for 1-dodecanethiol in the polymerization of styrene, $C_{ZH} = 19$) need only to be added in very small amounts (about 0.1% with respect to monomer). The simplest way of determining the transfer constant of such a regulator, using Eq. 3.12, is by polymerization experiments at constant initiator and monomer concentrations and varying concentrations of the transfer agent ZH.

In the absence of regulators one may write:

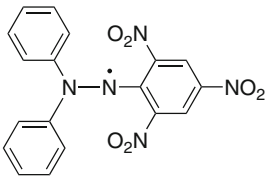
$$\frac{1}{P_{n,0}} = K \cdot \frac{[I]^{\frac{1}{2}}}{[M]} + C_M + C_I \cdot \frac{[I]}{[M]} + C_S \cdot \frac{[S]}{[M]} \tag{3.13}$$

Then with addition of regulator ZH:

$$\frac{1}{P_n} = \frac{1}{P_{n,0}} + C_{ZH} \cdot \frac{[ZH]}{[M]} \tag{3.14}$$

Plotting the reciprocal of the number-average degree of polymerization for polymers obtained at different regulator concentrations against $[ZH]/[M]$, a straight line is obtained which intersects the ordinate at $1/P_n$ and has a slope equal to the transfer constant of the regulator C_{ZH} (also see Sect. 2.2.5.5 and Example 3.8b).

Finally, many substances can inhibit polymerization reactions. Amongst these are molecular oxygen, Cu(I) ions, nitric oxide, phenols such as hydroquinone and 4-*tert*-butylpyrocatechol, quinones, certain aromatic amines such as *N*-phenyl-*ß*-naphthylamine, nitro compounds, and some sulfur compounds. The mechanism of action of most inhibitors is not yet fully clarified; the inhibitors react either with the primary radicals or with the growing chains to yield products that are no longer active in propagation. Stable free radicals such as *N*,*N*-diphenyl-*N*′-picrylhydrazyl are also effective inhibitors. Since this radical is strongly colored its consumption during the inhibition period can be followed photometrically:



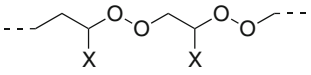
Inhibitors are frequently used to stop a polymerization quickly, for example, in kinetics investigations. Another important application is the stabilization of monomers against undesired polymerization during storage. Autoxidation of unsaturated monomers by the action of atmospheric oxygen frequently results in the

formation of peroxidic compounds that can generate radicals at relatively low temperatures, thus initiating polymerization; inhibitors are added as stabilizers to suppress this undesired and uncontrolled polymerization (see Sect. 2.2.5.5). These must of course be removed before using the monomer for polymerization reactions (see Example 3.1). Since the inhibitors are consumed by growing polymer chains, the time during which they prevent polymerization (incubation time, induction period) depends on their concentration in the stabilized monomer.

Molecular oxygen plays a special role in radical polymerizations. It is known to react very rapidly with hydrocarbon radicals with the formation of peroxy radicals:

$$R^{\bullet} + {}^{\bullet}O - O^{\bullet} \rightarrow R - O - O^{\bullet}$$

It is thus clear why atmospheric oxygen must be carefully excluded during radical polymerizations. Peroxy radicals are much less reactive than most alkyl (or aryl) radicals, but they can add a further monomer molecule, regenerating an alkyl radical, which can react again with oxygen. The rate of consumption of monomer, relative to that in the absence of oxygen, is substantially reduced. An alternating addition of unsaturated monomer and oxygen is observed, resulting in the formation of a polymeric peroxide (copolymerization with molecular oxygen):



Normal polymerization commences only after complete consumption of the oxygen; this is then accelerated by the formation of additional initiating radicals through the thermal decomposition of the polymeric peroxide. Thus, molecular oxygen at first inhibits the polymerization, but after its consumption there is an accelerating action.

Unlike ionic polymerizations, radical chain polymerizations have so far been found to occur only with unsaturated compounds. In some cases they can be induced purely thermally, or by means of light or high-energy radiation; generally, however, radical initiators such as peroxo compounds, azo compounds, and redox systems are used.

The initiation of a radical polymerization of a monomer can be achieved with practically every peroxo or azo compound. This means that in these cases the type of initiator influences only the rate and degree of polymerization, the nature of the end groups and branching but not the polymerizability of the monomer as such. This is not the case with redox systems as radical initiators. As a consequence, the determination of whether a new substance polymerizes radically or not is rather simple: to the purified compound (as a 30–50% solution) is added under nitrogen 1% of dibenzoyl peroxide and this mixture is heated for several hours to 60–120°C. The occurrence of turbidity or an increase of viscosity (if the polymer is soluble in the reaction mixture) are first indications that a polymerization has taken place. Final proof is the analysis of the reaction mixture after separation of the polymer

Table 3.2 Some parameters influencing radical polymerization

Parameter		Rate of polymerization/ conversion	Molecular weight	Example
Initiator concentration	↑	Increase	Decrease	3–6, 3–11b
Temperature	↑	Increase	Decrease	3–1
Monomer concentration	↑	Increase	Increase	3–7
Polymerization time	↑	Decrease	Decrease[a]	3–6
Chain transfer agent		Constant	Decrease	3–8b

[a]Exception: "Living polymerization"

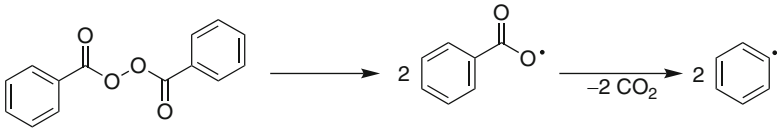
either by filtration or by precipitation in a solvent that is miscible with the monomer and does not keep the polymer in solution.

A short summary of the parameters which influence the radical polymerization are given in Table 3.2

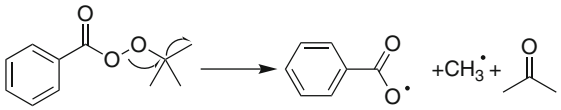
3.1.1 Polymerization with Peroxo Compounds as Initiators

Organic and inorganic peroxo compounds are especially important as initiators of radical polymerizations. Hydroperoxides, dialkyl peroxides, diacyl peroxides, and peresters are typical organic peroxo compounds. Since they dissolve not only in organic solvents but also in most monomers, they are suitable for solution polymerization as well as bulk or bead polymerization. Their decomposition into radicals can be brought about either thermally, or by irradiation with light, or by redox reactions (see Sect. 3.1.3). The rate of decomposition of organic peroxo compounds depends on their structure and on the temperature. For initiation by thermal decomposition of peroxo compounds an acceptable rate of polymerization is generally attained only above 50°C. Some peresters, for example, diethyl peroxydicarbonate, are exceptional and decompose rapidly at room temperature, thus, because of the danger of explosion, they should be added only in dilute solution.

A peroxo compound that is frequently used (concentration 0.1–1 wt% with respect to monomer) is dibenzoyl peroxide (see Example 3.4). It decomposes in solution at temperatures of about 50–80°C, mainly into benzoyloxy radicals; at higher temperatures phenyl radicals are formed to an increasing extent by elimination of carbon dioxide, so that the end groups of the resulting polymer are either hydrolyzable benzoic ester groups or non-hydrolyzable phenyl groups:

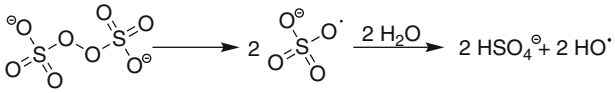


In practice *tert*-butyl peroxobenzoate is often used as a thermally decomposing radical initiator. It decomposes into benzoyloxy and methyl radicals, and acetone:



The kinetic relationship, according to which the rate of polymerization increases and the average degree of polymerization decreases with increasing initiator concentration, is satisfied by most monomers when either unsubstituted or substituted dibenzoyl peroxides are used as initiators.

Thermally activated organic peroxo compounds are generally used for polymerization in bulk or in organic solvents, as well as for bead polymerization; instead, inorganic peroxo compounds are the most suitable for initiating polymerization in aqueous solution or emulsion. Hydrogen peroxide is mainly used as a component of a redox initiator (see Example 3.9); in contrast, potassium or ammonium peroxodisulfate (concentration 0.1–1 wt% with respect to monomer) are very frequently used without a reducing agent, since even at 30°C they decompose thermally into radicals that can initiate polymerization.



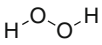
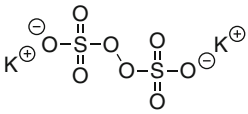
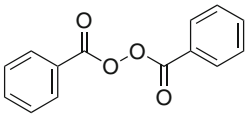
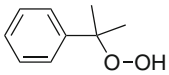
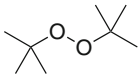
Ammonium peroxodisulfate is more soluble in water than the potassium salt; furthermore, it dissolves in more polar organic solvents (e.g., DMF), so that it is sometimes also used for initiating polymerizations in organic media. In polymerizations initiated by peroxodisulfates the reaction medium is liable to become acidic, so that buffering is generally necessary (see Example 3.2).

A list of some peroxo compounds that generate free radicals is given in Table 3.3, extensive information can be found in the literature. The initiators are selected according to their thermal half-lives to ensure that at the polymerization temperature they provide a source of free radicals. The rate equation for the thermal half-life is given by: $t_{1/2} = 0.693 \cdot k_d$, where k_d is the rate constant for the thermal decomposition. In technical applications one often uses the temperature at which within a certain time interval one half of the initiator is decomposed (e.g., quoted as 10 h half-life temperature).

Example 3.1 Thermal Polymerization of Styrene in Bulk (Effect of Temperature)

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.

Table 3.3 Peroxo compounds for initiation of radical polymerization

Peroxo compound	Formula	Suitable temperature for polymerizations [°C]
Hydrogen peroxide		30–80
Potassium peroxo-disulfate		40–100
Dibenzoyl peroxide		40–100
Cumyl hydroperoxide		50–120
Di-*tert*-butyl peroxide		80–150

Monomeric styrene is freed from phenolic inhibitors by shaking twice with 10% sodium hydroxide solution, washing three times with distilled water, drying over calcium chloride or silica gel and distilling into a receiver (see Sect. 2.2.5.3) under reduced pressure of nitrogen (bp 82°C/100 Torr, 46°C/20 Torr). It is stored in a refrigerator until required.

4 g (38.4 mmol) of destabilized styrene is weighed into each of five thick-walled Pyrex Schlenk tubes (content 15–20 ml). The tubes, equipped with a suitable adapter (see Sect. 2.2.5.4), are now cooled in a methylene chloride/dry ice cold bath, thereby freezing the styrene (mp −30.6°C); after evacuation with an oil pump and thawing, the tubes are filled with nitrogen. This sequence is repeated twice more. Finally the tubes are sealed off under nitrogen. The samples are polymerized at 80°C, 100°C, 110°C, 120°C, and 130°C, respectively, by placing them in an appropriately adjusted thermostat or vapor bath (Caution: the tubes may explode; place them behind shield, or cover them with cloth!). After exactly 6 h the sealed tubes are rapidly cooled by immersion in cold water (wear safety goggles) and then opened. The contents are each dissolved in 20–30 ml toluene and the solution run slowly from a dropping funnel into 200–300 ml methanol with stirring, thereby precipitating the polystyrene. The polymers are filtered off using sintered glass crucibles (porosity 2) and dried to constant weight in vacuum at 50°C. The observed yield (in %) is plotted as a function of polymerization temperature. Using an Ostwald viscometer (capillary diameter 0.3 mm) the limiting viscosity numbers of all samples are determined in toluene at 20°C, and the average degrees

of polymerization derived (see Sect. 2.3.3.3). These values are plotted as a function of temperature.

Example 3.2 Polymerization of Styrene with Potassium Peroxodisulfate in Emulsion

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 250-ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) is evacuated and filled with nitrogen three times. The following are then added under nitrogen: 122 mg (0.45 mmol) of potassium peroxodisulfate, 50 mg of NaH_2PO_4, 1.0 g of sodium oleate or sodium dodecyl sulfate, and 100 ml of water that has been boiled under nitrogen (sodium dihydrogen phosphate is added because styrene polymerizes best in weakly alkaline medium). When everything has dissolved, 50 ml of destabilized styrene are added with constant stirring; the resulting oil-in-water emulsion is heated at 60°C for 6 h with steady stirring under a slow stream of nitrogen. After cooling the polystyrene latex, 30 ml are pipetted into a beaker; the polymer is precipitated by addition of an equal volume of a concentrated solution of aluminum sulfate, if necessary by boiling; a further 30-ml sample is precipitated by dropping into 300 ml of methanol. Finally the latex remaining in the flask is coagulated by addition of concentrated hydrochloric acid. The samples are washed with water and methanol, filtered, and dried in vacuum at 50°C. The total yield and the limiting viscosity number (degree of polymerization) of one sample are determined. The values are compared with those obtained under similar conditions for polymerization conducted in bulk (Example 3.1) and in solution (Example 3.7).

Example 3.3 Polymerization of Vinyl Acetate with Ammonium Peroxodisulfate in Emulsion

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 500-ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) is evacuated and filled with nitrogen. 5 g of poly(vinyl alcohol) are then placed in the flask (see Example 5.1) and dissolved in 100 ml of distilled water by stirring at 60°C; next are added 2.2 g of oxethylated nonylphenol and 0.4 g (1.8 mmol) of ammonium peroxodisulfate buffered by the addition of 0.46 g sodium acetate in order to prevent the hydrolysis of the monomeric vinyl acetate.

The solution is heated to 72°C and 25 g (0.29 mol) of vinyl acetate (freshly distilled under nitrogen) are added dropwise. The temperature of the water bath is then raised to 80°C. As soon as the internal temperature reaches 75°C, a further 75 g (0.87 mol) of vinyl acetate are added dropwise at such a rate that the internal

temperature is maintained between 79°C and 83°C at moderate reflux (total time about 20 min); finally a further 0.1 g (0.44 mmol) of ammonium peroxodisulfate in 1 ml of distilled water is added. Refluxing soon abates and the internal temperature rises to about 86°C. The reaction mixture is allowed to polymerize for another 30 min on the water bath at 80°C. On cooling, a creamy dispersion is obtained that contains less than 1% monomer (corresponding to a solid content of about 50%). The polymer can now be precipitated by addition of a threefold excess of saturated sodium chloride solution. The poly(vinyl acetate) dispersion can also be spread out as a thin layer on a glass plate; on drying in air the polymer particles coalesce and form a homogeneous, very cohesive film that is resistant to water. These kinds of dispersions are very stable and insensitive to the addition of pigments or electrolytes, as well as to temperature variations (within certain limits) and are therefore extensively used as paints for wood or plaster surfaces, as well as for cementing wood and for impregnation of leather, paper, and textiles.

Example 3.4 Polymerization of Vinyl Acetate in Suspension (Bead Polymerization)

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.

0.15 g of a hydrolyzed copolymer of styrene and maleic anhydride (see Example 5.3) are dissolved in 150 ml of hot distilled water to give a 1% solution, which is then neutralized with a few drops of ammonia solution. The solution of the ammonium salt is placed in a standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) with dropping funnel (mounted on the reflux condenser), and heated to about 70°C by means of a water bath set at 80°C.

0.6 g (2.5 mmol) of dibenzoyl peroxide are dissolved in 100 g (1.16 mol) of freshly distilled vinyl acetate and the clear solution allowed to run in through the reflux condenser over a period of about 30 min with vigorous stirring. The water bath temperature is held steady at 80°C and the rate of addition of the vinyl acetate is so regulated that moderate refluxing is maintained. After the addition of monomer is complete the internal temperature rises to about 80°C, the reflux having ceased a few minutes previously.

In order to remove the small amount of unconverted vinyl acetate, steam is blown through the suspension for about 30 min, the flask being fitted with a condenser for distillation. The suspension is finally cooled externally to room temperature and diluted with cold water to about 500 ml. Only now is the stirrer switched off and after settlement of the bead polymer the aqueous layer is drawn off. The product is washed by repeated slurrying with cold water and subsequent decantation until the wash water no longer foams and is therefore free of suspending agent. The moist bead polymer is dried as a thin layer in vacuum at room temperature. The limiting viscosity number is determined in acetone at 30°C and the average molecular weight derived (see Sect. 2.3.3.3).

Example 3.5 Polymerization of Methacrylic Acid with Potassium Peroxodisulfate in Aqueous 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.

11 ml of distilled water are heated to 80°C in a 50-ml standard apparatus (round-bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) with two dropping funnels. At this temperature 6 g (0.07 mol) of methacrylic acid, purified by vacuum distillation under nitrogen, and a solution of 0.18 g (0.66 mmol) of potassium peroxodisulfate in 4 ml of water are slowly introduced dropwise into the flask over a period of 10–15 min, while stirring with a magnetic stirrer. The methacrylic acid polymerizes immediately, as may be seen from the increased viscosity of the solution. After the additions are complete, the temperature is held for another hour at 80°C.

After polymerization the rather viscous solution is added dropwise to 50 ml of 0.1 N HCl, whereupon the polymer precipitates. The polymer is filtered, if necessary broken up, extracted in a Soxhlet apparatus with petroleum ether for 5 h, and finally dried to constant weight in vacuum at 50°C. The yield is quantitative.

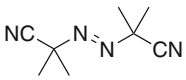
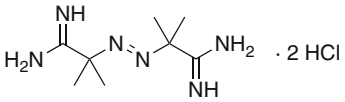
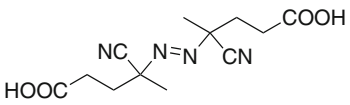
Poly(methacrylic acid) is soluble in water, methanol, 1,4-dioxane, and DMF. The solution viscosity of the polymer is measured in water at 20°C, using concentrations of 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 g/l (Ostwald viscometer, capillary diameter 0.3 mm). A plot of h_{sp}/c against c gives a curve that is typical of polyelectrolytes (see Sects. 1.3.1.2 and 2.3.3.3.1).

If, however, the viscosity is measured at the same concentrations in 1 N NaCl solution the behavior is identical with that for non-electrolyte polymers. It is best to proceed as follows. 30 g of NaCl are dissolved in water and made up to 100 ml in a graduated flask; this solution is 5.1 normal. To prepare the solutions for measurement at the aforementioned concentrations, the required amounts of poly (methacrylic acid) are weighed into 10-ml graduated flasks, dissolved in about 5 ml of water, and 2 ml of the 5.1 N NaCl solution added. The solutions are finally made up to the mark with water to give a solution of 1 N with respect to NaCl.

3.1.2 Polymerization with Azo Compounds as Initiator

Azo compounds that are especially suitable as initiators for radical polymerization are those in which the azo group is bonded on both sides to tertiary carbon atoms that carry nitrile or ester groups in addition to alkyl groups (Table 3.4). They are stable at room temperature, but decompose thermally above 40°C, or photochemically below 40°C, giving substituted alkyl radicals and liberating nitrogen. This nitrogen can be a nuisance at high initiator concentrations, both, in dilatometric measurements (gas bubbles in the measuring capillary) and in bulk polymerizations (the solid polymer is then frequently permeated with minute gas bubbles). Such azo compounds decompose in a manner that is essentially independent of solvent and strictly according to a first order rate law so that they are

Table 3.4 Azo-compounds for the initiation of radical polymerization

Azo-initiator	Formula	Suitable temperature for polymerization in °C
2,2′-Azobisisobutyronitrile (AIBN)		50–70
2,2′-Azobis (2-amidino-propane). 2HCl		40–60
2,2′-Azobis (4-cyano-pentanoic acid)		40–70

especially suited for kinetic investigations (see Sect. 3.1 and Examples 3.6 and 3.8). The most important azo compound in this connection is 2,2′-azobisisobutyronitrile (AIBN).

The yield of initiating radicals is, however, generally smaller than would be expected. In the case of AIBN this is because a certain amount of tetramethyl-succinic acid dinitrile is formed by combination of the primary radicals, while some methacrylonitrile and *iso*-butyronitrile are formed by disproportionation of the primary radicals. Azo compounds are especially suited as initiators for polymerization in bulk or in organic solvents.

Example 3.6 Bulk Polymerization of Styrene with 2,2′-Azobisisobutyronitrile in a Dilatometer

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 polymerization reaction can be followed very conveniently and with great accuracy by observing the resulting contraction of volume in a dilatometer. This contraction results from the considerable difference in density between monomer and polymer. Knowing the initial volume V and contraction ΔV during polymerization, the percentage conversion U in the absence of a diluent is given by the following Eq. 3.15.

$$U \cdot K = 100 \cdot \frac{\Delta V}{V} \tag{3.15}$$

Here, K is a constant that can be calculated from the specific volumes of the monomer and polymer at the appropriate temperature. One can, however, also determine the relationship between U and ΔU by direct experiment.

Dilatometric Measurements

The following amounts of 2,2′-azobisisobutyronitrile (AIBN) are weighed into 4 graduated 25-ml flasks: 35, 110, 180, and 250 mg (0. 21, 0.67, 1.10, and 1.52 mmol). The flasks are filled to the mark with destabilized styrene (at 20°C) and the amount of styrene divided by 25 ml gives the density at 20°C (neglecting the partial volume of AIBN).

Four dilatometers are filled with the above solutions of AIBN in styrene, and placed in a large water thermostat at 60°C (±0.05°C) so that the filled parts of the capillaries are completely immersed. The thermostat can easily be constructed from a large glass tank, a powerful stirrer, an immersion heater, a contact thermometer and a relay. The dilatometers are put into a metal test tube rack fitted with suitable mountings to hold them rigidly in the thermostat. After inserting a filled dilatometer in the thermostat the meniscus rises in the capillary until thermal equilibrium is reached (if necessary some of the styrene solution may be withdrawn from the capillaries by means of a syringe or thin glass capillary). The level remains steady for a short induction period because of the presence of dissolved oxygen, and then falls as polymerization commences. The meniscus level is read every minute after insertion of the dilatometer in the thermostat and plotted against time. When the reaction slows down, it is sufficient to take readings every 5 min. Zero reaction time is taken as the intersection of the horizontal line and the initial slope. When the volume has fallen by 0.1–0.2 ml the meniscus level is quickly noted and the reaction immediately quenched by immersion of the dilatometer in ice/water.

The dilatometers are emptied as follows. The dilatometer, cooled in ice to below 10°C, is inclined carefully over a small beaker, the capillary is lifted from the dilatometer, the polymer solution poured into a beaker and the capillary and dilatometer bulb washed out several times with small amounts of toluene. The polymer solutions are each added dropwise to an 8- to 10-fold excess of methanol. The amounts of polymers precipitated are determined gravimetrically.

Evaluation of the Dilatometric Measurements

The change in volume ΔV is determined from the initial and final dilatometer readings in each experiment, as given by the plot of meniscus level against time. The constant K can now be calculated by using Eq. 3.15 for each dilatometric measurement and the results can be averaged. The statistical error is estimated from the scatter of the data (without applying the Gaussian formula).

The rate of polymerization (in % conversion per hour) is plotted against the square root of the initiator concentration (in mol%), according to Eq. 3.6. The limiting viscosity numbers [η] and hence the degrees of polymerization are also determined and plotted against the reciprocal square root of the initiator concentration.

The statistical error determined for K is only a limited measure of the accuracy of the dilatometric measurements. Since the main errors will be similar for each

measurement, the accuracy of the method is best determined by estimating the limits of error of each individual measurement. The main source of error and its approximate magnitude should be indicated.

Example 3.7 Polymerization of Styrene with 2,2′-Azobisisobutyronitrile in Solution (Effect of Monomer Concentration)

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.

23 mg (0.14 mmol) of AIBN are weighed into each of seven tubes or Erlenmeyer flasks with ground joints. Using adapters attached with springs, the tubes are evacuated and filled with nitrogen three times. Under a flow of nitrogen 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ml (4.36, 8.72, 13.07, 17.42, 21.78, and 26.13 mmol) of destabilized styrene are pipetted into the tubes and each is diluted to 15 ml with pure toluene (distilled under nitrogen); the seventh tube is charged with 15 ml of styrene only (bulk polymerization). Using a slight positive pressure of nitrogen the adaptors are removed from the tubes and immediately closed with ground glass stoppers secured with springs. The tubes are placed in a boiling water bath and cooled after 6 h. After dilution with toluene the polymer solutions are run from a dropping funnel into 300 ml of stirred methanol. The polymer flakes are filtered off and dried at 50°C to constant weight.

The yield [Y] and degree of polymerization [P] are plotted against the monomer concentration. The results are compared with those for the sample polymerized in bulk.

Example 3.8 Polymerization of Methyl Methacrylate with 2,2′-Azobisisobutyronitrile in Bulk

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) Observation of the Trommsdorff Effect (Gel Effect)

100 ml of methyl methacrylate are distilled under nitrogen into a graduated receiver or dropping funnel with pressure-equalizing tube, into which 100 mg (0.61 mmol) of 2,2′-azobisisobutyronitrile (AIBN) have previously been weighed. Ten tubes with ground joints and suitable adapters are evacuated, filled with nitrogen, and 10 ml (93.6 mmol) of methyl methacrylate with AIBN introduced to each tube. The adapters are removed from the tubes under slight positive pressure of nitrogen, the tubes are immediately closed with glass stoppers secured with springs, and stored until needed in a refrigerator.

To start the experiment all the tubes are placed in a rack at the same time and allowed to warm to room temperature; finally they are placed in a thermostat at 50°C. The tubes are removed at intervals of 1 h and immediately cooled in an acetone/dry ice bath. The samples that are still fluid are diluted with approximately 50 ml of chloroform and dropped into about 500 ml of stirred heptane or petroleum

ether. For the very viscous or solid samples 1–2 g are dissolved in 50–100 ml of chloroform and the solution is added dropwise to 500–1,000 ml of heptane or petroleum ether with stirring. The polymers are filtered off and dried to constant weight in vacuum at 50°C. The yield, the limiting viscosity number (measured in chloroform at 20°C) and the degree of polymerization are plotted against reaction time.

The conversion can also be followed refractometrically, since the change of refractive index during polymerization is directly proportional to the conversion. The measurements can be made with an Abbé refractometer, by placing a drop of the still-liquid sample on the prism using a glass rod in the usual way. However, the determination of the refractive index of the highly viscous or solid samples can only be done with special equipment. The conversion corresponding to the measured refractive index is derived from a calibration line connecting the value of the pure monomer ($n_{20} = 1.4140$) and that of the pure polymer ($n_{20} = 1.4915$).

(b) Control of the Molecular Weight by Chain Transfer

Five tubes with ground joints are filled, as described in (a), with 10 ml (93.6 mmol) of methyl methacrylate (containing 0.1 wt% of AIBN). 0.1, 0.5, 1.0, and 2.0 mol% 1-dodecanethiol are added as regulator to four of the tubes, while the fifth serves as reference. The tubes are stoppered and stored in a refrigerator until needed. To begin the experiment the tubes are warmed up to room temperature at the same time and placed in a thermostat at 50°C. After 2 h the tubes are taken out, the contents each dissolved in 30 ml of chloroform and the solutions added dropwise to 300 ml of heptane or petroleum ether under stirring. The polymers are reprecipitated from chloroform into heptane or petroleum ether, filtered and dried in vacuum at 50°C. The limiting viscosity number of all samples is determined in chloroform at 20°C and the average degree of polymerization derived (see Sect. 2.3.3.3). The value for the transfer constant cannot be determined very accurately from these values since the chain transfer Eq. 3.14 is strictly valid only for the number-average degree of polymerization. To determine the transfer constant 1/Pn is plotted against the mole ratio of thiol to monomer, $[ZH]/[M]$. A straight line is obtained, intersecting the ordinate at $1/P_0$ (experiment without thiol); the slope gives the transfer constant C_{ZH}. On a second graph the yield is plotted against $[ZH]/[M]$. It can be seen that the rate of polymerization is unaffected by the occurrence of chain transfer.

3.1.3 Polymerization with Redox Systems as Initiators

Numerous redox reactions generate radicals that can initiate polymerization. Chief amongst oxidizing agents are organic and inorganic peroxides; reducing agents include either low valency metal ions or non-metallic compounds that are readily oxidized, for example, certain sulfur compounds. There are also redox systems that consist of a mixture of a peroxo compound with metal ions (e.g., Fe^{2+}) and a second reducing agent such as a hydrogen sulfite. In this case, the iron(III) ion produced by the redox reaction between the peroxo compound and an iron(II) compound is

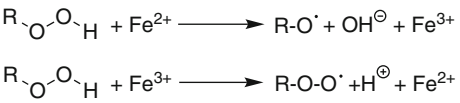
Table 3.5 Some common oxidizing and reducing agents that are suitable for initiating radical polymerization by redox reactions

Oxidizing agents	Reducing agents
Hydrogen peroxide	Ag^{+}, Fe^{2+}, Co^{2+}, Ti^{3+}
Peroxodisulfates	Hydrogen sulfites, sulfites, thiosulfates, mercaptans, sulfinic acids
Diacyl peroxides	Amines (e.g. *N*,*N*-dimethylaniline), certain sugars
Hydroperoxides	Benzoin/Fe^{2+}
Peracid ester	Hydrogen sulfite/Fe^{2+}

reduced again to the iron(II) state by the hydrogen sulfite, so that only a very small amount of iron(II) ions is required.

Table 3.5 lists some suitable oxidizing and reducing agents.

In a redox system consisting of a peroxo compound and an iron(II) salt, the initiating radicals are formed by electron transfer from Fe^{2+} to the peroxo compound, causing the peroxy link to be cleaved, with simultaneous formation of a radical and an anion. In a second step, the oxidized metal reacts with another hydroperoxide to form a peroxy radical and a proton:



It must be emphasized that, in contrast to the initiation of polymerization with peroxo compounds or azo compounds, not every redox system is suitable for initiating polymerization of every unsaturated monomer. Before attempting to polymerize a new compound with a redox system it is, therefore, advisable first to test its radical polymerizability with dibenzoyl peroxide.

Furthermore, the effectiveness of a redox system is influenced by a number of factors, and the redox components must be carefully balanced in order to attain optimum polymerization conditions. The most favorable conditions do not always correspond to a stoichiometric ratio of oxidizing and reducing agents. However, at constant molar ratio of oxidizing agent to reducing agent it is generally the rule that the rate of polymerization increases, and the mean degree of polymerization decreases, with increasing initiator concentration (see Example 3.11). The order of addition of the components can also be important; while it is normal to add the reducing agent first (in order to remove any oxygen which may be present), with subsequent dropwise addition of the oxidizing agent, there are cases where the reverse order must be applied. In aqueous medium, the pH value is also important; if it is necessary to work in alkaline medium, iron salts can only be used in combination with complexing agents such as sodium pyrophosphate ($Na_4P_2O_7$).

Redox polymerizations are usually carried out in aqueous solution, suspension, or emulsion; rarely in organic solvents. Their special importance lies in the fact that they proceed at relatively low temperatures with high rates and with the formation of high molecular weight polymers. Furthermore, transfer and branching reactions

are relatively unimportant. The first large-scale commercial application of redox polymerization was the production of synthetic rubber from butadiene and styrene (SBR1500) at temperatures below 5°C (see Example 3.44).

Example 3.9 Polymerization of Acrylamide with a Redox System in Aqueous 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.

5 g of pure acrylamide are dissolved in 500 ml of water (that has been boiled and distilled under nitrogen) in a 1 l standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath). To the solution are added 25 ml of a 0.1 M aqueous solution of iron(II) ammonium sulfate and 25 ml of a 0.1 M aqueous solution of hydrogen peroxide. The solution is gently stirred and nitrogen passed through the flask for 5 min in order to displace the atmospheric oxygen. The polymerization is conducted at room temperature (ca. 20°C). After 30 min the viscous solution is run dropwise with vigorous stirring into 4 l of methanol to which a few drops of concentrated hydrochloric acid have been added. The precipitate, colored brown by iron(III) hydroxide, is filtered off and dissolved in 50 ml of water. To this solution ammonia solution is added, the precipitated iron(III) hydroxide is filtered off, and the polymer solution is added dropwise to 500 ml of methanol. After filtration, the poly(acrylamide) is dried to constant weight in vacuum at 20°C; yield about 50%. Poly(acrylamide) is soluble in water but is not fusible. The limiting viscosity number is determined in water at 25°C (capillary diameter 0.35 mm).

Example 3.10 Fractionation of Polyacrylamide by Gel Permeation Chromatography in Water

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 Sephadex G100 are placed in a beaker and swollen with 400 ml water for 2 days. In a 2 m chromatography column (diameter 1.5–2 cm) a layer of glass wool and some glass beads are placed above the outlet tap. The tube is then partially filled with water and the swollen Sephadex is carefully run in to avoid trapping air bubbles. The gel particles gradually settle and the supernatant water is drawn off. The gel is now washed with fresh water until the runnings no longer show turbidity when added to methanol. (Fresh Sephadex often contains a small amount of water-soluble material that may have an adverse effect on the fractionation.) Finally the water is run off until the liquid meniscus is a few mm above the gel particles; the liquid level must never be allowed to fall below the level of the gel.

A solution of 250 mg of poly(acrylamide) from Example 3.9 in 25 ml of distilled water is introduced at the top of the column. At the same time the collection of the

eluate is commenced, taking 10 ml portions (measuring cylinder) for each fraction. The flow time under these conditions is about 10 ml/h. When the meniscus of the poly(acrylamide) solution reaches the gel layer, distilled water is added to the column as eluting agent.

The fractions collected are each run dropwise into 100 ml of stirred methanol to which two drops of concentrated hydrochloric acid have been added. Turbidity or precipitation will be observed from about the 6th fraction to about the 20th fraction. The precipitated fractions are filtered off, washed with methanol and dried to constant weight in vacuum at 20°C. For each fraction the viscosity is measured in water at 25°C using a capillary viscometer (capillary diameter 0.35 mm) and at as high a concentration as possible (10 g/l) in order to minimize errors. The limiting viscosity number, and hence the molecular weight, is estimated (see Sect. 2.3.3.3). Adjacent fractions for which there may be insufficient material for a viscosity measurement, can be combined where necessary.

After the fractionation, the amount of the individual fractions in mg is plotted against the elution volume. One can test whether there has been any loss of polymer by comparing the total mass of all the fractions with the initial amount; the loss should not be more than 3%.

The integral and differential molecular weight distribution curves are finally determined as described in Sect. 2.3.3.4. For summing the percentage amounts of the fractions, one proceeds from the last fraction having the lowest molecular weight to the first fraction having the highest molecular weight.

Example 3.11 Polymerization of Acrylonitrile with a Redox System in Aqueous Solution (Precipitation Polymerization)

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) Effect of the Ratio of Oxidizing Agent to Reducing Agent

The following solutions are prepared in distilled water:

5% solution of sodium disulfite ($Na_2S_2O_5$),

5% solution of potassium peroxodisulfate ($K_2S_2O_8$),

$$0.010\,\text{g}\ FeSO_4 \cdot 7H_2O\ \text{in}\ 100\,\text{ml water}\ + 2\,\text{ml conc.}\ H_2SO_4.$$

Four 250-ml round-bottomed flasks are evacuated and filled with nitrogen using a suitable adapter (see Sect. 2.2.5.2). The reagents listed in Table 3.6 are then introduced; the potassium peroxodisulfate solution is added last to all four samples at about the same time. The flasks are shaken briefly and allowed to stand under nitrogen at 20°C. For each sample the time of appearance of the first turbidity is noted. After 20 min the precipitated polymer is filtered off by suction from the four samples, washed with water, then with methanol, and dried overnight at 50°C in vacuum. The yield, the rate of polymerization and the limiting viscosity number (measured in DMF at 25°C) are plotted against the mole ratio of oxidizing agent to reducing agent.

Table 3.6 Test series for Example 3.11a

Sample	H_2O[a]	Acrylonitrile[b]	$Na_2S_2O_5$		$FeSO_4$		$K_2S_2O_8$	
	ml	ml	ml sol.	mmol	ml sol.	mmol	ml sol.	mmol
1	175	15	0.5	0.13	2.5	$9{\cdot}10^{-4}$	2.5	0.46
2	173	15	2.5	0.66	2.5	$9{\cdot}10^{-4}$	2.5	0.46
3	170	15	5.0	1.32	2.5	$9{\cdot}10^{-4}$	2.5	0.46
4	165	15	10.0	2.63	2.5	$9{\cdot}10^{-4}$	2.5	0.46

[a]The water is previously boiled under nitrogen
[b]Destabilized by distillation under nitrogen

Table 3.7 Test series for Example 3.11b

Sample	H_2O[a] ml	Acrylonitrile[b] ml	$Na_2S_2O_5$ ml sol.	mmol	$FeSO_4$ ml sol.	mmol	$K_2S_2O_8$ ml sol.	mmol
1	181	15	0.5	0.13	0.5	$1.8{\cdot}10^{-4}$	0.5	0.09
2	175	15	2.5	0.66	2.5	$9.0{\cdot}10^{-4}$	2.5	0.46
3	167	15	5.0	1.32	5.0	$1.8{\cdot}10^{-3}$	5.0	0.93
4	152	15	10.0	2.63	10.0	$3.6{\cdot}10^{-3}$	10.0	1.85

[a]The water is previously boiled under nitrogen
[b]Destabilized by distillation under nitrogen

(b) Effect of Initiator Concentration at Constant Ratio of Oxidizing Agent to Reducing Agent

Four 250-ml flasks are filled with the components listed in Table 3.7 as described above under (a).

The samples are allowed to react for 20 min at 20°C and then worked up as described above under (a). The rate of polymerization (in % conversion per minute) is plotted against the square root of the initiator concentration c_i (in mol $K_2S_2O_8$ per liter); the limiting viscosity number and the degree of polymerization are plotted against $c_i^{-1/2}$.

(c) Inhibition of Polymerization

5, 20, 100, and 200 mg of hydroquinone are weighed into four 250-ml round-bottomed flasks that are then evacuated and filled with nitrogen. To each are then added 15 ml of acrylonitrile (destabilized by distillation under nitrogen), 165 ml of degassed water, 10 ml of $Na_2S_2O_5$ solution, and 2.5 ml of $FeSO_4$ solution; finally 2.5 ml of $K_2S_2O_8$ solution are added to all four samples (20°C) at about the same time. The time required for the appearance of the first turbidity (incubation time, induction period) is noted. The induction periods are compared with each other and with that for sample 4 of experiment (a).

(d) Solution-Spinning of Poly(acrylonitrile)

3.5 g of one of the poly(acrylonitrile)s obtained above are dissolved in 25 ml of DMF. The viscous solution is poured into a 1-cm-wide glass tube which is drawn out to a jet at the lower end and dips into a dish of cold water. The polymer solution flows continuously out of the jet under its own weight, the poly(acrylonitrile) being precipitated in the form of an endless filament. This is guided through the water

bath and wound on to a rotating drum driven slowly by a motor. It is also possible to use a hypodermic syringe in place of the drawn-out glass tube; the filament thickness and rate of spinning can then be varied easily.

Example 3.12 Polymerization of Isoprene with a Redox System in Emulsion

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.

Most emulsion polymerizations are performed with water-soluble initiators; however, the following experiment describes a redox polymerization where one component (dibenzoyl peroxide) is water-insoluble, while the other is water-soluble.

A 100-ml standard apparatus (round-bottomed flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) is evacuated and filled with nitrogen three times. The following solutions are prepared: (a) 500 mg of sodium oleate (or sodium dodecyl sulfate) in 16 ml of degassed water; (b) 125 mg (0.32 mmol) of iron(II) ammonium sulfate and 125 mg of sodium pyrophosphate (as buffer) in 4 ml of degassed water. The latter solution is maintained at 60–70°C for about 15 min, with occasional shaking, and is then poured into the flask together with solution (a).

The mixture is cooled to room temperature and 20 ml (0.2 mol) of isoprene (distilled under nitrogen) containing 50 mg (0.21 mmol) of dissolved dibenzoyl peroxide are added. Vigorous stirring produces a stable emulsion that becomes more viscous as polymerizations proceeds. After 6 h at room temperature the isoprene is almost completely polymerized. The polymer is precipitated from the latex in the form of large flakes by adding it dropwise to 500 ml of methanol containing 500 mg of *N*-phenyl-β-naphthylamine as stabilizer for the polyisoprene; flocculation can be improved by the addition of a few drops of concentrated hydrochloric acid. The solid elastic product is filtered off, washed with methanol, and dried in vacuum at 50°C. The solubility is tested in different solvents, the limiting viscosity number determined (toluene, 25°C), also the proportion of 1,2- and 1,4-repeating units, and the *cis*/*trans* ratio. These values are compared with those obtained in the polymerization of isoprene with butyllithium (Example 3.21). The main application of polyisopren is in tires.

3.1.4 Polymerization Using Photolabile Compounds as Initiators

Radical polymerization can in several cases be initiated by subjecting the unsaturated monomer to light or high energy radiation. A very versatile variant of photopolymerization is the use of photolabile compounds as initiators which upon irradiation are fragmented to form radicals. This generation of radicals can occur in two ways. In the first case the photoinitiator itself absorbs light and decomposes. In the second case the photoinitiator is not able to absorb the light directly. Instead, a second compound (sensitizer) is needed to absorb the light and to transfer the

energy to the photoinitiator which than decomposes immediately. Some typical UV-initiators are benzoin, benzoin ether, benzil, and benzil ketals. Especially useful for the initiation of a radical polymerization in the visible spectral range of light is the yellow-colored campherquinone.

Photoinitiation is limited to thin layers due to the low penetration of light, nevertheless it possesses several advantages compared to the common techniques. Thus, it is possible to control the rate and degree of polymerization and also the number and length of crosslinks, by the intensity of light.

These advantages are commercially used in the so-called photolithography, a technique that allows the production of very tiny and accurate nanometer scale structures on the surface of semiconductors (e.g., silicon wafers).

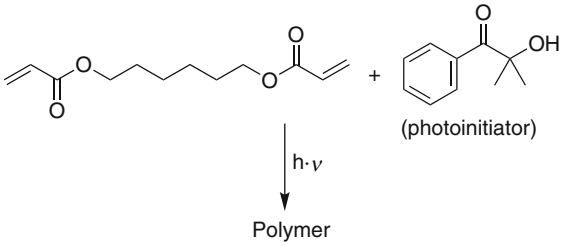
The principles of photolithography are as follows: Onto the surface of a semiconductor is spread a thin film of a photosensitive composition that consists of several chemicals. This composition is called photoresist and it is characterized by the effect that it changes its solubility upon irradiation. Thus, when the thin film is irradiated through a mask, the structure of this mask is projected onto the film which changes its solubility at the exposed segments. If the photoresist contains also bi- or higher functional monomers (Example 3.13), then crosslinked and insoluble polymers are formed. By treatment with a solvent the nonirradiated parts of the photoresist-film are removed while the crosslinked polymer remains on the surface of the substrate as an image of the structured mask, i.e., the structure of the integrated circuit. Without photolithography the modern microelectronics would not be possible.

The same principle is also applied in the manufacturing of printing plates for modern printing processes. Moreover, photopolymerization is used for coating of metals or wood and it finds also application in dentistry.

Example 3.13 Photopolymerization of Hexamethylene Bisacrylate

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 50-ml round-bottomed flask 5 g hexamethylene bisacrylate and 0.2 g of 2-hydroxy-2-methyl-1-phenylpropane-1-one as a photoinitiator are stirred until a homogeneous solution is obtained. The flask is evacuated for a short time to remove bubbles from the solution. An IR spectrum is taken of the homogeneous solution.



Part of this solution is now spread on a glass plate with a spatula and irradiated with UV light (Hg medium-pressure lamp), until a hard crosslinked and insoluble

film is obtained (5 min). The distance between the source of radiation and the substrate should be about 20 cm. This is an example of a photo-cured coating.

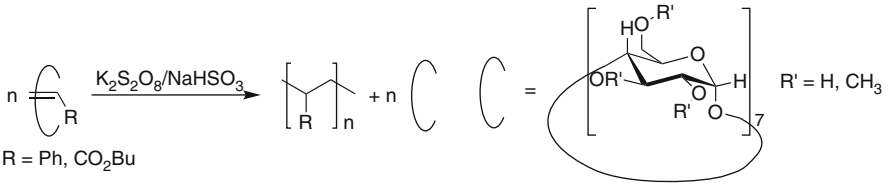
In a second experiment a mask, e.g., a coin, is placed between the substrate and the source of radiation by means of a holder. After 5 min the unexposed part of the film is removed by treating with an organic solvent. This is an example of surface structuring by photolithography.

The irradiated film shows an absorption band in IR spectrum (KBr pellet) at 1,635 cm^{-1}. The increase in intensity of this absorption with time is a measure of the conversion rate. Parallel to this the solubility/swelling of the film in THF or toluene should be qualitatively determined.

3.1.5 Polymerization of Cyclodextrin Host-Guest Complexes in Water

Polymerization reactions in aqueous medium can be carried out in homogeneous solution if the monomers and the polymers are soluble in water as in the case of acrylamide or methacrylic acid (see Examples 3.5, 3.9, and 3.35). Since most of the monomers are only sparingly soluble in water, suspension or emulsion techniques have to be applied in these cases.

Very recently a new method was developed that opens the possibility to polymerize even hydrophobic monomers in aqueous solution. This method is based on the finding that hydrophobic monomers can be made water-soluble by incorporation in the cavities of cyclodextrins. It has to be mentioned that no covalent bonds are formed by the interaction of the cyclodextrin host and the water-insoluble guest molecule. Obviously only hydrogen bonds or hydrophobic interactions are responsible for the spontaneous formation and the stability of these host-guest complexes. X-ray diffraction pattern support this hypothesis. Radical polymerization then occurs via these host-guest complexes using water-soluble initiators. Only after a few percent conversion the homogeneous solution becomes turbid and the polymer precipitates.



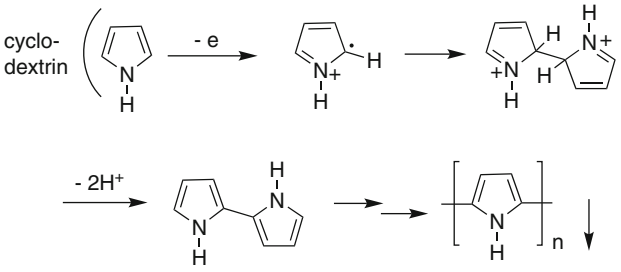
While the polymer precipitates, the cyclodextrin stays in solution and can be reused again as host-molecule.

Variations of this method are possible in several ways. First of all, cyclodextrin which is available on a large scale by enzymatically catalyzed modification of starch can be tailored by chemical reactions. Furthermore, copolymerizations

between different host-guest complexes are possible whereby in some cases the reactivity ratios differ from those reported in literature.

Cyclodextrin can also be used in order to stabilize monomers that would otherwise oxidize upon contact with air. The cyclodextrin host shields the monomer from oxygen in the air. Monomers such as pyrrole can be stored as a cyclodextrin complex for months without any noticeable degradation. The complex is a colorless powder that does not change color over time unlike pure pyrrole, which would oxidize and therefore turn black via yellow. Another advantage of the method is the fact, that the complex is odorless whereas pyrrole itself has an unpleasant smell.

In general, polypyrrole can be prepared via electrochemical or chemical oxidative polymerization of pyrrole involving different highly reactive intermediates. Also, the pyrrole/cyclodextrin complex can be polymerized in aqueous solution under oxidative conditions by adding potassium peroxodisulfate as an oxidizing agent. Polypyrrole is insoluble and infusible but achieved high interest since it can be used as conductive polymer. Its conjugated double bonds are able to conduct electricity if the polymer is doped. In the undoped state the polymer behaves as a semiconductor.



Example 3.14a Free Radical Polymerization of Cyclodextrin Host-Guest Complexes of Butyl Acrylate from Homogeneous Aqueous Solution (Precipitation Polymerization)

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.

27.1 g (20.35 mmol) of 1.8-fold methylated ß-cyclodextrin (m-ß-CD) are dissolved in 70 ml of deionized water in a 250-ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) fitted with magnetic stirrer. The resulting solution is flushed with nitrogen for 15 min. To this solution 2.0 g (15.61 mmol) of *n*-butyl acrylate are added. The shaken yellowish dispersion is sonicated for 20 min yielding a clear solution of the complexed monomer *n*-butyl acrylate/m-ß-CD. After complexation, 0.21 g (0.78 mmol) of potassium peroxodisulfate and 0.08 g (0.78 mmol) of sodium hydrogen sulfite are added to the solution. The polymerization is conducted at room temperature (20–25°C). After some minutes the clear monomer solution changes to

a colorless cloudy polymer dispersion. The polymerization can be stopped after 3 h by cooling the reaction mixture in an ice bath and adding 100 ml of water. The precipitate is filtered off. After dissolving the crude polymer in 15 ml of THF the solution is poured dropwise under vigorous stirring into 200 ml of water, yielding colorless polymeric products. After filtration the material is free of monomers and m-β-CD which can be proved by TLC using iodine for visualizing. Conversion 80%; $M_n = 20{,}000$ (GPC in THF at 25°C).

Example 3.14b Oxidative Polymerization of a Cyclodextrin Host-Guest Complex of Pyrrole from Homogeneous Aqueous Solution (Conducting Polymer)

4 g (4.11 mmol) α-cyclodextrin are dissolved in 40 ml of water. 0.24 ml (0.23 g = 3.43 mmol) pyrrole are added to the solution. The mixture is stirred for 4 h at room temperature (20–25°C). The complex precipitates as colorless crystals. The complex is filtered off and washed with 5 ml of cold water. The complex may be allowed to dry at room temperature on the filter paper or it can be used as it is.

1 g of the complex is completely dissolved in 25 ml of water at 60°C. 0.65 g potassium peroxodisulfate are added as an oxidizing agent. As the polymerization progresses a black precipitate forms. The polymer is filtered off after approximately 30 min reaction time, washed with hot water and dried in an oven at 50°C.

After drying, the filter paper displays a resistance of 40–100 kΩ, measured with a multimeter by pressing the electrodes into the polypyrrole powder at a distance of 1 cm. The resistance may vary depending on the location of measurement, since the polypyrrole thickness and distribution may vary on the filter paper. Without the polypyrrole, the filter paper has a resistance of at least 10^{10} Ω, which in most cases lies beyond the measuring range of the multimeter. Thus it can be shown that the polypyrrole reduces the resistance significantly.

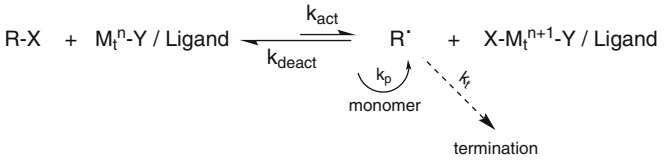
3.1.6 Controlled Radical Polymerization

Recently there has been progress in achieving higher control in free radical chain addition polymerization by suppressing chain termination reactions and reducing the content of free radicals in the system. All basic concepts involve a reversible chain termination reaction leading to a "dormant" chain which "sleeps" most of the time and is active only for a very short time to allow monomer "insertion" into the lable bond. These systems are called "quasiliving" or controlled radical polymerizations and show features of the "living" ionic chain addition reaction. In a well controlled radical system the monomer conversion is first order, molar mass increases linearly with monomer conversion and the molar mass distribution M_w/M_n is below 1.5. In addition, chain-end functionalionization as well as subsequent monomer addition allow the preparation of well-controlled polymer architectures, e.g., block copolymers and star polymers by a radical mechanism which had been up to now reserved for ionic chain growth polymerization techniques.

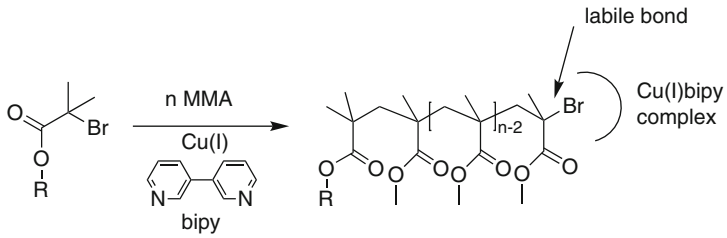
Three major systems are distinguished so far:

(a) Atom transfer radical polymerization (ATRP)
(b) Stable free radical polymerization (SFRP) or nitroxy-mediated radical polymerization (NMP)
(c) Reversible addition-fragmentation termination (RAFT)

The mechanism of the ATRP is based on the reversible activation of alkyl halides by redox reaction of a complexed metal with the halogen terminal group of the initiator or the growing chain end. Thus, the initiating step is the homolytic cleavage of the carbon-halogen bond in the organic halide R-X by oxidation of the metal M_t in the metal complex M_t^n-Y/ligand. Consequently. the initiating radical species $R^\bullet$ and the oxidized metal complex are formed. At this point, $R^\bullet$ can add monomer units to enable chain propagation, or else it can react with the halogen on the oxidized metal to regenerate the dormant species R-X. The activation constant K_{act} leading to a free radical at the growing chain end is low compared to the deactivation constant K_{deact} and therefore the equilibrium is strongly on the side of the dormant species reducing the amount of free radicals. Secondary or tertiary chloride or bromide compounds can be used as initiator in combination with copper (1)chloride and, e.g., (substituted) bypyridine or tetradendates (e.g., MeTREN) are applied as ligand. The ratio initiator/copper/ligand as well as the reaction temperature has to be optimized for each monomer system, however, a broad variety of monomers including styrenics as well as acrylates and methacrylates, was polymerized under controlled conditions so far.



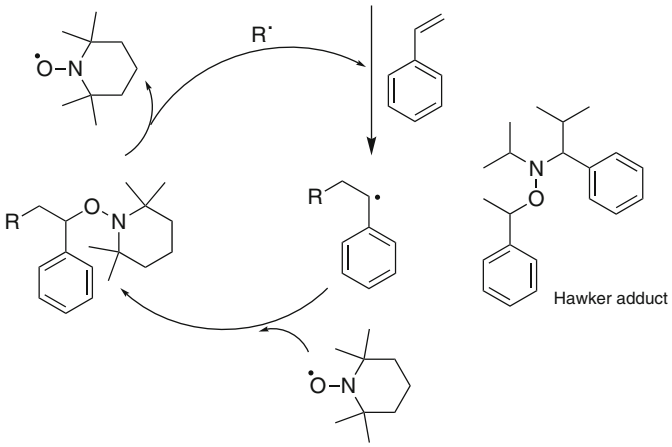
ATRP is a very potent method for preparing block copolymers by sequential monomer addition as well as star polymers using multifunctional initators. Furthermore, it can be applied also in heterogenous polymerization systems, e.g., emulsion or dispersion polymerization. In Example 3.15a the ATRP of MMA in miniemulsion (see also Sect. 2.2.4.2) is described.



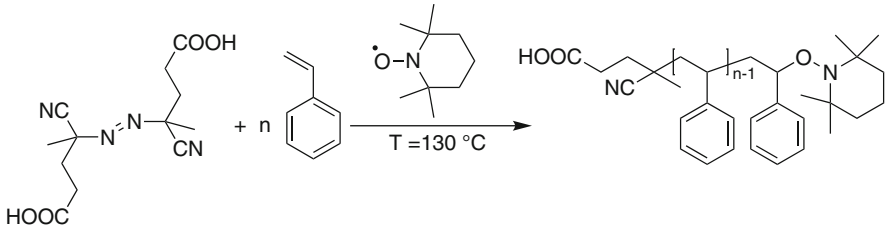
The SFRP or NMP has been studied mainly using the stable free radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or its adducts with, e.g., styrene derivatives. It is based on the formation of a labile bond between the growing radical chain end

or monomeric radical and the nitroxy radical. Monomer is inserted into this bond when it opens thermally. The free radical necessary to start the reaction can be created by adding a conventional radical initiator in combination with, e.g., TEMPO or by starting the reaction with a preformed adduct of the monomer with the nitroxy radical using so-called unimolecular initiators (Hawker adducts).

The thermal lability of the R–C–O–N bond system controls the reversibility of the chain termination and limits also the use of NMP. SFRP of styrene at about 130°C is studied intensively. In this case, high control and high-molar-mass products could be achieved. It was found that the thermal autopolymerization of the styrene monomer plays an important role in the mechanism of the reaction. Therefore, first experiments using different monomers in the presence of TEMPO and a radical initiator failed with regard of the control. However, new nitroxy adducts with a different R–O–N bond stability have been developed, e.g., by Hawker which work also for styrene derivatives as well as for acrylates.

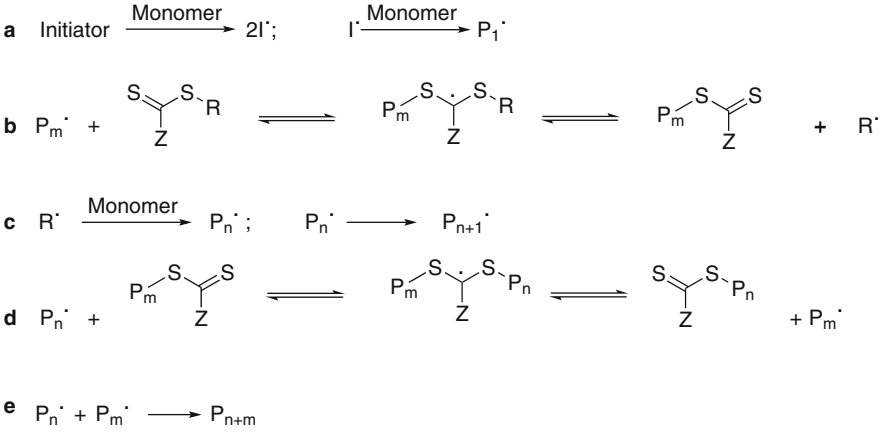


End-group functionalization in NMP can be achieved by using a functional radical initiator in combination with TEMPO.



In the RAFT mechanism, the chain equilibrium process is based on a transfer reaction, no radicals are formed or destroyed, and, when the RAFT agents behave ideally, the kinetics can be compared to the one of a conventional free radical polymerization. The release of initiating radicals through chain transfer (b) at the

beginning and the addition-fragmentation step (d), necessary to minimize the irreversible termination events, are the basis on which RAFT mechanism relies. During the reaction, chains are alternatively converted from propagating radicals to polymeric transfer agents and vice versa, generating an equilibrium. This enables the incremental growths of the chains with conversion, giving living character to the process. The choice of RAFT agents is very important for the achievement of well-defined products: they should have a high transfer constant regarding the monomers being polymerized, which means a high rate of addition, and suitable leaving groups for the propagating radical. As a result, dithioesters, trithiocarbonates, and certain dithiocarbamates can be successfully employed to obtain narrow polydispersity for styrenes and (meth)acrylates in batch polymerization. RAFT can be performed at a broad temperature range and has a high tolerance to a large variety of functionalities (e.g., OH, COOH, NR_2). Very similar is the MADIX (macromolecuelar design via interchange of xanthates) approach which employs xanthates.



Example 3.15a Controlled Radical Polymerization (ARTP) of Methyl Methacrylate in Miniemulsion

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 described in this example is carried out in miniemulsion. Miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobe. In contrast to the classical emulsion polymerization (see Sect. 2.2.4.2), here the polymerization starts and proceeds directly within the preformed micellar "nanoreactors" (= monomer droplets). This means that the droplets have to become the primary locus of the nucleation of the polymer reaction. With the concept of "nanoreactors" one can take advantage of a potential thermodynamic

control for the design of nanoparticles. Polymerizations in such miniemulsions, when carefully prepared, result in latex particles which have about the same size as the initial droplets. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials, or with respect to the stability of the formed latexes.

Experimental Conditions

All ingredients are carefully degassed and brought under an atmosphere of nitrogen prior to use. All material transfers are carried out using degassed syringes (see also Example 3.19). All reactions are carried out under an atmosphere of nitrogen in 10-ml round-bottom flasks closed by a rubber septum which can be passed by syringe needles. A solution of *n*-decane (0.422 g, hydrophobic) and poly(methyl methacrylate) (0.075 g; co-hydrophobic) in the monomeric methyl methacrylate (3 g, 29.96 mmol) is transferred into the 10-ml reaction flask containing a mixture of 4,4′-dinonyl-2,2′-bipyridine (0.081 g, 0.198 mmol) and CuCl (0.009 g, 0.099 mmol). Stirring at room temperature for several minutes leads to an intensively brown solution of the formed copper(I) complex. Stirring is continued until all copper salt has disappeared.

In a second 10-ml reaction flask, water (18 g) and Brij 78 [poly(oxyethylene stearyl ether); 0.45 g, 15 wt%] are mixed under vigorous stirring. The above solution of copper complex, hydrophob and co-hydrophob in MMA is then added to the resulting clear solution of the emulsifier, and the resulting mixture is vigorously stirred at room temperature using a magnetic stirring bar until a fine primary emulsion has been formed. Subsequently, the emulsion is sonicated for approx. 20 min in a conventional ultrasonic bath. Here, it is possible to follow the decrease of droplet size – and thus the increase of internal surface – via surface tension measurements. The resulting miniemulsion is heated in an oil bath to 70°C and then the initiator 2-bromo-2-methylpropionic acid methyl ester (0.018 g, 0.099 mmol) is added. Heating and stirring of the reaction mixture is continued for further 3 h (Table 3.8).

At regular intervals, samples are taken of the emulsion for GC (0.3 ml each) and SEC (0.5 ml each) analysis using degassed syringes. The following reaction times proved to be appropriate for taking samples for GC and SEC: 1: immediately after addition of the initiator; 2: after 15 min; 3: after 30 min; 4: after 60 min; 5: after 90 min; 6: after 120 min; 7: after 150 min; 8: after 160 min; 9: after 180 min; 10: after full reaction time.

For GC analysis, the emulsion samples are diluted in THF or acetone (1.5 ml). For SEC samples, the emulsions are dissolved in THF (3–5 ml, containing 0.06% toluene as an internal SEC standard). The solution SEC is filtered over aluminum oxide (to remove the copper residues) and then through a syringe filter prior to the injection into the SEC.

For the evaluation of the obtained GC data, the decrease of MMA concentration is plotted vs. time. From the plot the apparent rate of conversion can be determined.

Table 3.8 Recipe for Example 3.15 (T = 333 K/P_n ~ 300)

	n:*n*	*n* [mmol]	Weight [g]	Volume [ml]
MMA	300	29.96	3	3
MbiB	1	0.099	0.018	
CuCl	1	0.099	0.009	
dNbPy	2	0.198	0.081	
		***m* [g]**	**wt%**[a]	***v*:*v***
Water		18		6
MMA		3		1
Brij 78		0.45	15	
D/PMMA		0.422/0.075		

MMA	Methyl methacrylate	Monomer
MbiB	2-Bromo-2-methylpropionic acid methyl ester	Initiator
dNbPy	4,4′-Dinonyl-2,2′-bipyridine	Ligand
D	Decane	Hydrophob/GC-Standard
PMMA	Poly(methyl methacrylate) (7H, Röhm)	Co-hydrophob
Brij 78	Poly(oxyethylene stearyl ether)	Emulsifier

[a]wt% of emulsifier with respect to monomer

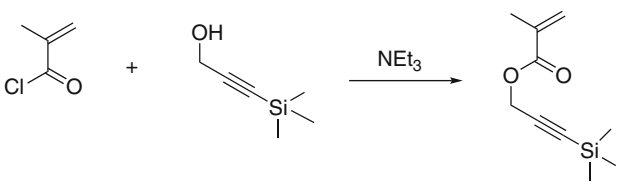
Also, the degree of conversion can be calculated for each data point. The resulting plot shows until what time the process occurs in a controlled manner and where the uncontrolled free radical polymerization sets in.

For the evaluation of the SEC measurements, a second plot can be created where the obtained values of M_n (left coordinate, should increase linearly with conversion) and the polydispersity indices (PDI, right coordinate, should be lower than 1.3) are plotted vs. the conversion. This plot again can be used to discuss the degree of control, and the time period where control was achieved during the chain growth process. This time is in general approx. 2 h.

Example 3.15b Controlled Radical Polymerization (RAFT) of Trimethylsilylpropargyl Methacrylate and Subsequent Polymer Analogous Click Reaction

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) Synthesis of the monomer trimethylsilyl propargylmethacrylate

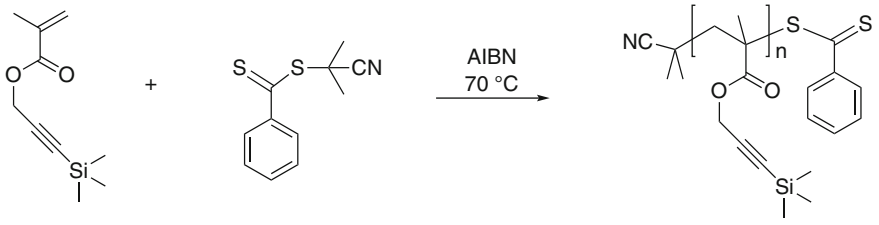


In a 500 ml inert gas flask, 3-(trimethylsilyl)prop-2-in-1-ol (3 g , 23.4 mmol) and triethyl-amine (12 ml, 86.3 mmol) are dissolved in THF (200 ml). The clear,

colorless solution is cooled down by using an ice bath and in an inert gas stream methacryloyl chloride (2.4 ml, 24.8 mmol) is added slowly via a syringe. After completed addition, the ice bath is removed and the solution is stirred at room temperature further 2 h. Subsequently, remains of methacryloyl chloride are neutralized by careful addition of water (2 ml). The white precipitation is filtered off, all solvents are removed using a rotary evaporator and the residue is dissolved again in a little amount of chloroform. Next, the product is purified by column chromatography (solvent: chloroform) to obtain the monomer as a clear, colorless liquid. Yield: 3.83 g (19.5 mmol; 83%).

^{1}H-NMR: δ_H (500,13 MHz, $CDCl_3$) 6.17 (1H), 5.61 (1H), 4.76 (2H), 1.96 (3H), 0.18 (9H) ppm.

(b) RAFT polymerization of trimethylsilyl propargylmethacrylate



CTA **P1**

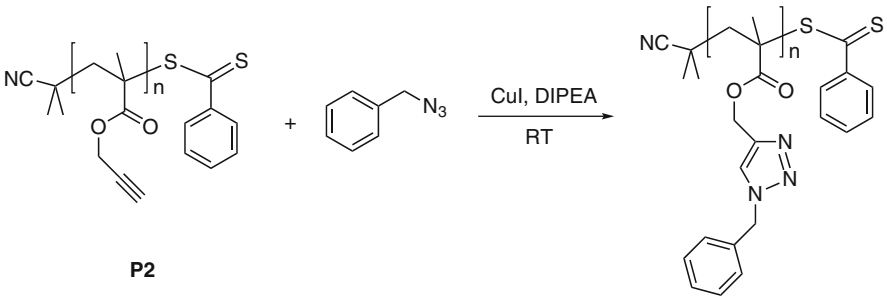
A 20 ml Schlenk tube is equipped with the CTA 2-cyanoprop-2-yl-dithiobenzoate (see Bibliography) (11.6 mg, 0.0524 mmol), the monomer (1 g, 5.09 mmol) and the initiator 2,2′-azobis(isobutyronitrile) (AIBN) (0.8 mg, 0.00487 mmol) in anisole (0.8 ml). The clear, pink colored solution is degassed by using three freeze-pump-thaw cycles. Next, the tube is immerged into a 70°C heated oil bath for 22 h. The polymerization is stopped by immersion of the reaction tube into liquid nitrogen for about 5 min. Then, the product mixture is diluted by roughly the same volume of deuterated chloroform ($CDCl_3$) to take a sample for NMR analysis (determination of conversion). The product P1 is obtained via precipitation in a methanol/water (1:1) mixture followed by filtration over a G4 frit and drying in vacuum. The polymer P1 is isolated in 50–60% yield and unde the given condition as a monomer conversion of about 80% is obtained as verified by NMR. The product is characterized by ^{1}H NMR and SEC. The obtained molar masses are in good agreement as the theoretical ones.

^{1}H-NMR: δ_H (500.13 MHz, $CDCl_3$) 4.6 (2H), 2.15–1.4 (2H), 1.35–0.7 (3H), 0.2 (9H) ppm. SEC (RI-detector): M_n: 16,900 g/mol, M_w: 20,000 g/mol, PDI: 1.18.

In the following step, the trimethylsilyl propargyl units are deprotected. In a 50 ml round flask, the protected polymer P1 (0.401 g, 2.045 mmol) is dissolved in THF (20 ml) and the solution is cooled down with an ice bath. Next, 2.7 ml (2.7 mmol) of a 1 M THF solution of tetrabutylammonium fluoride (TBAF) are added dropwise via a syringe. After 10 min, the ice bath is removed and the solution is stirred further 1.5 h. Subsequently, the product is precipitated in a methanol/water

(1:1) mixture, filtered (G4 frit) and dried in vacuum. The completely deprotected polymer P2 is obtained as a white solid in 60–70% yield and with a molar mass somewhat lower than the parent polymer (M_n: 14,000 g/mol, M_w: 16,000 g/mol). The success of the deprotection can be verified by NMR by the loss of the signals of the trimethylsilylgroup (0.2 ppm) and the appearance of the CH signal at 2.49 ppm (when measured in $CDCl_3$)

(c) 1,3-Dipolar cycloaddition of polymer P2 with benzyl azide



P2 **P3**

In a 100 ml inert gas flask, 110 mg (0.89 mmol) of the deprotected polymer P2 are dissolved in 20 ml DMF. Afterwards, benzyl azide (Alfa Aesar, 94%) (200 mg; 1.41 mmol), a minimal amount of copper iodide and 200 mg (1.55 mmol) of diisopropylethylamine (DIEA) are added. The addition of the substances is done in an inert gas stream. Subsequently, the reaction vessel is sealed and the mixture is stirred at room temperature over night (15 h). Next, the solution is added dropwise to a methanol/water mixture (1:1) leading to precipitation of the polymer. The product (P3) is filtered (G4 frit), washed with water and ethanol and dried in vacuum. A yield of 80–90% is achieved and complete reaction of the propargyl groups with the azide through formation of the triozole can be verified by ^{1}H NMR. SEC analysis shows some increase in molar mass.

^{1}H-NMR: δ_H (500, 13 MHz, $CDCl_3$): 8.1–7.6 (1H), 7.6–6.9 (5H), 5.8–5.3 (2H), 5.3–4.6 (2H), 2.15–1.15 (2H), 1.15–0.2 (3H) ppm. SEC (RI-detector): M_n: 19.000 g/mol, M_w: 24.000 g/mol, PDI: 1.2–1.3.3.2

3.2 Ionic Homopolymerization

Like radical polymerizations, ionic polymerizations also occur by a chain mechanism. In contrast to radical polymerizations the chain carriers are macroions:

carbonium ions in the case of cationic polymerizations and carbanions in the case of anionic polymerization of C = C compounds:

Cationic Polymerization

Anionic Polymerization

Again, in contrast to radical polymerization, there is no chain termination by combination, since the growing chains (macroions) repel each other electrostatically because of their like charges. Chain termination occurs only by reaction of the growing chain ends with substances such as water, alcohols, acids, and amines. The ions produced by reaction of these substances can sometimes initiate new chains (chain transfer). Under certain conditions the ionic propagation species retain their ability to grow over extended periods of time, even after complete consumption of monomer ("living polymers", see Sect. 3.2.1).

Radical initiators have so far been employed successfully only for the polymerization of compounds containing C = C bonds. The number of ionically polymerizable monomers is considerably larger, and includes also compounds containing a C = O or a C = N group, and a series of heterocyclic compounds. In some cases migration of an atom or group occurs during polymerization (isomerization polymerization). A particular characteristic of some ionic polymerizations is that they proceed stereospecifically, leading to tactic polymers.

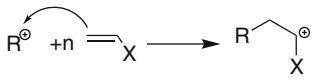
In contrast to radical polymerizations, ionic polymerizations proceed at high rates even at low temperatures, since the initiation and propagation reactions have only small activation energies. For example, isobutylene is polymerized commercially with boron trifluoride in liquid propane at −100°C (see Example 3.16). The polymerization temperature often has a considerable influence on the structure of the resulting polymer.

3.2.1 Ionic Polymerization Via C = C Bonds

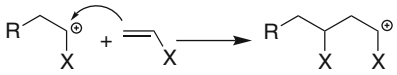
The tendency of unsaturated compounds to undergo cationic or anionic polymerization differs greatly according to the type of substituent at the double bond. Some monomers can polymerize only cationically or only anionically but there are also some that can polymerize by both mechanisms (see Table 2.2). Electron-repelling groups (alkyl, phenyl, alkoxy) cause polarization, such that the unsubstituted carbon atom of the double bond carries a partial negative charge; hence, protons or other suitable cations can attach themselves to this unsubstituted carbon atom with the positive charge being transferred to the substituted carbon atom which can likewise add monomer by the propagating reaction. In cationic polymerization the propagating chains can be terminated only by addition of reactive anions, since the

combination of two macrocations is not possible; b-elimination of a proton from the chain end may also take place in a transfer reaction.

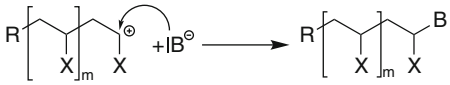
Initiation:



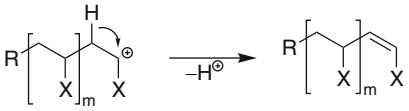
Propagation:



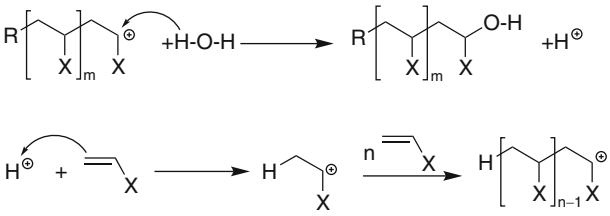
Termination:



Transfer:

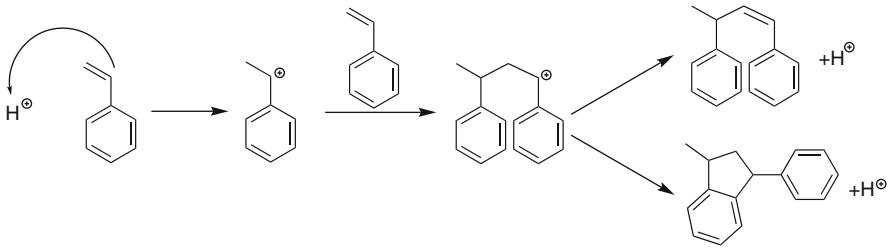


Nucleophiles such as water, alcohols, esters, acetals, and ethers can also act as transfer agents by reacting with the macrocations, at the same time forming a new cation that initiates the growth of a new chain; the kinetic chain thus remains unbroken.



Cationic polymerizations can be initiated with protic acids (e.g., sulfuric, perchloric, trifluoroacetic acid), with Lewis acids (see Sect. 3.2.1.1), and with compounds that form suitable cations (e.g., iodine, acetyl perchlorate). Some monomers are also polymerized by high-energy radiation according to a cationic mechanism.

By choice of appropriate conditions it is sometimes possible to stop the reaction at the dimer stage; for example, in the case of styrene this leads to an unsaturated linear dimer, or, by ring closure, to a cyclic dimer:

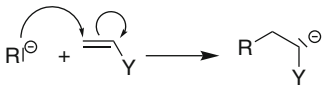


According to this reaction, the dimerization of divinylbenzene leads to polyindane.

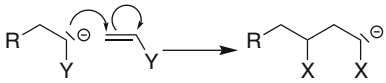
For unsaturated compounds with electron-withdrawing substituents (carboxyalkyl, nitro, nitrile, vinyl), polymerization can be initiated anionically (e.g., by OH^-, NH_2^-, or carbanions).

The addition of the anion takes place at the unsubstituted carbon atom, which, in this case, carries a partial positive charge. Since the growing chain end is a genuine anion, chain termination can occur by addition of a reactive cation. As in cationic polymerization, combination of two growing ends is not possible. Chain transfer with electrophiles can also occur.

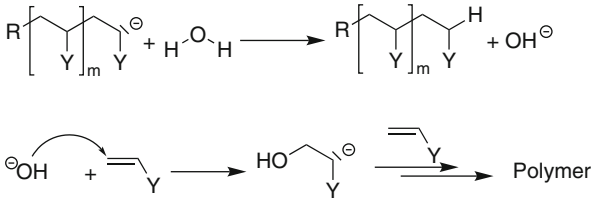
Initiation:



Propagation:

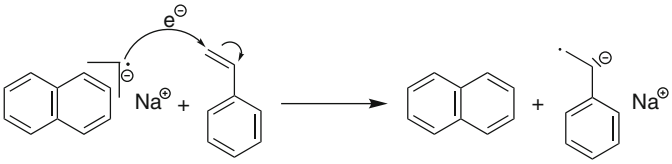


Chain transfer:

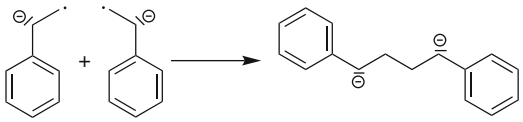


For some monomers (e.g., nitroethylene and 2-cyano-2,4-hexadienoic acid ester, CH_3–CH = CH–CH = C(CN)–COOR), anionic polymerization can be conducted in aqueous alkaline solution. Other anionic initiators are Lewis bases, e.g., tertiary amines or phosphines, and organometallic compounds (see Sect. 3.2.1.2). Since the polarizability of unsaturated compounds depends very much on the substituents and on the solvent used, there are considerable differences in the effectiveness of the initiators mentioned.

Another way to initiate anionic polymerization is by electron transfer. The reaction of sodium with naphthalene gives sodium naphthalene (sodium dihydronaphthylide) in which the sodium has not replaced a hydrogen atom, but has transferred an electron to the electronic levels of the naphthalene; this electron can be transferred to styrene or α-methylstyrene, forming a radical anion:



Such radical anions combine very quickly forming a dianion which can then add styrene at both ends:



Provided that the reaction mixture is prepared under stringent conditions, that reaction of the dianions with impurities (e.g., water) is prevented, the polymer chains can grow until the monomer is completely consumed. If another batch of styrene is added, the "living polymer" can grow further. Finally a "dead" polymer results, if a chain breaker is added (e.g., proton donor).

Under ideal conditions, i.e., complete exclusion of impurities and very rapid mixing of monomer and initiator solution, two sodium naphthalene molecules give rise to one polymer chain. Provided that initiation is rapid compared with propagation, the degree of polymerization is then given by:

$$P = \frac{2 \cdot [M]}{[I]} \tag{3.16}$$

The polydispersity of polymers prepared in this way is usually very low; for example, a value M_w/M_n of 1.05 was found for a sample of poly(α-methylstyrene). Living polymers can also be used for the preparation of block copolymers; after the consumption of the first monomer, a second anionically polymerizable monomer is added which then grows onto both ends of the initially formed block. By termination of the living polymer with electrophilic compounds the polymer chains can be provided with specific end groups; for example, living polystyrene reacts with carbon dioxide to give polystyrene with carboxylic end groups.

In the anionic polymerization of α-methylstyrene with sodium naphthalene the reaction proceeds to an equilibrium and it is possible to observe the temperature dependence of the equilibrium between monomer and polymer. After addition of the monomer, the deep green color of the initiator solution is transformed into the red color of the carbanions. At low temperatures (−70 to −40°C) the living polymer is formed and the solution becomes viscous. After warming, the macroanions

depolymerize again, but reform reversibly on cooling. The temperature at which the equilibrium is established is called the ceiling temperature for the given monomer concentration; for α-methylstyrene it lies at about 60°C, but for most vinyl monomers it occurs above 250°C. For some monomers with polymerizable C = O bonds, or for cyclic monomers, the ceiling temperature is relatively low, for example, formaldehyde or trioxane (126°C) and THF (85°C). In spite of its thermodynamic instability, poly(α-methylstyrene) can be isolated if the living anionic chain ends are capped, e.g., by reaction with water or carbon dioxide. The thermal degradation of poly(α-methylstyrene) with stable end groups to monomer proceeds with measurable speed only above 200°C where chain scission begins to occur (see Example 5.12).

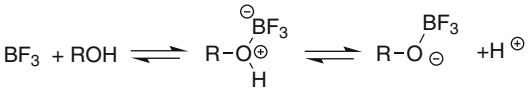
In certain cases of ionic polymerization the chain growth is stereoregular. It was first shown to be possible to make tactic polymers by stereospecific catalysis using organometallic catalysts (see Sect. 3.2.1.2), but other initiators have since been found that are suitable for stereoregular polymerization. For example, under certain conditions styrene can be polymerized with many organo-alkali-metal compounds to give tactic polystyrene. A certain degree of stereoregulation during chain growth has also been observed in cationic and even in radical polymerizations of some monomers.

Stereospecific polymerization has particular significance for the preparation of stereoregular polymeric dienes. In the radical polymerization of butadiene or isoprene the molecular chains always consist of varying proportions of adjacent *cis*- and *trans*-1,4-units as well as 1,2- and 3,4- linked units, depending on the polymerization conditions; but it is now possible, using particular ionic initiation systems to make a "synthetic natural rubber" that contains more than 90% *cis*-1,4-isoprene repeating units (see Example 3.21).

It can be seen that both the solvent and the catalyst affect the structure of the polymer produced. For example, the structure of the polyisoprene differs strongly with the alkali metal, even when used in the same solvent medium. Experiments with a typical organometallic complex catalyst, consisting of trialkylaluminum and titanium tetrachloride, show that the same initiator can lead to quite different structures in the products of polymerization of isoprene and of butadiene.

3.2.1.1 Cationic Polymerization with Lewis Acids as Initiators

The following Lewis acids are suitable for initiating cationic polymerization: BF_3, $AlCl_3$, $TiCl_4$, $SnCl_2$, $SnCl_4$, and $FeCl_3$. So-called co-initiators (cocatalysts) play an essential part in the initiation mechanism. Among these are proton-donating compounds (protic acids, water, alcohols) and compounds such as alkyl halides that form ionic complexes with Lewis acids which can then dissociate to give cations capable of initiating polymerization. Thus, in the case of water or alcohol as cocatalyst the real initiator is a proton:



and, when alkyl halides are used, an alkyl cation:

$$SnCl_4 + RCl \rightleftharpoons [RClSnCl_4] \rightleftharpoons R^{\oplus} + {}^{\ominus}SnCl_5$$

The initiator concentrations required for cationic polymerizations are smaller than those for radical polymerizations; frequently 10^{-3}–10^{-5} mol of initiator per mol monomer is sufficient to achieve a high rate of reaction. The effect of initiator concentration on the rate and average degree of polymerization depends on the monomer and a variety of other factors and does not follow a consistent pattern.

The type and amount of cocatalyst required for optimum polymerization conditions must be determined for each case; generally the amount of cocatalyst required (in mol) is much less than that of the initiator.

In polymerizations of unsaturated compounds with Lewis acids the required reaction temperatures are below room temperature, down to −100°C or even lower (see Example 3.16). On the other hand, cyclic monomers (see Sect. 3.2.3) frequently require higher temperatures.

Cationic polymerizations of unsaturated compounds are practically always carried out in solution. In radical polymerization, dilution with a solvent, under otherwise similar conditions, always results in a decrease of rate and molecular weight; but in cationic polymerization, addition of one to four parts by volume of a suitable solvent (with respect to monomer) often causes a significant increase of the molecular weight and sometimes also of the rate. The main reasons for this behavior reside in the effect of solvent polarity and the cocatalytic action of the solvent. The choice of solvent is thus extremely important. The rate of polymerization and the molecular weight generally increase with increasing polarity and relative permittivity (dielectric constant) of the solvent; some solvents can form complexes with Lewis acids that then initiate polymerization by a carbonium ion mechanism. The solvent can also interfere with the course of a cationic polymerization through chain transfer reactions. Taking into account the above-mentioned limitations, the following solvents are suitable for cationic polymerizations: toluene, cyclohexane, methylene chloride, carbon tetrachloride, dichloroethylene, trichloroethylene, chlorotoluene, nitrotoluene, and liquid sulfur dioxide.

In solution polymerizations catalyzed by Lewis acids, the polymerization frequently does not begin immediately after addition of the initiator, and there is an induction period that cannot be completely eliminated even by careful purification of the starting materials. In contrast, some cationic polymerizations proceed so quickly (flash polymerization), even after dilution, that conversion is already complete after a few minutes (e.g., isobutylene, Example 3.16).

Finally, it should be noted that cationic polymerizations are very sensitive to impurities. These can act as cocatalysts, accelerating the polymerization, or as inhibitors (e.g., tertiary amines); they can also give rise to chain transfer or chain termination and so cause a lowering of the degree of polymerization. Since these

effects can be caused by very small amounts of impurities (10^{-3} mol% or less), careful purification and drying of all materials and equipment is imperative.

Example 3.16 Cationic Polymerization of Isobutylene with Gaseous BF_3 at Low Temperatures in Bulk

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.

Monomeric isobutylene is passed from a cylinder through a drying column filled with solid potassium hydroxide pellets or *IA* zeolith and condensed in a dry cold trap. 10 ml of the condensate are collected in a dropping funnel installed directly below the trap.

A dry 100-ml standard apparatus (round-bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) is cooled to −80°C in a methanol/dry ice bath; 10 ml isobutylene and 5 g of dry ice are then added while stirring (the dry ice should be taken from the middle of a larger piece in order to be as free from water as possible). A dry 10-ml syringe pipette is filled with gaseous boron trifluoride (see Example 3.24) from a cylinder via an empty wash bottle; this is then injected into the liquid monomer. Polymerization begins immediately and gives a rubber-elastic product. The cold bath is removed after 45 min so that excess monomer slowly evaporates on warming to room temperature. The polyisobutylene obtained in this way is soluble in aliphatic, cycloaliphatic, and chlorinated hydrocarbons. The limiting viscosity number is determined in cyclohexane at 24°C and the molecular weight is derived (see Sect. 2.3.3.3). Depending on the molar mass polyisobutylene finds use as rubber and additive.

Example 3.17 Cationic Polymerization of Isobutyl Vinyl Ether with BF_3-Etherate at Low Temperatures

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.

35 ml of dry isobutyl vinyl ether are washed five times with distilled water, dried over $MgSO_4$ and distilled (bp 80°C) under nitrogen over solid NaOH into a dry receiver (see Sect. 2.2.5.3). About 80 ml of propane, taken from a cylinder, are passed through a drying column filled with solid KOH pellets and condensed in a dry cold trap.

A dry 500-ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) is heated under vacuum with a heat gun in order to remove traces of water. It is then filled with nitrogen and cooled to −70°C in an acetone/dry ice bath, the gas outlet being protected against back diffusion (see Sect. 2.2.5.2). The propane in the cold trap is transferred to the flask and 20 ml (0.15 mol) of isobutyl vinyl ether are added from the receiver. 0.30 ml (0.39 mmol) of freshly distilled BF_3-etherate are added dropwise with vigorous stirring and the mixture is held at −70°C for 30 min; another 0.3 ml of BF_3-etherate are then dropped in and stirring is continued at

this temperature for a further 90 min. During polymerization, which takes place at the surface of the initiator droplets, a very slow stream of nitrogen is passed through the apparatus. Finally the initiator is destroyed by addition of an excess of cyclohexylamine and the mixture is slowly warmed to room temperature; the propane evaporates, leaving the polymer behind in the form of small lumps. It is dried in vacuum at 50°C. Before drying, a small sample is dissolved in toluene and reprecipitated in petroleum ether; this is used for the determination of the limiting viscosity number in toluene at 20°C and also for the determination of the melting point (90°C) with the product being crystalline (see Sects. 2.3.3.2 and 2.3.5.4). Polyisobutylvinylether finds use as an adhesive.

Example 3.18 Cationic Polymerization of α-Methylstyrene 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.

Monomeric α-methylstyrene is freed from phenolic inhibitors by shaking twice with 10% sodium hydroxide. It is then washed three times with distilled water, dried over calcium hydride, and distilled before use over calcium hydride under reduced pressure of nitrogen (bp 54°C/12 Torr).

Methylene chloride is refluxed over P_2O_5 (best deposited on a solid carrier) for 1 h and then distilled into a dry receiver.

A carefully dried 100-ml three-necked flask, fitted with stirrer, thermometer, and nitrogen inlet, is evacuated and filled with nitrogen; 5.9 g (0.05 mol) of α-methylstyrene and 50 ml of methylene chloride are pipetted in and cooled to −78°C in a methanol/dry ice bath. 0.040 ml (0.075 mmol) of concentrated sulfuric acid are now added, causing polymerization to begin immediately, as shown by the slight temperature rise. After 3 h the viscous solution is added dropwise to about 500 ml of methanol in order to precipitate the polymer that is filtered off after settling and washed with methanol; a portion of the polymer is reprecipitated from a 2% toluene solution into methanol. Both samples are dried to constant weight in vacuum at 50°C; yield: about 70%. The reprecipitated sample is used to determine the softening range (150–200°C) and the limiting viscosity number in toluene at 25°C. This experiment can also be carried out with styrene; boron trifluoride or tin tetrachloride may also be used as initiators.

3.2.1.2 Anionic Polymerization with Organometallic Compounds as Initiators

There are numerous organometallic compounds that are capable of initiating the polymerization of unsaturated monomers. The following ones are of general importance: organic compounds of the alkali metals (e.g., butyllithium), organic compounds of zinc and cadmium (e.g., diethylzinc, diisobutylzinc), and organomagnesium compounds. Polymerizations with organometallic compounds as initiators are generally carried out in solution. The following solvents can be used: aliphatic and aromatic hydrocarbons (hexane, heptane, decalin, benzene, toluene), and cyclic ethers (THF, 1,4-dioxane). Polarity and solvating power of

the solvent have a major effect on the course of the polymerization and on the structure of the resulting polymer when stereospecific initiators are used (see Example 3.20).

For the polymerization of unsaturated monomers with organometallic compounds, the initiator concentration must generally be between 10^{-1} and 10^{-4}/mol of monomer; cocatalysts are usually unnecessary. Polymerization frequently occurs at temperatures below 20°C. Raising the temperature increases the rate of polymerization, but usually decreases the tacticity or tactic content when stereospecific initiators are used. An induction period is rarely observed.

All the above-mentioned initiators are very sensitive towards substances with active hydrogen. Care must therefore be taken to exclude acids, water, thiols, amines, and acetylene derivatives. Oxygen, carbon dioxide, carbon monoxide, carbonyl compounds, and alkyl halides which can react with the initiator, also interfere with the reaction. Careful purification and drying of the starting materials and apparatus is, therefore, absolutely essential, especially when dealing with "living polymers" (see Example 3.19).

Example 3.19 Anionic Polymerization of α-Methylstyrene with Sodium Naphthalene in Solution ("Living Polymerization")

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.

All operations must be carried out under especially careful exclusion of air and moisture, otherwise the experiment will fail.

Purification of the Monomer and Solvent

Monomeric α-methylstyrene is destabilized and dried as described in Example 3.18. Pure THF (previously distilled through a column) is refluxed over potassium under nitrogen for at least a day. A small amount of pure benzophenone is then added; if the THF is sufficiently pure a blue color appears, due to the formation of metal ketyl. If the blue color fails to appear, the purification with potassium must be continued. The THF is distilled from this ketyl solution under nitrogen before use.

Preparation of the Initiator Solution

First of all the parts of the apparatus (see Fig. 3.1) are carefully cleaned and assembled, evacuated under a flame, and filled with dry nitrogen three times.

Very reactive, finely divided sodium, that is easy to handle and relatively safe, can be prepared by mixing 5 g of sodium and 50 g of neutral aluminum oxide powder under nitrogen with vigorous stirring at 150–170°C. A fine powder is obtained that can easily be dosed under nitrogen using the burette shown in Fig. 3.1.

To prepare the initiator solution, 1.28 g (10 mmol) of very pure naphthalene are introduced into tube (1) through the joint (8), while passing a slow stream of nitrogen through stopcock (6). After inserting a magnetic stirrer, 100 ml of purified

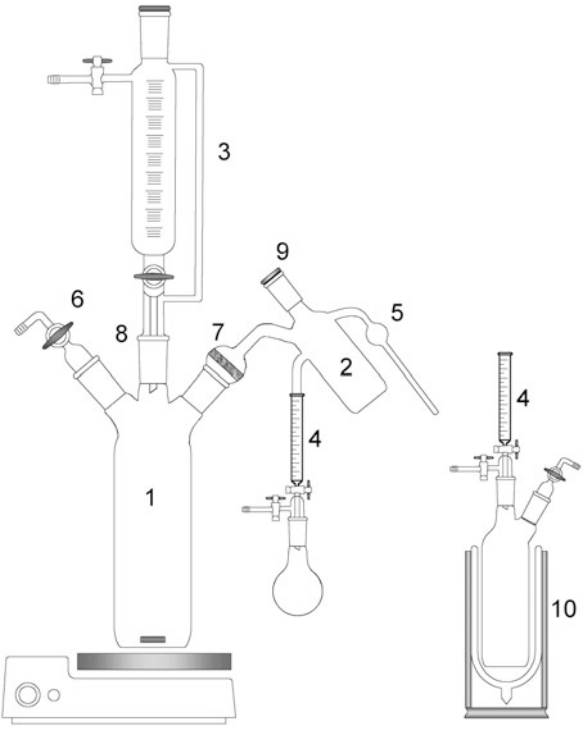


Fig. 3.1 Apparatus for the preparation of the initiator solution (explanation see text)

THF are run in through joint (8) with exclusion of air. The 10-ml burette (3) (bore of the stopcock barrel of this powder burette is 4 mm) is filled with the sodium/aluminum oxide powder and mounted on joint (8). The apparatus is now completely closed to the external atmosphere. 5 ml of the sodium powder are then run into the stirred solution in tube (1); the burette can now be removed and replaced with a ground-glass stopper. The sodium is allowed to react with the naphthalene for 30 min, while stirring is continued; the solution in tube (1) is then transferred to tube (2) by tilting the apparatus and applying a pressure of nitrogen. The aluminum oxide powder is held back by means of the sintered disc (7) (porosity 1). Capillary (5) can now be filled and sealed off after cooling to −78°C; this solution can be used to obtain the electron spin resonance spectrum and thus to demonstrate the radical character of sodium naphthalene. 10 ml of the initiator solution are run from burette (4) into a conical flask containing some distilled water.

The content of sodium naphthalene is determined by titration of the hydrolysis product with 0.1 M hydrochloric acid. The solution made by this procedure should contain about 100 mmol of initiator per liter.

Polymerization Procedure

A Schlenk tube is dried by heating under vacuum and is then charged with 50 ml of purified THF under nitrogen. The tube is attached through the joint to the burette (4) under a gentle stream of nitrogen. To remove traces of impurities that might still be present, a few drops of initiator solution are run into the vessel. As soon as the green color persists 1 mmol of initiator (about 10 ml depending of the result of the titration) is run into the reaction vessel from burette (4). The vessel is removed from the burette under nitrogen, closed with a stopper and cooled to −78°C in a Dewar vessel (10). 5.90 g (0.05 mol ≈ 6.5 ml) of α-methylstyrene are now injected in one dose from a hypodermic syringe, the solution being vigorously shaken. The solution immediately turns red as a result of the formation of the carbanions.

After 1 h at −78°C an aliquot of the solution is removed from the reaction vessel under a nitrogen stream using a syringe filled with nitrogen; this is dropped into a tenfold excess of methanol in order to precipitate the poly(α-methylstyrene). Another 5.9 g of α-methylstyrene are now added to the solution remaining in the reaction vessel, the red color of which should not be affected by the removal of the sample aliquot. After a further hour another sample is taken and a fresh batch of monomer added. The experiment is finally brought to an end after another hour, the remaining solution being dropped into methanol to precipitate the polymer. The polymers obtained during the experiment are reprecipitated from THF into methanol, filtered and dried in vacuum at 50°C.

This experiment can be carried out under identical conditions also with styrene.

Determination of the Molecular Weight of the Poly(α-Methylstyrene)s

If the polymerization of α-methylstyrene with sodium naphthalene proceeds without termination according to the above mechanism, the degree of polymerization can be represented by the following simple relation:

$$P = 2 \cdot \frac{\text{amount of monomer consumed (in mol)}}{\text{amount of initiator (in mol)}} \tag{3.17}$$

Thus, for 0.05 mol of α-methylstyrene and 0.001 mol of initiator the polymer should have a degree of polymerization of 100, corresponding to a molecular weight of 11,800 g/mol.

The limiting viscosity numbers of the samples are determined in toluene at 25°C and the molecular weights are derived. The observed and calculated values are tabulated and compared.

Example 3.20 Preparation of Isotactic and Syndiotactic Poly(Methyl Methacrylate) with Butyllithium 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.

Preparation of the Initiator Solution

0.5 g (72 mmol) of finely cut lithium and 4.64 g (50.1 mmol) of freshly distilled butyl chloride are added to 50 ml of pure toluene under nitrogen in a well-dried, nitrogen-filled, 250 ml three-necked flask, fitted with stirrer and nitrogen inlet. A reflux condenser is then attached and the reaction started by stirring and slowly heating to about 80°C. The mixture is refluxed for a further 4 h and then allowed to stand. The butyllithium solution so obtained is about 1 M. For the exact determination of the butyllithium content, 2 ml of this solution are withdrawn under nitrogen with the aid of a hypodermic syringe, added to 20 ml of pure methanol and titrated with 0.1 M hydrochloric acid using methyl red as indicator.

Polymerization Procedure

Methyl methacrylate, toluene, and 1,2-dimethoxyethane are fractionated using a column, and finally distilled over calcium hydride into a receiver under dry nitrogen (see Sect. 2.2.5.3).

Two 250 ml three-necked flasks are baked out under vacuum, fitted with stirrer, nitrogen inlet, and self-sealing closure (see Sect. 2.2.5.2), evacuated and filled several times with dry nitrogen. 100 ml of toluene are introduced to one of the flasks and 100 ml of 1,2-dimethoxyethane to the other; to both are added 0.006 mol of butyllithium (about 6 ml of 1 M solution) using a hypodermic syringe, and the solutions cooled to −78°C; 10 ml (0.1 mol) of methyl methacrylate are then injected into each. After 30 min the polymerizations are terminated by addition of 10 ml of methanol, and the polymers precipitated by dropping each solution into 1.5 l of low-boiling petroleum ether. The polymers are filtered off, the damp polymer then being dissolved in toluene and centrifuged for about 30 min at 4,000 rpm in order to separate insoluble residues (inorganic hydrolysis products and some crosslinked polymers). The polymer is reprecipitated in a 15-fold amount of petroleum ether, filtered, and dried in vacuum at 40°C. Yield in toluene as solvent: 60–70% (isotactic polymer); yield in 1,2-dimethoxyethane as solvent: 20–30% (syndiotactic polymer). The limiting viscosity numbers of the two samples are measured in acetone at 25°C (see Sect. 2.3.3.3); also the IR spectra in potassium bromide discs (see Sect. 2.3.2.2) are recorded. From the latter, the isotactic and syndiotactic content can be determined both qualitatively and quantitatively.

Example 3.21 Stereospecific Polymerization of Isoprene with Butyllithium 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.

(a) Preparation of 3,4-Polyisoprene

Monomeric isoprene is purified as described for styrene in Example 3.1; before use it is run under nitrogen through a 30-cm column packed with neutral aluminum oxide; cyclohexane and 1,2-dimethoxyethane are refluxed over sodium for 6 h and distilled off under nitrogen.

A carefully dried 250 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) fitted with a glass-sealed magnetic stirrer, is evacuated and filled with nitrogen (dried over phosphorus pentoxide) three times. 20 ml of 1,2-dimethoxyethane, 100 ml of cyclohexane, and 6.8 g (0.1 mol) of isoprene are pipetted in under a stream of nitrogen. The magnetic stirrer is switched on and 0.1 mmol of butyllithium (0.5 ml of a 0.2 M solution in toluene) is added; the solution turns lemon yellow and gradually warms up, a sign that polymerization has been triggered. The reaction may fail to commence on account of impurities present in the system, in which case more initiator solution is pipetted in until the yellow color of the reaction mixture persists. Polymerization ceases after 3 h, and the polymer is precipitated by dropping the solution into ethanol. It is filtered off and the polymer is dried in vacuum at 50°C. Yield: 90–95%. Before characterizing the polymer as described under (c), about 1 g is reprecipitated from 2% toluene solution into a tenfold excess of ethanol.

(b) Structural Investigations of Polymeric Dienes by IR Spectroscopy

The type of arrangement of the monomeric units in polymeric dienes can be determined qualitatively and quantitatively by IR spectroscopy. For this purpose thin films are prepared by dropping an approximately 2% solution in carbon disulfide (spectroscopically pure) on to suitable rock salt plates and allowing the solvent to evaporate at room temperature. The plates are placed in the spectrometer beam and the IR spectrum is recorded. The different types of chemical linkages are associated with characteristic IR bands as summarized in Table 3.9.

The spectra may first be evaluated qualitatively. The polyisoprene prepared in solution shows a pronounced band at 888 cm^{-1}, which indicates a high proportion of 3,4-linkages. For the product of bulk polymerization this band is much reduced in favor of absorptions at 1,127 and 1,315 cm^{-1}, indicating predominantly *cis*-1,4-linkage of the monomeric units in this case. The polymer made by radical polymerization in emulsion (see Example 3.12) shows the presence of all possible structural units, although the proportion of *cis*-1,4-linkages is low.

A distinction between 1,2- and 1,4-arrangement is possible through selective epoxidation of the olefinic components using *m*-chloroperbenzoic acid. Double bonds in the polymer main chain with higher electron density are more nucleophilic and therefore more reactive than pendant double bonds. In addition, a good distinction can be drawn by NMR spectroscopy.

3.2.2 Ionic Polymerization Via C = O Bonds

Polymerization by opening of C = O bonds was investigated many years ago in the case of formaldehyde. As may be expected from its polar mesomeric structure formaldehyde can polymerize both anionically and cationically:

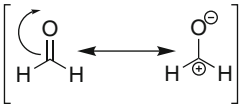
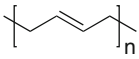
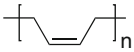
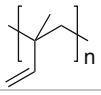
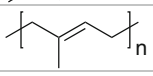
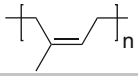
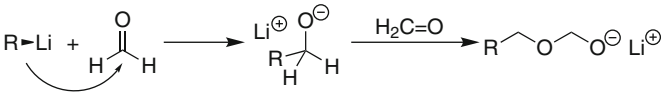


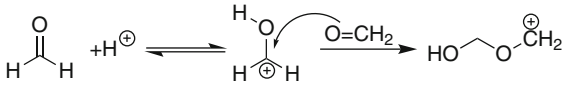
Table 3.9 Characteristic IR absorption bands for the different possible repeat units in polymeric dienes

Polybutadiene	Structure	Wavenumber in cm^{-1}
1,2		909
trans-1,4		1355/971
cis-1,4		1311/741–725
Polyisoprene		
1,2		909
3,4		888
trans-1,4		1325/1148
cis-1,4		1315/1127

Anionic polymerization can be initiated with tertiary phosphines or amines, with organometallic compounds or with alcoholates. With all of these, initiation occurs by nucleophilic attack on the positive carbonyl carbon atom:



Cationic polymerization of formaldehyde (which should be carried out under the driest possible conditions to avoid transfer reactions) can be initiated with protic acids, Lewis acids (see Sect. 3.2.1.1), or other compounds that yield cations such as acetyl perchlorate or iodine:



Polymers of formaldehyde with semiacetal end groups are thermally unstable; they decompose at temperatures as low as 150°C, splitting off monomeric formaldehyde. Upon acetylation of the hydroxy end groups, thermal stability up to 220°C is achieved; alkylations also provides stability against alkali, but not against acids

since these are capable of splitting the acetal bonds in the polymer chains (see Example 5.13).

Other carbonyl compounds, such as acetaldehyde or propionaldehyde can also be polymerized to high-molecular-weight products; however, their stability is lower than that of polyoxymethylenes with protected end groups.

The industrial synthesis of polyformaldehyde [poly(oxymethylene)] occurs by anionic polymerization of formaldehyde in suspension. For this the purification and handling of monomeric formaldehyde is of special importance since it tends to form solid paraformaldehyde. After the polymerization the semiacetal end groups have to be protected in order to avoid thermal depolymerization (Example 5.13). This is achieved by esterfication with acetic anhydride (see Example 5.7). As in the case of trioxane copolymers (see Sect. 3.2.3.2) the homopolymers of formaldehyde find application as engineering plastics.

Example 3.22 Anionic Polymerization of Formaldehyde in Solution (Precipitation Polymerization)

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: All operations with formaldehyde have to be carried out in a closed hood.

Preparation of a Solution of Monomeric Formaldehyde

The apparatus for the preparation of monomeric formaldehyde consists of a 1 l two-necked flask (A), one neck of which is closed with a loosely fitting stopper so that it can be removed quickly in the event of development of excess pressure. To the second neck is fitted a 2 m long, angled tube (diameter at least 2 cm), to the end of which is attached another 500 ml two-necked flask (B) filled with Raschig rings. The second neck of flask B serves as gas outlet and is connected to a 1 l cold trap. The outlet of the trap is fitted with a suitable device (see Sect. 2.2.5.2) to prevent the ingress of atmospheric moisture and CO_2, the latter being a powerful inhibitor of polymerization. In the first flask (A), which is not yet connected to the rest of the apparatus, are mixed 100 g of polyoxymethylene (or alternatively paraformaldehyde) and 100 g of dry paraffin oil. This is then heated in an oil bath to 130°C until about 10–15% of the polyoxymethylene has decomposed; the resulting gaseous formaldehyde is not yet passed into the apparatus, but into a washing bottle with dry ethylene glycol or glycerin; this procedure serves to remove water from the polyoxymethylene to be decomposed.

In the meantime the rest of the apparatus is flamed out under vacuum and filled with dry nitrogen; the cold trap is filled with 500 ml of sodium-dried ether and cooled to −78°C. Flask A is now attached via the 2 m glass tube. The gaseous formaldehyde generated by further pyrolysis polymerizes partially in the glass tube

and in flask B to low-molecular-weight polyoxymethylene, which contains as end groups most of the water formed during depolymerization (thus resulting in purification by prepolymerization). Care must be taken that the polymer deposited does not block the glass tube; if necessary the pyrolysis must be interrupted so that the tube can be cleaned. Sticking of the ground joints can be prevented by generous greasing. The pyrolysis should be carried out rather quickly (within about 1 h), since otherwise too much monomer is lost by prepolymerization; an oil bath temperature up to 200°C is required. The resulting ether solution contains about 70 g of formaldehyde (about 4 M). Another method of preparing very pure monomeric formaldehyde is from 1,3,5-trioxane, which can be decomposed in the gas phase at 220°C on a supported phosphoric acid catalyst.

Polymerization Procedure

150 ml of the ethereal formaldehyde solution are placed in a previously flamed 250 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) cooled to −78°C, taking care to exclude atmospheric moisture. (For larger quantities care must be taken to make adequate provision for the removal of the heat of polymerization.) The flask is fitted with a self-sealing closure and a pressure equalizer protected with a soda-lime tube. 1 mg of pyridine, dissolved in 5 ml of dry ether, is used as initiator; this is carefully injected into the formaldehyde solution (cooled to −78°C) over a period of 15 min, with vigorous stirring. After 1 h at −78°C the conversion reaches more than 90%. Should the rate of polymerization be lower because of impurities, the amount of initiator can be raised. The precipitated polyoxymethylene is filtered off, washed with ether and dried in vacuum at room temperature; it melts between 176°C and 178°C. The limiting viscosity number is determined on a 1% solution in DMF at 140°C ($\eta_{sp}/c \approx 0.08$ l/g, corresponding to an average molecular weight of 80,000). The thermal stability can be tested before and after blocking the hydroxy end groups (see Examples 5.7 and 5.13).

Polyoxymethylene, obtained by the polymerization either of formaldehyde or of 1,3,5-trioxane, is a highly crystalline product which is insoluble in all solvents at room temperature with the exception of hexafluoroacetone hydrate; at higher temperatures it dissolves in some polar solvents (e.g., at 130°C in DMF or DMSO). If the unstable semi-acetal end groups are blocked (see Example 5.7) polyoxymethylene can be processed without decomposition as a thermoplastic at elevated temperatures in the presence of stabilizers.

3.2.3 Ring-Opening Polymerization

Many heterocyclic compounds can be polymerized by ring opening under certain conditions with ionic initiators, to produce linear macromolecules. Amongst these are cyclic ethers, cyclic sulfides, cyclic acetals, cyclic esters (lactones), cyclic

amides (lactams), and cyclic amines. Ring-opening polymerizations are carried out under similar conditions, and frequently with similar initiators to those used for ionic polymerizations of unsaturated monomers (see Sect. 3.2.1); they are likewise sensitive to impurities. In some cases one succeeds in the ring-opening polymerization of cyclic olefins with formation of straight-chain unsaturated polymers (metathesis polymerization, see Example 3.33).

3.2.3.1 Ring-Opening Polymerization of Cyclic Ethers

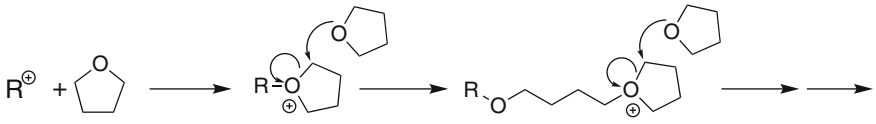
The ring-opening polymerization of cyclic ethers having 3-, 4-, and 5-membered rings (e.g., epoxides, oxetanes, THF) yields polymeric ethers. Six-membered rings (1,4-dioxane) are not capable of polymerization.

Epoxides such as epoxyethane (ethylene oxide) can be polymerized cationically (e.g., with Lewis acids) and anionically (e.g., with alcoholates or organometallic compounds).

Polymers with extremely high molecular weights result from the polymerization of ethylene oxide initiated by the carbonates of the alkaline earth metals, e.g., strontium carbonate, which must, however, be very pure. Poly(ethylene oxides) having molecular weights up to about 600 are viscous liquids; above that they are wax-like or solid, crystalline products that are readily soluble not only in water but also in organic solvents such as benzene or chloroform. Polymers of propylene oxide and generally substituted ethylene oxides can be produced in both atactic amorphous and isotactic crystalline forms. Optically active poly(propylene oxide)s can be obtained from propylene oxide.

Polymerization of four-membered cyclic ethers (oxetanes) is also brought about by cationic initiators (e.g., Lewis acids) and by anionic initiators (e.g., organometallic compounds). The polymer of 3,3-bis(chloromethyl)oxetane is distinguished by its very high softening point and by its unusual chemical stability.

THF can be polymerized only with cationic initiators, for example, boron trifluoride or antimony pentachloride. The initial step consists of the formation of a cyclic oxonium ion; one of two activated methylene groups in the a-position to the oxonium ion is then attacked by a monomer molecule in an S_N2-reaction, resulting in the opening of the ring. Further chain growth proceeds again via tertiary oxonium ions and not, as formerly assumed, via free carbonium ions:



Deviations from this mechanism are observed when so-called superacids (e.g., fluorosulfonic acid, FSO_3H) are used as initiators (macroion/macroester equilibrium).

Poly(oxytetramethylene), poly(tetrahydrofuran), may assume the state of a viscous oil, a wax, or a crystalline solid (melting range around 55°C), depending on the molecular weight. Poly(tetrahydrofuran) telechelics prepared with two OH end groups and in molar masses of 500–4,000 g/mol are used widely as soft block in segmented polyurethanes and polyesters (see Sect. 3.4.2.1).

Example 3.23 Polymerization of THF with Antimony Pentachloride in Bulk

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.

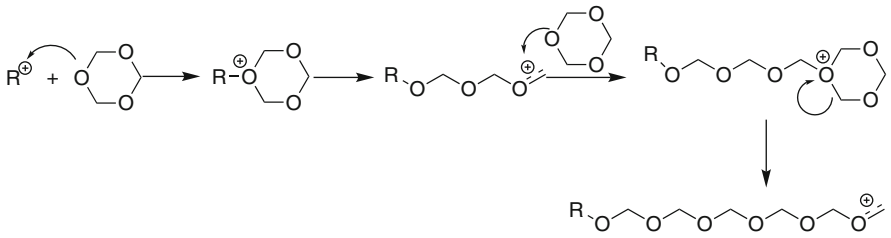
THF is purified as described in Example 3.19 and distilled shortly before use into a dry receiver (see Sect. 2.2.5.3).

A dry 250 ml round-bottomed flask, fitted with an adapter (see Sect. 2.2.5.4) is flamed under vacuum and filled with nitrogen. 15 g (0.21 mol) of THF are then added by connecting the receiver to the adapter and applying a slight vacuum to the flask while admitting nitrogen to the receiver through a side arm and stopcock. The flask is cooled to −30°C and 0.6 g (2.0 mmol) of freshly distilled antimony pentachloride are added under nitrogen. The flask is now detached from the adapter under a slight positive pressure of nitrogen and immediately closed with a ground glass stopper, secured with springs. The mixture is swirled around and allowed to stand at room temperature for 24 h, during which time the mixture becomes viscous. It is then treated with 2 ml of water and 150 ml of THF, and refluxed for about 30 min until a homogeneous solution is produced. The still viscous solution is diluted with a further 100 ml of THF and filtered to remove the insoluble portion (hydrolysis product of the initiator). The polymer is precipitated by dropping the solution into 3 l of water with vigorous stirring; it is filtered off and dried in vacuum at 20°C. The polymer obtained in the above preparation is a somewhat sticky solid material with a melting range around 40°C. It is soluble in toluene, carbon tetrachloride, chlorobenzene, THF, 1,4-dioxane, and acetic acid; it is insoluble in water, methanol, and acetone. The limiting viscosity number is determined in toluene at 20°C (see Sect. 2.3.3.3).

3.2.3.2 Ring-Opening Polymerization of Cyclic Acetals

Like THF, cyclic acetals (e.g., 1,3-dioxolane and 1,3,5-trioxane) are polymerizable only with cationic initiators. The ring-opening polymerization of 1,3,5-trioxane (cyclic trimer of formaldehyde) leads to polyoxymethylenes (see Example 3.24), which have the same chain structure as polyformaldehyde (see Example 3.22). They are thermally unstable unless the semiacetal hydroxy end groups have been protected in a suitable way (see Example 5.7). Like the cyclic ethers, the polymerization of 1,3,5-trioxane proceeds via the addition of an initiator cation to a ring oxygen atom, with the formation of an oxonium ion which is transformed to

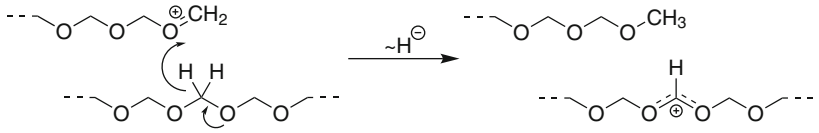
a carbenium ion by ring opening. The chain propagates by the addition of further 1,3,5-trioxane molecules:



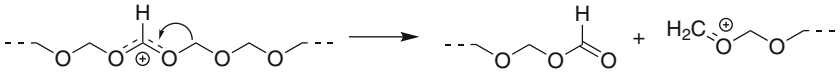
The solubility of polyoxymethylene is very poor so that the ring-opening polymerization of 1,3,5-trioxane proceeds heterogeneously both in bulk (melt) and in solution. 1,3,5-Trioxane can also be readily polymerized in the solid state; this polymerization can be initiated both by high-energy radiation and by cationic initiators (see Example 3.24).

Generally, the molecular weight and the molecular-weight distribution are determined by two side reactions. Moreover, the end groups and in case of copolymers, their sequence length distribution are determined by the following two side reactions:

Hydride transfer or hydride migration is initiated by the electrophilic attack of the poly(oxymethylene) cation from the methylene bridge of its own or of a neighboring macromolecule. A hydride ion is thus split off, and a methoxy end group is formed.

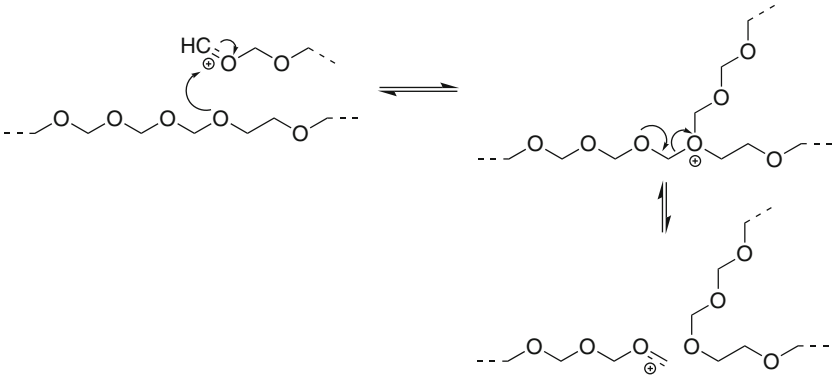


The newly created cation is stabilized through conjugation with the free electron pairs of the neighboring O atoms and is broken into a chain with the formate end group and another poly(oxymethylene) cation.



Both end groups can be determined quantitatively. A second side reaction is the transacetalization. Here a poly(oxymethylene) cation attacks an oxygen of a poly (oxymethylene) chain with formation of an oxonium ion that decomposes. Through continued cleavage and recombination of poly(oxymethylene) chains one obtains polymers which are chemically and molecularly largely homogeneous. For the case

of a trioxane/ethylene oxide copolymer the following reaction scheme can be formulated:



The transacetalization also proceeds intramolecularly. It then leads to the formation of cyclic acetals which participate as monomers in the propagation reaction.

The industrial production of copolymers of trioxane with ethylene oxide or dioxolane (1–5%) is conducted as a bulk polymerization in special equipment. The incorporation of small amounts of C–C bonds into the C–O chain has a remarkable effect on the thermal and chemical stability. In homopolymers the thermal decomposition starts at the semiacetal end groups ("unzipping") and leads to a complete destruction of the polymer chain, whereas this reaction stops in copolymers already at the first C–C bond. A thermally stable OH end group is thus formed which, in addition, contributes to a much better alkali resistance compared to ester group-terminated homopolymers (see Examples 3.40 and 5.13).

Trioxane copolymers (often called polyacetals) are used as engineering plastics in automotive, machinery, and electric industry.

Example 3.24 Polymerization of Trioxane with BF_3-Etherate as Initiator

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 the polymerizations have to be carried out in a closed hood.

(a) Polymerization in the Melt

150 g of commercial 1,3,5-trioxane are refluxed (bp 115°C) with 9 g of sodium or potassium under nitrogen for 48 h, using an air condenser with suitable protection against ingress of atmospheric moisture. 20 g of the purified monomer are distilled into a 50 ml flask that has previously been flamed in vacuum. The flask contains a glass-sealed magnetic stirrer and is equipped with a self-sealing closure (see Sect. 2.2.5.2). The contents are heated to 70°C and 0.05 ml (0.4 mmol) of

BF_3-etherate ($d_{20} = 1.125$ g/ml) are injected as an approximately 10% solution in nitrobenzene. Special care must be taken that the molten 1,3,5-trioxane is mixed thoroughly with the initiator and a homogeneous mixture is obtained as quickly as possible. Immediately after the addition of initiator to the molten monomer the polyoxymethylene begins to precipitate; after only 10 s the whole reaction mixture has solidified. The polymerization is terminated with acetone and the polymer filtered off on a glass sinter after thorough mixing and, if necessary grinding. The polymer is boiled twice with acetone for 20 min, filtered, and dried in vacuum at room temperature. Yield: about 50%; melting range 177–180°C. The viscosity number is determined for a 1% solution in DMF at 140°C ($\eta_{sp}/c \approx 0.06$ l/g, corresponding to an average molecular weight of 60,000). The thermal degradation can also be studied before and after blocking the hydroxy end groups (see Examples 5.7 and 5.13).

(b) Polymerization in the Solid State

Gaseous boron trifluoride is required for this experiment. Suitable gas cylinders are available commercially. If necessary boron trifluoride can be prepared as follows: 15 g of powdered sodium tetrafluoroborate are mixed in a 100-ml flask with 2.5 g of boron trioxide and 15 ml of concentrated sulfuric acid. The flask is fitted with a gas delivery tube, to which is attached a piece of PVC tubing, pinched tight at the open end having a slit in the side to allow pressure equalization. The gaseous BF_3 is generated by heating to 160–170°C and can be withdrawn by means of a hypodermic syringe through the PVC tubing.

Commercial 1,3,5-trioxane is purified by sublimation under normal pressure at 50°C, followed by recrystallization of 60 g from 500 ml of dry cyclohexane (yield: about 36 g). Especially well-formed crystalline needles are obtained which, after filtering off the solvent, can be used without further drying.

20 g of 1,3,5-trioxane are placed in a 300 ml conical flask that is then flushed with nitrogen and sealed with a polyethylene film. 10 ml of BF_3 gas are injected through the film.

After a short time the trioxane crystals which initially have a glassy appearance, become cloudy. After 1 min the polymerization has advanced so far that a sample is nearly totally insoluble in methanol. The conical flask is kept for another hour at 80°C to allow the polymerization to die away. The product can be worked up and treated further as described under (a). Yield: >50%.

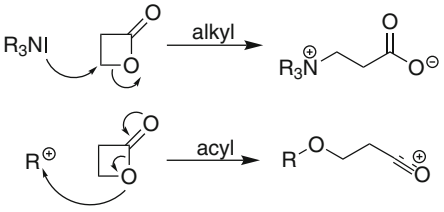
(c) Polymerization in Solution (Precipitation Polymerization)

90 g of 1,3,5-trioxane, purified as in (a), are distilled into a 500 ml flask (that has previously been flamed under vacuum) containing 200 ml of 1,2-dichloroethane that has been dried over P_2O_5; atmospheric moisture must be excluded. The flask is closed with a self-sealing closure (see Sect. 2.2.5.2). 0.06 ml (0.5 mmol) of BF_3-etherate dissolved in 7 ml of 1,2-dichloroethane are now injected while shaking the flask, which is then warmed to 45°C. After an induction period of about 1 min, solid poly (oxymethylene) begins to separate, until finally the contents of the flask are completely solidified. After 1 h the product is well ground with 200 ml of acetone,

filtered, boiled well with acetone as under (a) and dried. In order to remove occluded initiator residues the polymer is boiled with 1 l of ether containing 2 wt% of tributylamine; it is finally filtered and dried in vacuum at room temperature. Yield: 90–95%; melting range: 176–178°C. The limiting viscosity is determined in DMF at 140°C (molecular weight ~60,000). The thermal stability can also be measured; see under (a). The amount of initiator can be reduced dramatically if the trioxane is purified very carefully. For this, trioxane is refluxed over sodium/potassium alloy for 4 days under a nitrogen atmosphere and distilled into the polymerization flask.

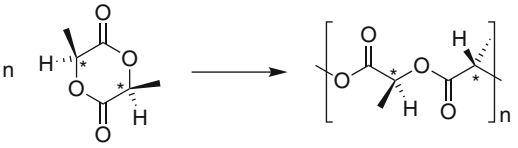
3.2.3.3 Ring-Opening Polymerization of Cyclic Esters (Lactones)

Cyclic esters of ω-hydroxycarboxylic acids can be polymerized by ring-opening to give linear aliphatic polyesters. According to the type of initiator and monomer the polymerization occurs either by alkyl or by acyl cleavage:



The polymerizability depends on the ring size and on the number, size, and position of the substituents.

The ring-opening polymerization of dilactide (dimeric cyclic ester of lactic acid) allows the preparation of high molecular weight, optically active polyesters of lactic acid. The configuration of the asymmetric carbon atoms of the monomer is retained when the polymerization is initiated with $SnCl_4$ or Et_2Zn, for example:



Example 3.25a Ring-Opening Polymerization of Dilactide with Cationic Initiators 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.

NOTE: L-Lactide is hygroscopic and should be stored over P_4O_{10}.

5 g of L-lactide, 50 ml of pure toluene, and a magnetic stirrer are placed in a reaction vessel that has been flamed under vacuum and flushed with nitrogen. The vessel is closed with a pressure-tight rubber cap and heated to 110°C in an oil bath. 0.5 ml of initiator solution (3.32 g of $SnCl_4$/100 ml of toluene) is then injected

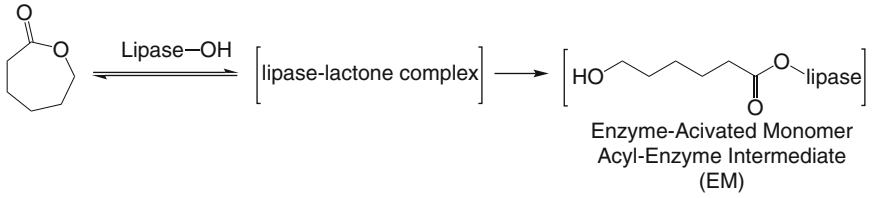
through the rubber cap with a hypodermic syringe. After about 3 h the viscous solution is cooled and added dropwise to 300 ml of vigorously stirred methanol. The filtered polymer is dissolved in 50 ml of 1,4-dioxane and reprecipitated in methanol. After drying in vacuum at about 70°C one obtains 4.2 g (yield 74%) of a white polymer with a crystalline melting point (DTA) of 153°C. It is soluble in 1,4-dioxane, chloroform, and acetonitrile, and insoluble in methanol, ether, and hexane. The solution viscosity (see Sect. 2.3.3.3) is determined in 1,4-dioxane at 25°C using an Ostwald viscometer (capillary diameter = 0.4 mm). The polymer can be characterized by IR spectroscopy and by ORD and CD measurements.

Enzyme Calaysed Ring-Opening Polymerization of ε-Caprolacton

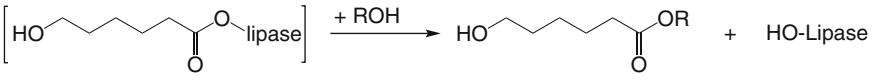
Lipase-catalysed ring opening polymerization was first disolved in 1993 for ε-caprolacton (ε-CL) and δ-valerolactone (δ-VL) by two independent groups. Lipase (triacylglycerol acylhydrolase, EC Sect. 3.1.1.3) is an enzyme that catalyzes both the hydrolysis of a fatty acid lycerol ester in vivo with bond-cleaving and the polymerization reaction to give polyester in vitro with bond-forming, when the lipase catalyst an substrate monomer are appropooriately combined for the reaction.

Among the various lactones, ε-CL is the most extensively studied monomer. The ROP was induced by many lipases from different origin. *Candida antarctica* [lipase CA or CA lipase B (CALB) immobilized on an acrylic resin, produced commercially as Novozym 435] was found to be the most effective lipase for the ROP of ε-CL.

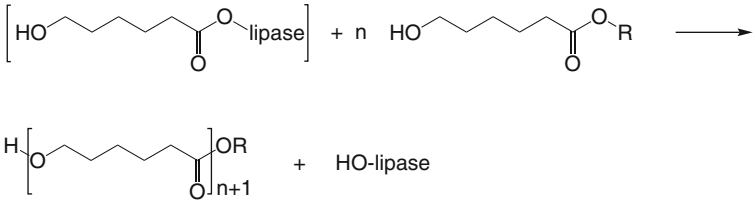
Monomer activation



Initiation: nucleophilic attack of water or alcohol



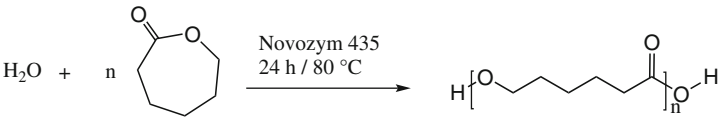
Propagation



The reaction can be either performed in solvent or in bulk. By considering the principal reaction course involving an acyl-enzyme intermediate, the postulated mechanism for the lipase-catalyzed ROP of ε-CL is as follows. The polymerization via an "activated monomer mechanism". The reaction of lactone with lipase catalyst involving an enzyme-lipase complex and its ring-opening to give an acyl-enzyme intermediate (EM) is the key step of this reaction. In the initiation stage, is a nucleophilic attack of a nucleophile, such as water or an alkohol, which is present in the reaction mixture, on the acyl carbon of the intermediate to produce ω-hydroxycaroxylic acid (n = 1). It is followed by the propagation, in which EM is nucleophilically attacked by the terminal hydroxyl group of a propagation chain end to produce a one-monomer-unit elongated polymer chain.

Example 3.25b Novozym 435 Catalyzed Ring-Opening Polymerization of ε-Caprolactone in Bulk

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.



ε-Caprolactone was purchased from Aldrich, dried over calcium hydride, distilled under reduced pressure, stored over 4 Å molecular sieves and under an argon atmosphere.

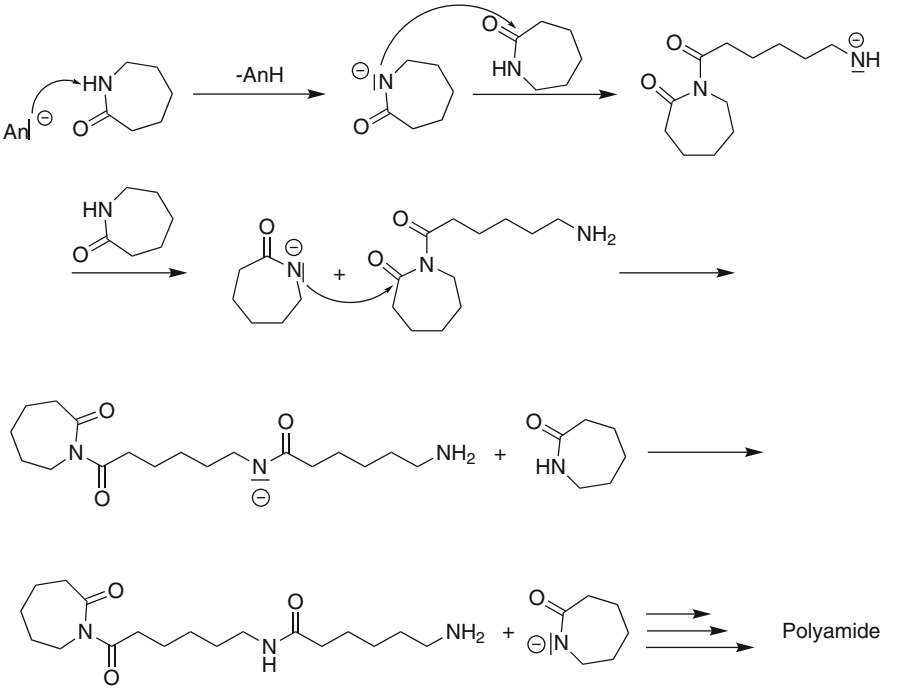
10.0 g (87.6 mmol) of ε-CL and 1.0 g (10 wt%) of Novozym 435 are added to a 25 ml round-bottom flask. The suspension is heated to 80°C under stirring and refluxing for 24 h. The reaction mixture slowly becomes viscous. The suspension is diluted with 5 ml chloroform. The lipase is removed from the solution by filtrating. The filtrate is poured into 250 ml of cold methanol. The precipitated polymer is isolated by filtration and dried under vacuum. (Yield: 90–95%).

3.2.3.4 Ring-Opening Polymerization of Cyclic Amides (Lactams)

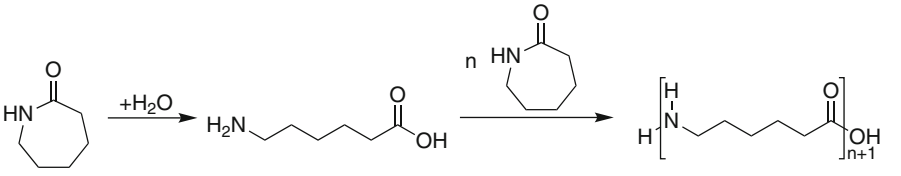
The ring-opening polymerization of cyclic amides gives linear polyamides. This very important reaction can be initiated ionically. There is a pronounced dependence of the polymerizability of lactams on the ring size and on the number and position of the substituents. The five-membered lactam (γ-butyrolactam) can be polymerized anionically at low temperature; the polyamide depolymerizes again to the monomer in the presence of the initiator at 60–80°C. The corresponding 6-membered ring, δ-valerolactam, is likewise polymerizable. The seven-membered ring, ε-caprolactam, can be polymerized both cationically and anionically to high-molecular-weight polyamides.

Polymers made from ε-caprolactam in the presence of anionic catalysts at high temperatures have average molecular weights that are initially high but decrease on

prolonged heating of the molten reaction mixture, finally attaining an equilibrium value. This change of molecular-weight distribution is caused by a transamidation reaction of the growing chains with the dead polyamide molecules. The polymerization of ε-caprolactam with anionic initiators can be considered as a true addition polymerization reaction:



whereas the reaction initiated by catalytic amounts of water, e-aminocaproic acid, or benzoic acid as applied industrially, may be conceived as a stepwise addition polymerization involving migration of hydrogen atoms. The reaction starts with the addition of water or acid to ε-caprolactam; the resulting NH_2 or NH_3^+ end groups then add further lactam:



The molecular weight increases with increasing conversion. Regulation of the molecular weight can be achieved by adding small amounts of substances (e.g., benzoic acid) that can react with the polyamide chains by transamidation. Because

of the transamidation reaction and hydrolysis of amide bonds, an equilibrium molecular-weight distribution is finally attained (see Sect. 4.1).

Polymers prepared at 250–270°C contain an equilibrium concentration of up to 10% of cyclic monomer and partly cyclic higher oligomers: after cooling, the monomer and oligomers can be recovered by extraction with water or lower alcohols. The oligomers can be separated and identified chromatographically (see Example 4.9).

Aliphatic polyamides of ε-caprolactam (Nylon-6) possess great importance as fibers and plastics.

Example 3.26 Bulk Polymerization of ε-Caprolactam with Anionic Initiators (Flash Polymerization)

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.

ε-Caprolactam is recrystallized twice from cyclohexane and dried in vacuum at room temperature over P_4O_{10} for 48 h; mp 68–69°C.

(a) Preparation of N-Acetylcaprolactam

A mixture of 67.8 g (0.6 mol) ε-caprolactam and 67 g (0.665 mol) of acetic anhydride is heated for 4 h in a 250-ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath). Finally, most of the excess anhydride, as well as the acetic acid, is distilled off and the remainder submitted to fractional distillation at low pressure, using an oil pump; bp 134–136°C/26–27 Torr;

$$n_D^{25} = 1.4885;\ \text{yield} : 77.5\text{g}\ (83.5\%)$$

(b) Polymerization Procedure

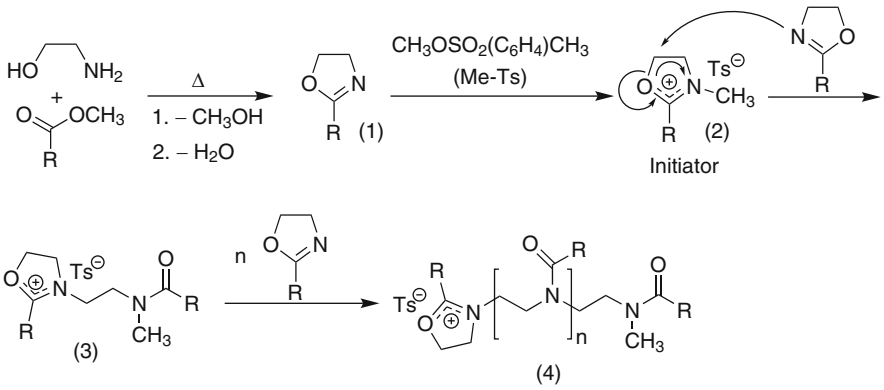
25 g (0.22 mol) of ε-caprolactam and 0.6 g (0.025 mol) of sodium hydride are placed in a flask, which is then evacuated and filled with nitrogen several times. The sample is melted to allow the sodium hydride to react. When the evolution of hydrogen has ceased, 0.33 g (0.002 mol) of *N*-acetylcaprolactam are added, the flask is well shaken, and then heated in an oil bath to 140°C. The contents rapidly solidify and after 30 min can be cooled and ground up.

The limiting viscosity number is determined in *m*-cresol or concentrated sulfuric acid. The polyamide-6 (Nylon-6) so obtained has a crystallite melting point around 216°C. It still contains monomer and low-molecular-weight cyclic oligomers which can be removed by extraction with water or lower alcohols. These oligomers can be separated and identified chromatographically (see Example 4.9).

3.2.3.5 Ring-Opening Polymerization of Oxazolines

The reaction of a nucleophilic monomer with an electrophilic monomer can, under suitable circumstances, lead to the formation of macromolecules that carry at least one charge at a chain end. Although the reaction has been known for a long time, it

has gained importance for technical applications only recently. On the basis of the following scheme, the reaction mechanism can be explained by the homopolymerization of an oxazoline using methyl tosylate as an alkylating initiator.



First of all a 2-substituted oxazoline (1) is formed by cyclocondensation of a carboxylic acid ester with 2-aminoethanol and a small amount of (1) is converted with an alkylating agent (e.g., methyl tosylate) to the activated, ionic form (2).

This *N*-alkylated heterocycle (2) acts as the actual initiator because it is attacked rapidly under ring-opening by an oxazoline molecule, present in excess. The newly formed dimer (3) contains an ionic ring function, which is subjected to the same attack as the initiator molecule. The molecular weight of the polymers is controlled by the amount of the alkylating agent. Other suitable initiators for the polymerization of oxazolines are Lewis acids, protic acids, and alkyl chloroformates.

In principle, one can obtain an unbranched polyethyleneimine by saponifying the amide groups that are located on the polymer (Example 5.4). It is important to note that the ring-opening polymerization of aziridine does not yield linear polyethyleneimines but rather highly branched polymer structures.

Example 3.27 Synthesis of a Linear, N*-Acylated Polyethyleneimine Through Cationic Polymerization of 2-Methyl-2-Oxazoline in Bulk*

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 100 ml three-necked flask with stirrer and thermometer 1 mol% of *p*-toluenesulfonic acid methyl ester (methyl tosylate) are added to 3 g (0.03 mol) of anhydrous 2-methyl-2-oxazoline. The reaction mixture is stirred under nitrogen at 100–120°C. The bulk polymerization sets in immediately. After 30 min. the viscous polymer melt is poured in a dish where it solidifies within minutes. After cooling to room temperature about 2 g are dissolved in 20 ml ethanol and precipitated in 500 ml THF. The collected precipitate is dried under vacuum.

The polymer is fully amorphous with a glass transition temperature of 68°C. It is soluble in water, methanol, ethanol, propanol, $CHCl_3$, and DMF. Characterization

can be carried out by IR-spectroscopy ($\nu_{C=O}$ = 1,633 cm^{-1}) and by NMR spectroscopy ($CDCl_3$, δ = 3.47 ppm, –N–CH_2–CH_2–, 2.13 ppm, CH_3).

The polymer can readily be hydrolized yielding a linear polyethyleneimine (see Example 5.4).

3.3 Metal-Catalyzed Polymerization

The initiation of polymerizations by metal-containing catalysts broadens the synthetic possibilities significantly. In many cases it is the only useful method to polymerize certain kinds of monomers or to polymerize them in a stereospecific way. Examples for metal-containing catalysts are chromium oxide-containing catalysts (Phillips-Catalysts) for ethylene polymerization, metal organic coordination catalysts (Ziegler-Natta catalysts) for the polymerization of ethylene, α-olefins and dienes (see Sect. 3.3.1), palladium catalysts and the metallocene catalysts (see Sect. 3.3.2) that initiate not only the polymerization of (cyclo)olefins and dienes but also of some polar monomers. More recently, progress in catalytic developments led to a number of new materials by Ring-Opening Metathesis Polymerization (ROMP) (see Sect. 3.3.3).

In all these cases and in contrast to starting a polymerization by initiators, there are no fragments of the starting molecule incorporated in the polymer chain. Consequently, the mechanisms are different to those of radical, anionic, or cationic polymerizations.

3.3.1 Polymerization with Ziegler-Natta-Catalysts

In 1953 K. Ziegler and coworkers discovered a class of heterogeneous catalysts that allowed ethylene to be polymerized at low pressures and low temperatures (low-pressure polyethylene = high-density polyethylene = PEHD).

These catalysts are made by mixing organometallic compounds of transition group elements IV–VIII with metal alkyls or metal hydrides of the groups I–III of the periodic system – for that reason they often are called metal organic mixed catalysts. Very efficient are combinations of the transition group compounds $TiCl_4$, $TiCl_3$, or $VOCl_3$ with alkylaluminum or alkylaluminum halide reagents, for example, $Al(alkyl)_3$, $Al(alkyl)_2halogen$, and $Al_2(alkyl)_3halogen_3$.

The transition group compound (catalyst) and the metal alkyl compound (activator) form an organometallic complex through alkylation of the transition metal by the activator which is the active center of polymerization (Cat). With these catalysts not only can ethylene be polymerized but also α-olefins (propylene, 1-butylene, styrene) and dienes. In these cases the polymerization can be regio- and stereoselective so that tactic polymers are obtained. The possibilities of combination between catalyst and activator are limited because the catalytic systems are specific to a certain substrate. This means that a given combination is mostly useful only for a certain monomer. Thus conjugated dienes can be polymerized by catalyst systems

containing cobalt or nickel, whereas those systems do not work with ethylene and α-olefins. The latter can be polymerized with titanium-, vanadium-, or chromium-containing catalysts. A further restriction for the industrial process can be the activity of the catalyst and the stereoselectivity; in many cases both are not high enough. So-called carrier catalysts led to a considerable advance. They are obtained by precipitation of a transition metal compound onto an inert ($MgCl_2$) or reactive [$Mg(OH)_2$] solid. The polymerization activities achieved are very high (1,000 kg polyethylene per g titanium, corresponding to catalyst concentrations of a few ppm) so that the removal of the catalyst residue is not necessary, thus making the manufacturing process much easier (see Example 3.28). Further progress has been obtained by utilization of metallocenes (see Sect. 3.3.2).

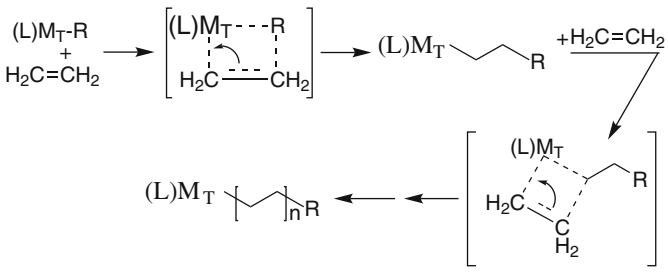
By adding suitable electron donors (for example, ether or amines) the stereoselectivity of the propylene polymerization can be increased. Finally, a particular class of organometallic - catalysts should be mentioned thatcan bring about the ring-opening metathesis polymerization (ROMP) of cycloolefins to linear unsaturated polymers, e.g., of cyclopentene to poly(1-pentenylene) (see Example 3.33). Originally, tungsten compounds (e.g., $WCl_6/C_2H_5OH/C_2H_5AlCl_2$) have been applied for ROMP which are now largely substituted by the more effective Grubbs and Schrock catalysts.

The polymerization mechanism with Ziegler-Natta catalysts can be explained as follows:

The primary step consists in the formation of a π-complex between ethylene and the catalytic active center (Cat) that was already alkylated by the activator (R-M). This complexed monomer is then inserted into the metal-carbon bond with chain extension of two C-atoms. The propagation reaction consists of consecutive insertion steps. Termination occurs by β-elimination or by reaction with hydrogen. In both cases the active center Cat is maintained.

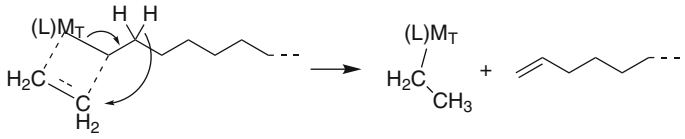
Formation of the catalyst (Cat):

Propagation:

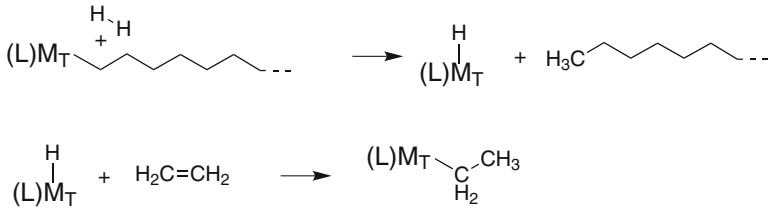


Termination:

(a) By β-elimination:



(b) By reaction with hydrogen:



All factors that influence the stability of the transition metal-carbon bond (M_T-R) and/or the stability of the transition metal-ethylene bond (M_T-ethylene) are liable to affect the course of the reaction. Such factors are:

- Type and valence state of the transition metals M_T
- Type and number of ligands L at the transition metal M_T
- Type of the metal alkyl species (activator) R-M
- Catalyst morphology (crystallinity, porosity, external and internal surface).

The polymerization process consists of a series of consecutive and concurrent steps:

- Transfer of monomer and the molecular weight regulator, H_2, from the gas phase to the suspension medium,
- Diffusion of these components to the active center Cat; with increasing conversion, the diffusion will be affected by the increasing amount of partially crystalline polymer phase,
- Adsorption or complex formation of the monomer with the active center Cat,
- Occurrence of chemical reactions,
- Formation of a steadily growing partially crystalline polymer phase around the active center Cat. This can result in the catalyst particle breaking off from the polymer (disintegration), whereby under certain circumstances a new active center Cat can be formed; the diffusion of the reactants (monomer, H_2) can also be hindered by the growing polymer phase.

The polymerization of ethylene is carried out as follows with exclusion of air and water: the organometallic catalyst and the activator are suspended in an aliphatic hydrocarbon, the active centers Cat thereby being formed. Ethylene is passed in and the polymerization allowed to proceed at or slightly above atmospheric pressure, at

a temperature below 100°C. The polyethylene precipitates as a swollen powder. As soon as the mixture has developed into a thick, dark-colored slurry, the reaction is terminated by destroying the catalyst (e.g., with butanol). The polymer is freed from most of the disperse medium by filtration, the remainder being removed by steam distillation. The damp polyethylene is finally dried.

Besides ethylene, higher olefins (propylene, 1-butylene), dienes, and a number of other monomers can be polymerized with organometallic mixed catalysts; the polymerization frequently proceeds stereospecifically, leading to tactic polymers (see Examples 3.29–3.31).

Example 3.28 Polymerization of Ethylene on a Supported Catalyst in Organic Suspension

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: The greatest possible care must be exercised when working with organoaluminum compounds since they ignite very easily on contact with air and water. All operations must, therefore, be carried out with the complete exclusion of air and moisture and pipettes must be flushed with nitrogen. Moreover, these substances cause wounds that are slow to heal, so that the wearing of safety goggles is mandatory and all contact with the skin must be avoided. The pipettes are cleaned as follows: After all the $AlEt_3$ has been run out, the pipette is filled with petroleum ether and allowed to drain again. It is then washed with acetone, dried and later cleaned with a solution of dichromate in concentrated sulfuric acid.

The polymerization apparatus (see Fig. 3.2) consists of a 1 l three-necked flask, fitted with stirrer, thermometer, gas inlet with tap, and gas outlet. On the inlet side the gas stream passes through three wash bottles: one as a safety bottle (A), one for the purification of ethylene, filled with 30 ml of petroleum ether (bp 100–140°C) and 5 ml of diethylaluminum chloride (B), and one filled with molecular sieves 5 Å (C). The last of these dries the ethylene further and also serves to trap aluminum hydroxide carried over from B. On the outlet side there are two wash bottles: the first is a safety bottle (D), and the second, (E), is filled with 50 ml of dry bis (2-hydroxyethyl) ether (diglycol), and isolates the apparatus from the external atmosphere.

(a) Preparation of the Supported Catalyst

1.1 g (10 mmol) of magnesium ethoxide (carrier) are suspended in 5 ml toluene. 20 ml of a 1 M $TiCl_4$ solution in toluene are added. The suspension is refluxed for 15 h. The precipitate is washed by decanting and stirring six times with 15 ml of toluene. The toluene above the solid should be free of titanium compounds. The volume of the suspension is filled up to 25 ml. The content of titanium of the suspension can be determined by colorimetric measurements with H_2O_2; 10 ml suspension contains approx. 2 mmol titanium compound.

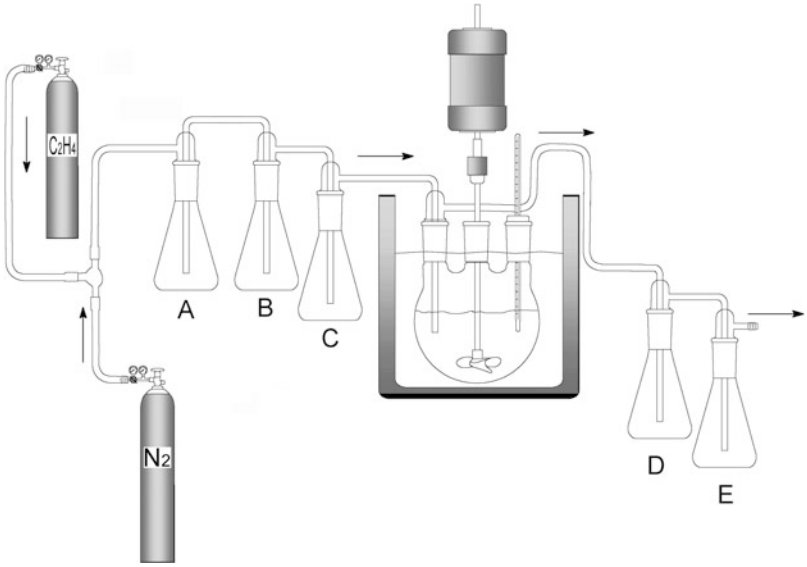


Fig. 3.2 Setup for the suspension polymerization of olefins in anhydrous medium

(b) Polymerization of Ethylene

Following the experimental arrangement in Fig. 3.2, the reaction vessel is a baked-out 500 ml four-necked flask with stirrer, gas inlet tube, and a condenser. A washing bottle with concentrated sulfuric acid, a washing bottle with KOH chips, and a washing bottle with toluene are attached to the gas inlet tube, so that the gas flow can pass through these bottles in the mentioned order. The condenser is attached to an empty washing bottle and to one filled with paraffin. Then 200 ml of absolutely dry toluene are placed into the flask under a nitrogen flow. The gas inlet tube has to reach into the liquid. Then, a solution of 0.5 g (3.1 mmol) triethylaluminum in 10 ml toluene and 2 ml of the supported catalyst suspension are added. The solution of the triethylaluminum is not allowed to come into contact with air and moisture. Now, the reaction flask is warmed up to 85°C and the nitrogen flow is stopped. Instead, ethylene from the pressure flask is passed into the solution. The gas flow is tuned in such a way that only a few or no gas bubbles can escape from the washing bottle. The start of the reaction can be observed by the fact that the initially finely distributed catalyst particles form a black coarse-grained precipitate and the toluene solution becomes colorless. In the course of the reaction the formed polyethylene grows around these grains as a dark-colored bulk. The stirrer has to work powerfully. After 4–6 h the polymerization is terminated by stopping the ethylene flow and by the addition of 100 ml of isopropanol. The resulting polyethylene is filtered off, repeatedly washed with methanol and dried in vacuum. Yield: 10–20 g polyethylene.

Polyethylene is, depending on the molecular weight, a waxy or solid, crystalline substance. Following the above-mentioned procedure, a high molecular crystalline product with a melting range around 130°C is obtained. At room temperature it is insoluble in all solvents. At higher temperatures (100–150°C) it can be dissolved in aliphatic and aromatic hydrocarbons. Viscosity measurements can be performed in xylene, tetralin or decalin at 135°C. To prevent the polymer from oxidative degradation, 0.2% of a commercially available stabilizer (for example, 2,6-di-*tert*-butyl-4-methylphenol or *N*-phenyl- b-naphthylamine) are added as antioxidant. Polyethylene can be formed to thin films by pressing between two metal plates (pressing time: 2 min at 180–190°C, see Sect. 2.5.2.1). After quenching with cold water, the films can be detached from the plates. They are convenient for recording infrared spectra, from which, for example, the crystallinity (see Sect. 2.3.5.5) or the degree of branching (see Sect. 2.3.2.2) can be determined.

Example 3.29 Stereospecific Polymerization of Propylene with Ziegler-Natta-Catalysts in Organic Suspension

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: Aluminum alkyls must be handled under total exclusion of oxygen and moisture (see Example 3.28).

(a) Preparation of Isotactic Polypropylene

The polymerization apparatus (Fig. 3.2) is flushed with nitrogen and the reaction flask filled with 500 ml of dry petroleum ether (distilled over sodium under nitrogen, bp 100–140°C). The flask is then heated to 60°C (±2°C) in a thermostatted oil bath and the petroleum ether is saturated with propylene (about 15 min) while stirring (about 500 rpm). 1.26 ml (10 mmol) of diethylaluminum chloride and about 1 g (5 mmol) of $TiCl_3 \cdot 1/3\ AlCl_3$ (Stauffer AA, handled with exclusion of air and moisture) are added through the thermometer neck. The flow of propylene is adjusted such that very little escapes through the protective wash bottle E. The polymer separates out as a red-violet powder. The temperature is held steady by thermostatting at 60 ± 2°C. The stirring speed during polymerization is about 700 rpm.

After 2 h the polymerization is terminated by addition of 20 ml of 2-propanol, and stirring continued for another 30 min at 60°C; the reaction mixture decolorizes and becomes white. After filtration using a Büchner funnel and several washings with warm petroleum ether the polymer is dried to constant weight in vacuum at 70°C. Yield: 29.5 g.

The polypropylene so obtained has a high molecular weight and is crystalline. The proportion of isotactic polymer, determined by extracting with heptane for 10 h in a Soxhlet apparatus, is 98.5%. Isotactic polypropylene shows similar solubility behavior to polyethylene, but has a higher melting point (crystalline melting range 165–171°C).

(b) Effect of Heterogeneous Nucleation on the Crystallization of Isotactic Polypropylene

In the crystallization of isotactic polypropylene from the melt, the number and size of the spherulites (and hence the rate of crystallization) can be influenced by the addition of certain nucleating agents. The smaller the spherulites, the greater is the transparency of the polypropylene film. The mechanical properties can also be affected in some cases.

The effect of heterogeneous nucleation on the crystallization of isotactic polypropylene from the melt can be easily established as follows. A small amount of powdered polypropylene is well mixed with about 0.1 wt% of sodium benzoate in a mortar or by means of an analytical mill. Some of the mixture is transferred with a spatula to a microscope slide and melted at about 250°C on a hot block. A cover slip is pressed on to the melt with a cork to obtain as thin a film as possible. The sample is held at 200–250°C for some minutes and then allowed to crystallize at about 130°C on the hot stage of the microscope; an unadulterated polypropylene sample is crystallized in the same way. Both samples are observed under a polarizing microscope during crystallization, the difference in spherulite size between nucleated and untreated polypropylene can be seen very clearly. An ordinary microscope can also be used by placing polarizers on the condenser and eyepiece, and adjusting these to give maximum darkness.

Example 3.30 Stereospecific Polymerization of Styrene with Ziegler-Natta-Catalysts

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: Alkylaluminum reagents must be handled under total exclusion of atmospheric oxygen and moisture (see Example 3.28).

A dry 1 l three-necked flask, fitted with stirrer, thermometer, nitrogen inlet, and dropping funnel with pressure equalizer (according to Fig. 3.2), is evacuated and filled with nitrogen three times. 1.0 ml (9.1 mmol) of $TiCl_4$ is added by means of a syringe pipette under a brisk flow of nitrogen, and 27 ml (24 mmol) of triethylaluminum (0.9 M in hexane) (or triisobutylaluminum) are dropped in from the dropping funnel over a period of 10 min, with stirring. The reaction of the two catalyst components is initially strongly exothermic and the flask must therefore be cooled externally to about −20°C. As a precaution against possible breakage of the flask, the cooling bath must not contain water since it reacts extremely violently with triethylaluminium. A dry ice/1,2-dimethoxyethane bath can be used. When the additions are complete, the cooling bath is removed and stirring is continued for 5 min at room temperature, then 90 g of carefully dried styrene (seeExample 3.1) are added quickly from a second dropping funnel. The stirring rate is now increased and the oil bath heated to 50°C. After 1–2 h the contents of the flask become viscous and eventually gel-like after 2–3 h. The hot bath is removed and 30 ml of methanol are added over a period of 10 min through the dropping funnel, with vigorous stirring, in order to destroy the catalyst. The addition of methanol must be done very carefully; above all one must ensure immediate and thorough mixing. After the catalyst has been destroyed a further 350 ml of methanol are added, once again with

vigorous stirring; the polystyrene then precipitates from the gel-like reaction mixture in the form of fine flakes. Stirring is continued for another 10 min, and the polymer is filtered off and washed with methanol. In order to remove catalyst residues the polymer is stirred for 1 h in a mixture of 500 ml of methanol and 5 ml of concentrated hydrochloric acid. It is then filtered off, washed with methanol and dried in vacuum at 60°C. Yield: 5–30%.

For the separation of the amorphous portion the dried polymer is stirred for 3 h in 500 ml of acetone, to which 2 ml of concentrated hydrochloric acid has been added. The insoluble portion is filtered off and dried in vacuum at 60°C. Yield: 85–95% of crystallizable polystyrene.

The crystallization of the acetone-insoluble polystyrene is completed by boiling for 2 h in freshly distilled butanone; it is then allowed to stand overnight at room temperature and finally filtered and dried in vacuum at 60°C. Yield of crystalline isotactic polystyrene: 95–100% of the acetone insoluble portion. The crystalline melting range and the density (see Sect. 2.3.5.1) are determined, as is also the limiting viscosity number in toluene at 20°C.

Crystallization and Characterization of Isotactic Polystyrene

The atactic polystyrene is precipitated by dropping the acetone/HCl solution into methanol and it is filtered through a sintered glass crucible; the atactic and crystalline portions are dried in vacuum at 50°C and finally weighed. The X-ray diffraction patterns of the two samples are compared with each other and with that of a polystyrene made by radical polymerization; likewise for the IR spectra (see Sects. 2.3.5.2 and 2.3.2.2).

The melting range of the isotactic, crystalline sample is determined with the aid of a hot-stage microscope; the following conditions of the sample can be distinguished:

1. Clearly defined particles
2. Blurred edges
3. Beginning of sintering
4. Beginning of melting
5. Melt runs together
6. Clear melt

The melting range is defined by the temperature interval between steps 4 and 5; for the crystalline polystyrene prepared above, this lies between 205°C and 215°C.

Example 3.31 Stereospecific Polymerization of Butadiene with Ziegler-Natta-Catalysts: Preparation of cis*-1,4-Polybutadiene*

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: Aluminum sesquichloride must be handled under total exclusion of atmospheric oxygen and moisture (see Example 3.28).

A trap, to be used for condensing the butadiene (see Fig. 3.3), is dried for 1 h at 120°C, evacuated, and filled with pure dry nitrogen. A butadiene cylinder is

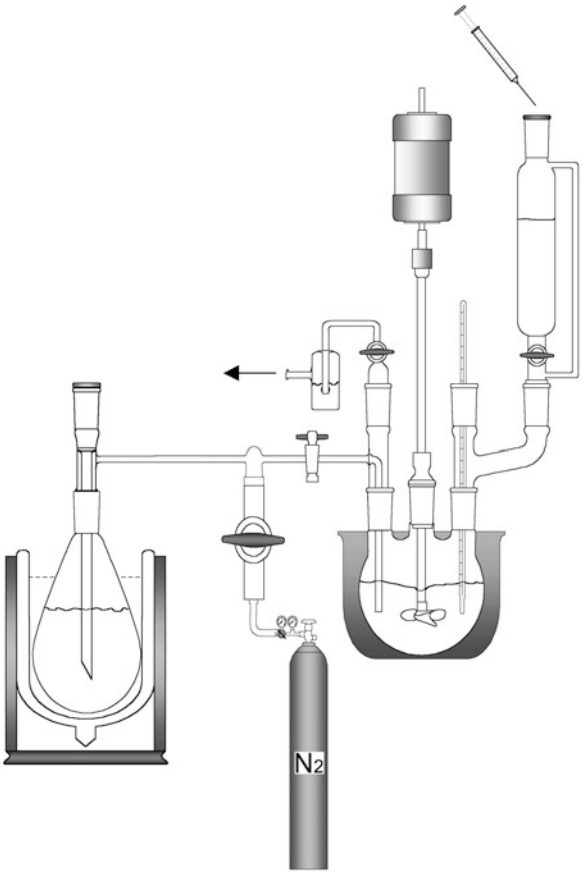


Fig. 3.3 Setup for the polymerization of butadiene

attached to the three-way tap via a P_2O_5 drying tube. The air in the tubing and drying tube between the three-way tap and cylinder is displaced by flushing with butadiene. The trap is then cooled in a dry ice/methanol bath and 20 g (33 ml) of butadiene condensed in.

Toluene is refluxed for a day over potassium. 200 ml are then distilled under nitrogen into a dry dropping funnel with pressure-equalizing tube. It is well stoppered for storage. 600 mg (1.68 mmol) of cobalt(III) acetylacetonate are weighed into a dry tube with attached stopcock. This is evacuated, filled with dry nitrogen, and 20 ml of dry toluene are then introduced through the bore of the tap with the aid of a hypodermic syringe. The closed tube is shaken until the cobalt compound has dissolved.

The polymerization is carried out in a 500 ml four-necked flask, fitted with stirrer, thermometer, adapter, and nitrogen inlet (see Fig. 3.3). The individual parts of the apparatus are previously dried for 1 h at 120°C, and while still hot are

assembled as quickly as possible; the whole is then evacuated and filled with P_2O_5-dried nitrogen three times.

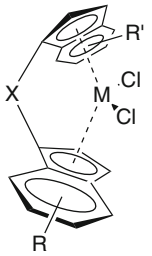
Finally, the dropping funnel containing the 200 ml of pure toluene is mounted and fitted with a self-sealing closure. Using a hypodermic syringe that has been dried at 120°C and flushed with dry nitrogen, 1.0 ml (4.6 mmol) of $Al_2Et_3Cl_3$ are injected through the self-sealing closure into the toluene in the dropping funnel; the syringe is washed out with the toluene by several strokes of the piston. The piston of the syringe should be smeared with a little paraffin in order to prevent its seizure in the cylinder. It should be washed with a mixture of 2-propanol and decalin (1:1 vol/vol) immediately after use. The toluene solution of the aluminum sesquichloride is now run into the flask, warmed on a water bath to 20–25°C, and 10 ml of the cobalt (III) salt solution added through the dropping funnel by means of a second hypodermic syringe, prepared in the same way as the first. The color now changes from green to gray-brown and the temperature rises to about 40°C. The two components of the catalyst are allowed to react with each other for 10 min. The cold bath round the butadiene is removed and the 20 g (0.37 mol) of butadiene are allowed to evaporate into the polymerization flask with stirring; this takes about 1 h. The reaction mixture is held at 20°C for another hour and a toluene solution of an antioxidant (e.g., 0.2% 2,6-di-*tert*-butyl-4-methylphenol) is then added to prevent crosslinking reactions during work-up. The polymer is precipitated by dropping the highly viscous solution into a fivefold amount of methanol. After settling, the supernatant liquid is decanted from the polymer which is then broken down into small pieces and stirred with fresh methanol for a few minutes; this purification process is repeated twice more, the polymer finally being filtered and dried in vacuum at 40°C. Yield: >90%. About 1 g of the polybutadiene is reprecipitated from toluene solution with methanol. The limiting viscosity number is determined in cyclohexane at 20°C and the molecular weight derived. The polymer may be further characterized as described in Example 3.21. Main applications of polybutadiene are in tires and in polystyrene/polybutadiene blends (high impact polystyrene, see Example 5.23).

3.3.2 Polymerization with Metallocene Catalysts

Metallocences are sandwich-like π-complexes derived, e.g., from dicyclopentadienylzirconium dichloride. At first, they were used only as soluble model systems (in combination with diethylaluminum chloride) in order to study Ziegler-Natta polymerizations. The discovery by Sinn and Kaminsky that, by using methylalumoxane (MAO), exceptionally high activities of polymerization were achieved and the results of Brintzinger that an additional bridging (linking) of the ligands in the metallocene results in outstandingly high regio- and stereoselectivities, make this class of catalysts very interesting, especially for industrial applications.

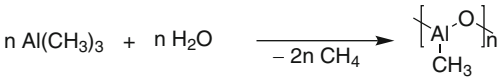
For example, it is possible to synthesize isotactic as well as syndiotactic polypropylene in high configurational purity and high yields. The same holds for syndiotactic polystyrene. Furthermore, metallocene catalysts open the possibility to absolutely new homopolymers and copolymers like, e.g., cycloolefin copolymers

(COC) and even (co)polymers of polar monomers. The simplest metallocene catalyst consists of two components. The first one is a π-complex (the actual metallocene) that can be bridged via a group X and therefore can become chiral:



X = e.g., $(CH_3)_2Si$ or CH_2
M = e.g., Zr, Ti

The second component is a special alumina-organic compound, methylalumoxane (MAO), that is prepared by partial hydrolysis of trimethylaluminum and that contains linear as well as cyclic structures in the molecules.



The mixture of metallocene and co-catalyst is soluble. Its active center, which is chiral, induces with a very low rate of defects only one type of monomer linkage ("single site catalysts"). That is why high activities (some 1,000 kg polymer/g zirconium), high molecular weights, narrow molecular weight distribution, and high steric homogeneity are achieved.

Example 3.32 Metallocene-Catalyzed Polymerization of Propylene to Highly Isotactic Polypropylene in Organic Suspension

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) Solvent

Caution: Refluxing of toluene over sodium/potassium alloy must be done under permanent supervision.

Highly dried toluene is the most useful reaction medium. It is obtained according to the following procedure. Pre-dried toluene (over molecular sieve) is refluxed over a liquid sodium/potassium alloy (5–10 ml for 2 l of toluene) for 4–5 days. An alternative method is the addition of *n*-butyllithium in small portions (ca. 10 ml for 2 l toluene) which can be visualized with benzophenone as indicator. When the toluene is sufficiently dried (change of color) it is distilled off and stored under

argon (The used syringes or pipettes have to be flushed prior to use with argon; after use they have to be cleaned immediately with toluene).

(b) Methylalumoxane (MAO)

Caution: Working with MAO has to be done under rigorous safety precautions! Wearing of safety goggles and protective gloves is a must. MAO is highly reactive! It reacts with moisture traces on the skin. If MAO is spilled, the contaminated area has to be covered with sand to prevent a fire. Then, MAO is hydrolyzed by the careful addition of 2-propanol or ethanol, followed by water (see also Example 3.28).

MAO is usually available as a 10% solution in toluene and is stable for approx. 2 months. If MAO should be stored over a longer period of time, the solvent has to be distilled off. Vacuum distillation at 40°C is therefore the method of choice (the cooling trap is cooled with liquid nitrogen!). The more and more viscous MAO solution should be stirred all the time. The solid MAO is then stored under argon.

(c) Polymerization of Propylene

A 250 ml flask with the equipment shown in Fig. 3.2 is flushed with argon. Then, 90 ml of the highly dried toluene are added with a syringe. Now are pipetted in under stirring: 5 ml of a 10% solution of MAO followed by 5 ml of a solution of *rac*-ethylene-bis(4,4,5,5′,6,6′,7,7-tetrahydro-1,1′-indenyl)zirconium dichloride (The used syringes or pipettes have to be flushed prior to use with argon; after use they have to be cleaned immediately with toluene).

Then the setup is evacuated until the vapor pressure of toluene is reached. Next, dry propylene is passed in until normal pressure is attained. The polymerization starts after approx. 15 min and the reaction mixture becomes turbid and might also warm up. A small flow of propylene into the reaction mixture is still maintained. After 1 h, the propylene flow is stopped and the polymerization is terminated by the addition of 10 ml ethanol. Then, the fluffy reaction mixture is added under stirring to 300 ml ethanol whereby the polymer precipitation is completed. MAO and metallocene residues are removed by the addition of 25 ml of a 10% HCl solution and stirring for 1 h. Finally, the solid polymer is filtered over a Büchner funnel, washed with ethanol and dried in vacuum at 40–60°C to constant weight (~12 h). Yield: 1–2 g. The obtained polypropylene is highly isotactic (determination by ^{13}C-NMR spectroscopy) and has a molecular weight of approx. 30,000.

3.3.3 Ring-Opening Metathesis Polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP) is a transition metal alkylidene-triggered process in which cyclic olefins, whether mono-, bi- or multicyclic, undergo ring-opening and are concomitantly joined together to form a polymer chain. ROMP is thus a chain-growth polymerization and belongs, together with Ziegler-Natta-type polymerizations and group transfer polymerizations, to the family of polyinsertions. The mechanism is based on olefin metathesis. The ring-opening process occurs at the most stable site of the monomer, i.e. at the double bond.

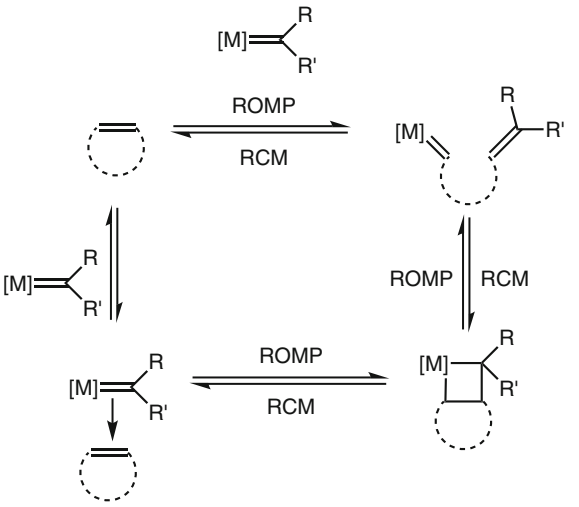
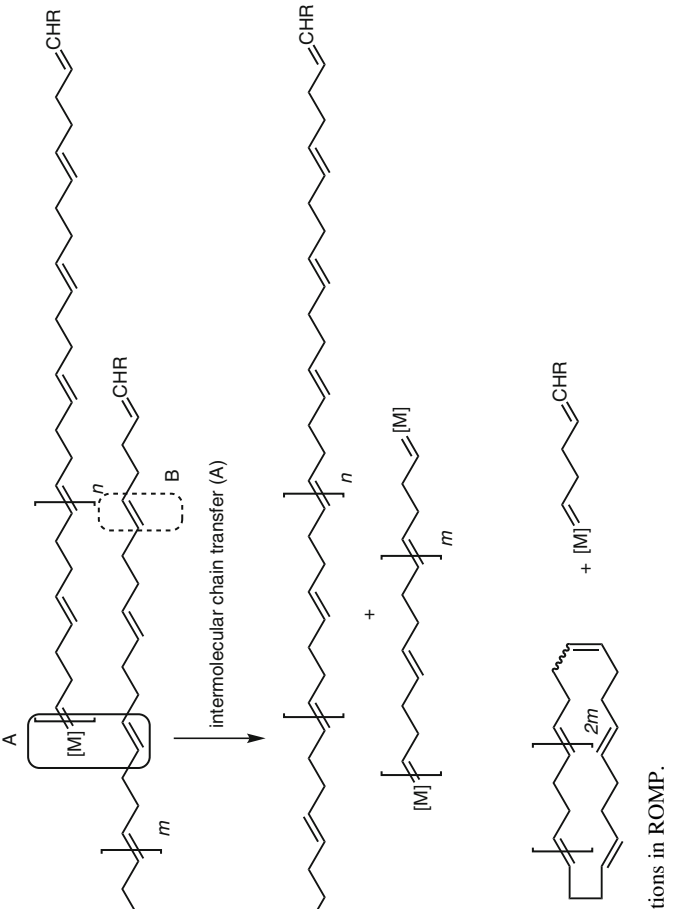


Illustration of the ROMP process

It is important to note that, as all metathesis reactions, all steps are in principle reversible. Furthermore, the double bond of the monomer is formally preserved, resulting in one double bond per repeat unit. ROMP may therefore be regarded as an inversed ring-closing metathesis (RCM) reaction. ROMP is driven by the thermodynamics that are entailed with the reduction in ring-strain that occurs during incorporation of the monomer into the growing chain. In general, the ring-opening of 3-, 4-, 8- and larger-membered rings is energetically favored. Finally, since the polymer itself still contains double bonds, i.e., one per repeat unit, an intramolecular chain transfer reaction, i.e., a backbiting process may occur, leading to cyclic oligomers/polymers.



Inter- (A) and intramolecular (B) chain transfer reactions in ROMP.

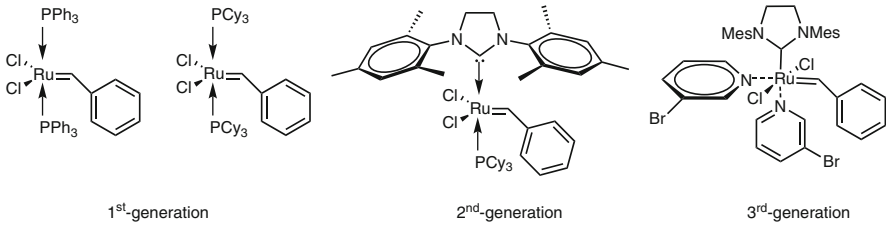
The extent of this process strongly depends on temperature, monomer concentration, *cis*/*trans* configuration of the double bonds within the polymer backbone, solvent, reaction time and, probably most important, on the steric bulk of the monomer used.

Historically, complex mixtures, usually based on a metal halide or oxohalide, a tin alkyl, an alcohol and an additive have been used to generate the metal alkylidene in situ. The chemical nature of these alkylidenes, however, is usually ill defined and in most cases only a low percentage (<20%) of metal alkylidene with respect to the total amount of metal present in the mixture forms. As a result, the polymers produced by such ill-defined systems display broad polydispersities. Furthermore, the structure of the polymer (i.e. *cis*/*trans* content and tacticity) cannot be controlled. With organometallic coordination catalyst systems containing molybdenum or tungsten, it is possible to bring about ring-opening polymerization of cycloolefins to linear unsaturated polymers, e.g., of cyclopentene to poly(1-pentenylene) (Example 3.33). The resulting polymer has rubber-like properties because of the remaining double bonds.

Tremendous efforts have been put into the development of well-defined "single-site" transition metal alkylidenes. Mainly the work of R.H. Grubbs and R.R. Schrock (awarded with the Chemistry Nobel Prize 2005, shared with Y. Chauvin) led to the development of well-defined transition metal alkylidenes that rapidly outrivaled the traditional initiator systems. These initiators have the advantage of being well-defined compounds and in particular of possessing preformed metal-alkylidenes.

"Schrock-catalysts" are high-oxidation state molybdenum (or tungsten) alkylidenes of the general formula $M(NAr')(OR')_2(CHR)\cdot L$, where M = Mo, W; Ar′ = phenyl, a substituted phenyl group or adamantyl; R = ethyl, phenyl, trimethylsilyl, CMe_2Ph or *t*-butyl; R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, etc. and L = quinuclidine, trialkylphosphane, THF, etc. Generally speaking, Schrock initiators are highly active in the ROMP of a vast variety of cyclic alkenes such as substituted norborn-2-enes, norbornadienes, 7-oxanorbornenes, cyclooctatetraenes (COTs), 1,4-cyclooctadienes (CODs), etc. or polycyclic alkenes such as certain quadricyclanes. In addition, they may be used for 1-alkyne polymerization and the cyclopolymerization of 1,6-heptadiynes. The "living" polymerizations triggered by Mo-bis(*t*-butoxide)-derived initiators usually lead to the formation of all-*trans,* highly tactic polymers. Living, Schrock initiator-triggered polymerizations are best terminated by aldehydes in a Wittig-type reaction.

Grubbs-type initiators are well-defined ruthenium alkylidenes. First-generation Grubbs initiators are based on phosphanes, while the second-generation Grubbs initiators bear both an N-heterocyclic carbene (NHC) and a phosphane. The third-generation Grubbs-initiators, finally, contain one NHC and one or two (substituted) pyridines. Another breakthrough in catalyst activity was the development of Grubbs-type initiators with an internally oxygen-chelated ruthenium alkylidene. They are usually referred to Grubbs-Hoveyda catalysts and exhibit pronounced stability and longevity, e.g. in RCM reactions.

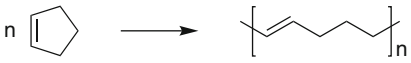


Selection of Grubbs-type initiators

Compared to molybdenum- or tungsten-based Schrock catalysts, the reactivity of ruthenium-based Grubbs catalysts is somewhat different. Reactivity in $RuCl_2(PR_3)_2(CHPh)$ may efficiently be tuned rather via the use of different phosphanes than by the nature of the alkylidene moiety or by substitution of the chlorides by other, more electron-withdrawing groups. The stability as well as the reactivity order that can be deduced there from is $PPh_3 < PBz_3 < PCyPh_2 < PCy_2Ph <$ P-*i*-$Bu_3 <$ P-*i*-$Pr_3 < PCy_3$. In terms of polymer structure, ROMP of norborn-2-enes and norbornadienes using ruthenium-based systems generally results in the formation of polymers that, in most cases, predominantly contain *trans*-vinylene units. Polymerizations initiated by Grubbs-type initiators are best terminated by the use of ethyl vinyl ether, yielding methylidene-terminated polymers.

Example 3.33 Poly(1-Pentenylene) by Metathesis Polymerization of Cyclopentene with a Ziegler-Natta-Catalyst 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.



Caution: Aluminum alkyls must be handled under total exclusion of oxygen and moisture (see Example 3.28).

(a) Preparation of $W(OCH_2CH_2Cl)_2Cl_4$

2.64 g (6.67 mmol) of WCl_6 and 50 ml of dry toluene are transferred under nitrogen to a 100 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vacuum, thermometer, heating bath) three-necked flask, equipped with thermometer, nitrogen inlet, dropping funnel with a pressure-equalizing tube, and magnetic stirrer. A solution of 1.07 g (0.9 ml, 13.33 mmol) of 2-chloroethanol in 15 ml of dry toluene is added dropwise at room temperature with stirring, over a period of about 30 min. The temperature should not be allowed to exceed 35°C. Stirring is continued for 1 h. The brown solution of the tungsten compound (0.1 M) is stored under nitrogen.

(b) Preparation of a 0.5 M Solution of $(C_2H_5)_2AlCl$ in Toluene

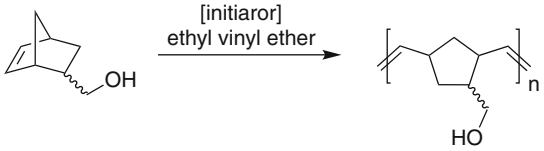
30 ml of dry toluene and 2 ml (1.95 g, 16.13 mmol) of diethylaluminum chloride are placed in a 50 ml round-bottomed flask under nitrogen. The solution is well mixed and stored under nitrogen.

(c) Polymerization of Cyclopentene

450 ml of pre-dried toluene are placed in a 500 ml flask equipped with stirrer, thermometer, nitrogen inlet, and condenser for distillation. 125 ml of the toluene are distilled off under a gentle stream of nitrogen. The flask is cooled to −15°C under a slight excess pressure of nitrogen, 50 ml (38.6 g, 0.567 mol) of dry cyclopentene and, finally, 2 ml of the 0.1 M solution of $W(OCH_2CH_2Cl)_2Cl_4$ and 2 ml of the 0.5 M solution of $(C_2H_5)_2AlCl$ are added. The polymerization commences immediately as can readily be seen from the marked increase in viscosity. The reaction temperature is kept at −10°C by external cooling. The polymerization is stopped after 5 h. To deactivate the catalyst a mixture of 0.5 g of 2,6 di-*tert*-butyl-4-methylphenol and 1 ml of ethanol dissolved in 15 ml of toluene are added with stirring; the solution is rapidly decolorized. The poly(1-pentenylene) is isolated by precipitation in about 1 l of propanol and drying to constant weight in vacuum at 50°C. Yield: about 70%. The solution viscosity is determined in toluene and the proportions of cis and trans double bonds estimated from the IR spectrum (see Table 3.9).

Example 3.34 ROMP of norborn-5-ene-2-methanol with a Grubbs-Type Initiator 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.



All manipulations are carried out in a N_2-mediated dry box or under standard Schlenk conditions similar as described in example 3.19. Prior to use, CH_2Cl_2 is dried and deoxygenated by distillation from CaH_2 under Ar.

0.002 mmol of $RuCl_2(PCy_3)_2(CHPh)$ (1st-generation Grubbs catalyst, Sigma-Aldrich or Materia Inc.) or $RuCl_2$(3-Br-pyridine)$(IMesH_2)(CHPh)$ (3rd-generation Grubbs catalyst, $IMesH_2$ = 1,3-dimesitylimidazolin-2-ylidene, Sigma Aldrich or Materia Inc., or synthesized according to T. L. Choi, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2003**, *42*, 1743–1746) are dissolved in 1 ml of CH_2Cl_2. Separately, 28 mg of norbornene-5-ene-2-ylmethanol (0.225 mmol, from Sigma-Aldrich) are dissolved in 2 ml of CH_2Cl_2 (monomer: initiator = 100:1). Under vigorous stirring, the initiator solution is quickly added to the monomer solution. Stirring is continued for another 20 min, then, ethyl vinyl ether is (0.5 ml) added. After another 20 min, the reaction mixture is poured onto 20 ml of pentane, the polymer is isolated by filtration and washed with diethyl ether. Isolated yield: >90%.

The *cis*/*trans* ratio of the double bonds can be estimated by IR-spectroscopy or determined quantitatively by ^{1}H-NMR spectroscopy. Here, the *cis:trans* ratio of the polymer can be estimated via integration of the olefinic protons. These can be found at $\delta = 5.6$–5.3 ppm and $\delta = 5.4$–5.1 ppm for the *trans*- and *cis*-double bonds, respectively. With the initiators used here, a *cis:trans* ratio of roughly 55:45 is obtained.

The solution viscosity can be determined in chloroform or THF. Additionally, the average degree of polymerization can be determined by ^{1}H-NMR-based end group analysis in THF-d_8 by determining the ratio of the phenyl protons over the protons of the double bond of the repeat unit.

3.4 Copolymerization

By copolymerization we understand the mutual polymerization of two or more monomers, with the resulting macromolecules containing repeating units of all the participating monomers. Depending on the distribution of the monomers in the macromolecules one differentiates four types of copolymers (nomenclature of copolymers see Sect. 1.2):

- Statistical copolymers
- Alternating copolymers
- Block copolymers
- Graft copolymers

Conventional polymerization methods yield macromolecules mostly with random (statistical) or nearly statistical and only very seldom with alternating distribution of the monomer units (see Sect. 3.4.1). Special methods are required in order to synthesize block and graft copolymers (Sect. 3.4.2).

3.4.1 Statistical and Alternating Copolymerization

When synthesizing random (statistical) and alternating copolymers two phenomena have to be kept in mind:

- Monomers that readily homopolymerize are not necessarily able to copolymerize well with another monomer. On the other hand, there are some monomers that are not able to homopolymerize but which can be induced to copolymerize.
- The tendency of monomers to copolymerize is strongly dependent on the nature of the growing chain end, e.g., on the type of the initiation. In nonradical polymerizations even the composition of the initiator or catalyst is important.

Copolymerization of two monomers has been very thoroughly investigated, but copolymerization of three or more compounds presents considerable difficulties on account of the multiplicity of variables. Nevertheless, terpolymers (from three monomers) are of technical importance and are produced on large scales. We limit ourselves here to the case of mutual polymerization of two monomers; there are then essentially four different possible propagation reactions: monomer M_1 can

react with a polymer chain whose growing chain end (radical or ionic) has been formed either from monomer M_1 or from monomer M_2; similarly for monomer M_2:

$$\begin{aligned} -M_1^{\bullet} + M_1 &\xrightarrow{k_{11}} -M_1^{\bullet} \\ -M_1^{\bullet} + M_2 &\xrightarrow{k_{12}} -M_2^{\bullet} \\ -M_2^{\bullet} + M_2 &\xrightarrow{k_{22}} -M_2^{\bullet} \\ -M_2^{\bullet} + M_1 &\xrightarrow{k_{21}} -M_1^{\bullet} \end{aligned}$$

where k_{11}, k_{12}, k_{21}, k_{22} represent the rate constants of these propagation reactions, the first number in the subscript indicating the type of active center, and the second, the nature of the monomer that is adding to it. As long as the chain length is relatively large, the propagation reactions are rate-determining; as in homopolymerization, a quasistationary state is set up. It can then be shown that at low conversion (<10%), the relative rates of consumption of the two monomers, and thus their relative amounts (in mol) in the copolymer, M_1/M_2, can be described by the following copolymerization equation:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \left(\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right) \tag{3.18}$$

in which $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are termed the reactivity ratios (copolymerization parameters). $[M_1]$ and $[M_2]$ represent the molar concentrations of monomer in the reaction mixture. The composition of a copolymer thus depends on the monomer feed ratio in the polymerization mixture. Since the parameters r_1 and r_2 are ratios of rate constants, they express the tendency of the growing chains to add either the same or the other monomer. If r is close to 1 it follows that a particular active chain end adds molecules of monomers M_1 and M_2 at random with approximately equal facility; $r > 1$ means that the addition of a monomer to a chain with the same end unit is strongly preferred. Reactivity ratios, being quotients of two rate constants, are not very temperature-dependent, but of course are strictly valid only for a particular polymerization temperature which must, therefore, always be indicated.

In some cases, the reactivity of the growing chain end depends on the nature of the last but one monomer unit. So, eight propagation constants have to be considered. This so-called penultimate effect can be the reason why the binary copolymerization cannot be described precisely enough by Eq. 3.18.

By rearranging Eq. 3.18 and inserting known values of the reactivity ratios r_1 and r_2, one can calculate the molar ratio of monomers that must be used in order to arrive at a copolymer with a chosen composition ($f = m_1/m_2$):

$$\frac{[M_1]}{[M_2]} = \frac{1}{2 \cdot r_1} \left\{ (f-1) + \left[(f-1)^2 + 4 \cdot r_1 \cdot r_2 \cdot f \right]^{0.5} \right\} \tag{3.19}$$

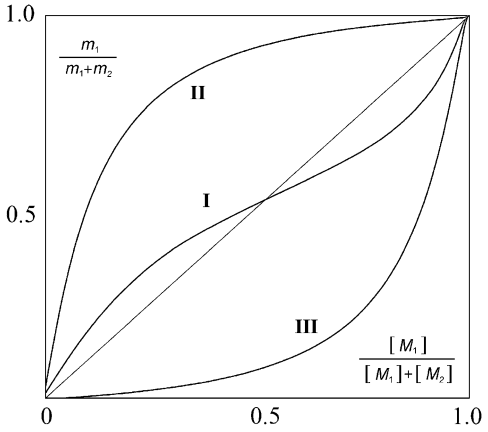


Fig. 3.4 Copolymerization diagram for the system styrene (M_1)/methyl methacrylate (M_2). I: radical copolymerization at 60°C; $r_1 = 0.52$, $r_2 = 0.46$; II: cationic copolymerization initiated by $SnBr_4$ at 25°C; $r_1 = 10.5$, $r_2 = 0.1$; III: anionic copolymerization initiated by Na in liquid NH_3 at −50°C; $r_1 = 0.12$, $r_2 = 6.4$

The dependence of the composition of the copolymer on the proportions of the monomers in the initial mixture can be portrayed graphically in a so-called copolymerization diagram (Fig. 3.4). The mole fraction of one of the two monomeric units in the resulting copolymer is plotted against the mole fraction of this monomer in the original reaction mixture; the curve can also be calculated from the reactivity ratios by means of Eq. 3.18.

As can be seen from Fig. 3.4, it is very rare for the polymer composition to correspond to that of the monomer mixture. For this reason the composition of the monomer mixture, and hence also that of the resulting polymer, generally changes as the copolymerization proceeds. Therefore, for the determination of the reactivity ratios one must work at the lowest possible conversion. In practical situations where, for various reasons, one is forced to polymerize to higher conversions, this leads to a chemical non-uniformity of the copolymers in addition to the usual non-uniformity of molecular weights.

If one wishes to attain high conversion at constant composition, the more reactive monomer must be added in a programmed manner. The procedure is as follows: from the copolymerization diagram (or from the reactivity ratios) one obtains the monomer composition that will lead, at low conversion, to the desired copolymer composition. A conversion/time curve is drawn up for this system and the composition of the copolymer determined from time to time. From this, one can find how much of the more reactive monomer is to be added at given times during the polymerization in order to maintain an approximately constant composition (see Example 3.39). Special computer software has already been developed for this.

From the copolymerization Eq. 3.18 and the copolymerization diagram (Fig. 3.4) some special cases can be derived (see Table 3.10). When the compositions of the

Table 3.10 Special cases of the copolymerization equation

r_1	r_2	$r_1 r_2$	Copolymerization equation	Comment
>0	~0	<<1	$\frac{m_1}{m_2} \approx r_1 \cdot \frac{[M_1]}{[M_2]} + 1$	M_2 has no tendency to give homopolymers
~0	~0	~0	$\frac{m_1}{m_2} \approx 1$	Both monomers have no tendency to give homopolymers→alternating copolymerization
$1/r_2$	$1/r_1$	~1	$\frac{m_1}{m_2} \approx r_1 \cdot \frac{[M_1]}{[M_2]}$	Ideal copolymerization without azeotrope
~1	~1	~1	$\frac{m_1}{m_2} \approx \frac{[M_1]}{[M_2]}$	Ideal copolymerization with azeotrope
<1	<1	<1	Normal equation	Non-ideal copolymerization, azeotrope at $\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1}$
>1	>1	>1		Not found yet

monomer feed and the resulting copolymer are the same, one speaks of "azeotropic" copolymerization; Eq. 3.18 then reduces to:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1} \tag{3.20}$$

In such cases the polymerization can be taken to relatively high conversion without change in composition of the copolymer formed (see Example 3.37). In the copolymerization diagram the azeotrope corresponds to the intersection point of the copolymerization curve with the diagonal. For example, from Fig. 3.4 it may be seen that in the radical copolymerization of styrene and methyl methacrylate the azeotropic composition corresponds to 53 mol% of styrene.

For the case where $r_2 = 0$, $k_{22} = 0$, M_2 does not add to growing chains having an M_2 end unit, so that homopolymerization of M_2 is also impossible. Eq. 3.18 then reduces to:

$$\frac{m_1}{m_2} = r_1 \cdot \frac{[M_1]}{[M_2]} + 1 \tag{3.21}$$

The resulting copolymer can contain at most 50 mol% M_2 units, even at high concentration of M_2 in the monomer mixture. This applies, for example, to maleic anhydride, and especially to such "monomers" as molecular oxygen or sulfur dioxide where, independent of the comonomer used, essentially alternating copolymers are obtained, with almost equal amounts of the two components.

Finally there are also cases in which two "monomers" copolymerize, both "monomers" being themselves incapable of homopolymerization ($k_{11} = k_{22} = 0$); this results in strict alternation of monomeric units of M_1 and M_2 in the copolymer (see Example 3.38).

If radical copolymerization is conducted in the presence of complexing agents it is sometimes possible to force monomers into forming alternating copolymers when they would otherwise give random copolymers. Lewis acids such as zinc chloride are especially suitable for this, also organoaluminum compounds. The reaction mechanism is not yet fully clarified; it is assumed that the additives form electron donor/acceptor complexes with the monomer or the active chain ends, leading to alternating insertion of the two monomers into the growing polymer chains.

It is important to note that the tendency of a monomer towards polymerization and therefore also towards copolymerization is strongly dependent on the nature of the growing chain end. In radical copolymerization the composition of the copolymer obtained from its given monomer feed is independent of the initiating system for a particular monomer pair, but for anionic or cationic initiation this is normally not the case. One sometimes observes quite different compositions of copolymer depending on the nature of the initiator and especially on the type of counterion. A dependence of the behavior of the copolymerization on the used catalyst is often observed with Ziegler-Natta or metallocene catalysts.

In the radical copolymerization of styrene and methyl methacrylate the reactivities are about the same, but for anionic initiation of an equimolar mixture of the two monomers the incorporation of methyl methacrylate is much preferred, while for cationic initiation of the same mixture the copolymer contains mostly styrene (see Fig. 3.4 and Example 3.35). Conversely, monomer pairs whose copolymerization behavior is well known can be used to test new initiator systems in order to draw conclusions about the polymerization mechanism.

As already indicated, values of reactivity ratios apply only to a given pair of monomers. There have been many attempts, especially for radical copolymerization, to derive parameters from the reactivity ratios, representing individual constants for each monomer which can be related to the structure of the monomers, and can be used to make predictions.

The basis of the scheme developed particularly by Alfrey and Price is the assumption that the activation energies of the propagation reactions, and hence the related rate constants and reactivity ratios, are governed primarily by resonance effects and by the interaction of the charges on the double bonds of the monomers with those in the active radicals. Accordingly, the rate constant of the reaction between a radical and a monomer is represented by:

$$k_{12} = P_1 \cdot Q_2 \cdot e^{-e_1 \cdot e_2} \tag{3.22}$$

where P_1 denotes the reactivity of a radical having an M_l unit at the reactive end, Q_2 is the reactivity of the monomer M_2, and e_1 and e_2 are proportional to the charges on the corresponding species. It is assumed that the e value of the monomer is the same as that of the corresponding radical. Hence, it follows that:

$$r_1 = \frac{Q_1}{Q_2} \cdot e^{-e_1(e_1 - e_2)} \qquad r_2 = \frac{Q_2}{Q_1} \cdot e^{-e_2(e_2 - e_1)} \tag{3.23}$$

and hence

$$e_1 = e_2 \pm \sqrt{-ln(r_1 \cdot r_2)} \tag{3.24}$$

$$Q_1 = \frac{Q_2}{r_2} \cdot e^{\pm e_2 \sqrt{-ln(r_1 \cdot r_2)}} \tag{3.25}$$

On this basis, values of Q and e can be calculated for each monomer, so long as two arbitrary reference values are assumed. For this purpose Price took the values for styrene as $Q = 1.0$ and $e = -0.8$. Q and e values can then be obtained for all monomers that are copolymerizable with styrene. These monomers in their turn can serve as reference compounds for further determinations with other monomers that do not copolymerize with styrene. One of the main advantages of the so-called *Q,e* scheme is that the data can be presented in the form of a diagram instead of very complex tables of reactivity ratios.

Obviously the precision of this procedure is not very great, since the assumptions underlying the calculations of Q and e values can be regarded as best as semiquantitative. However, it has been shown that when the reactivity ratios are back-calculated from the *Q,e* values, quite good agreement is obtained with the experimental values, so that it is possible to make useful predictions of reactivity ratios for monomer pairs not previously investigated. On the other hand, it is questionable whether any theoretical conclusions should be drawn from the Q and e values concerning the behavior of different monomers. Thus, the e value of a monomer as a measure of the charge should be dependent on the nature of the solvent used for polymerization; but it has been shown, for example, that the copolymerization of styrene with methyl methacrylate in solvents of different dielectric constant (benzene 2.28, methanol 33.7, acetonitrile 38.8) give the same reactivity ratios, which should not really be the case if the foregoing assumptions are correct. A broadening of the basis of the *Q,e* scheme has therefore been suggested by various people. These further considerations permit somewhat deeper theoretical conclusions.

In most cases one of the two monomers is preferentially incorporated into the copolymer, so that the composition of the monomer mixture changes with increasing conversion, as also does the composition of the polymer chains. Therefore it is important, when determining reactivity ratios, to work at low conversions, so that at the end of the experiment the ratio of monomer concentrations is essentially the same as at the beginning. However, if high conversions are needed for preparative purposes, constant composition can be achieved by adding the more reactive monomer in a programmed manner (see Example 3.39).

The determination of the reactivity ratios requires a knowledge of the composition of the copolymers made from particular monomer mixtures; numerous analytical methods are available (see Sect. 2.3.2). In principle, it is possible to calculate r_1 and r_2, using Eq. 3.18, from the composition of only two copolymers that have been obtained from two different mixtures of the two monomers M_l and M_2. However, it

is more precise to determine the composition of the copolymers from several monomer mixtures and to calculate, for each individual experiment, values of r_2 that would correspond to arbitrarily chosen values of r_1 from the rearranged copolymerization equation:

$$r_2 = \frac{[M_1]}{[M_2]} \cdot \left\{ \frac{m_2}{m_1} \left(1 + \frac{[M_1]}{[M_2]} . r_1 \right) - 1 \right\} \tag{3.26}$$

r_2 is then plotted against r_1, for each experiment to obtain a series of lines intersecting at the actual values of r_2 and r_1. In practice the lines do not intersect precisely at a point so that r_1 and r_2 are taken as the center of the smallest area that is cut or touched by all the lines. The size of this area allows an estimate of the limits of error.

A simpler method for determining the reactivity ratios is that of Fineman and Ross, in which the copolymerization Eq. 3.18 is rearranged to:

$$\frac{F}{f} \cdot (f - 1) = r_1 \cdot \frac{F^2}{f} - r_2 \tag{3.27}$$

or

$$\frac{f - 1}{F} = -r_2 \cdot \frac{f}{F^2} + r_1 \tag{3.28}$$

where $f = \frac{m_1}{m_2}$ and $F = \frac{[M_1]}{[M_2]}$

$(F/f)(f–1)$ is plotted against (F^2/f) to give a straight line (Eq. 3.27), of slope r_1 and intercept $-r_2$ on the ordinate. Alternatively, a plot of $(f-1)/F$ against f/F^2 according to Eq. 3.28 gives a line of slope $-r_2$ and intercept r_1 on the ordinate. The limits of error of r_1 and r_2 can be determined from the scatter of the points by the method of least squares. Besides these two classical methods, a number of further publications has recently appeared concerning the evaluation of copolymerization data. Among these, worthy of mention are not only the method of Kelen and Tüdös which is a graphical linear procedure, and perhaps the most ambitious but also the most exact method of Tidwell and Mortimer.

Under the condition that the reaction capability is only affected by the nature of the last monomer unit of the growing polymer chain end (terminal model, Bernoulli statistics), the copolymerization equation can be transformed according to Kelen and Tüdös:

$$\eta = r_1 \cdot \xi - \frac{r_2 \cdot (1 - \xi)}{\alpha} \tag{3.29}$$

where α is a arbitrarily chosen constant ($\alpha > 0$). The variable ξ can only adopt values between 0 and 1; η is plotted against ξ to a straight line with $(-r_2/\alpha)$ as the ordinate ($\xi = 0$) and the reactivity ratio r_1 where $\xi = 1$. Choosing the constant as

the geometric middle of the smallest ($F_{\min}$) and the largest ($F_{\max}$) F value, a homogeneous distribution of the ξ-values of the interval (0.1) is achieved:

$$\alpha = \sqrt{F_{min} \cdot F_{max}} \tag{3.30}$$

Because Eq. 3.26 is based on the differential form of the copolymerization equation, it is strongly valid only for infinitely low conversions, but this cannot be realized in real life. For higher conversions one has to start with an integrated form of the copolymerization equation. Fortunately, Kelen and Tüdös developed an elegant method of iteration. It allows the use of the earlier suggested method without the loss of graphical clearness.

In the literature one can find extensive compilations of reactivity ratios for numerous monomer pairs. For evaluation of the copolymerization experiments and for calculating the reactivity ratios, there is now extensive software available.

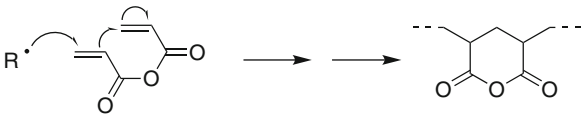
In copolymerizations of three monomers there are nine growing steps to be taken into account. From these, six reactivity ratios can be derived. They are difficult to obtain from terpolymerizations and are therefore taken from binary copolymerizations.

The statistical (random) copolymerization is an often used possibility in industry to change the properties of a polymeric compound. By incorporation of small amounts of a comonomer, the mechanical properties (hardness, stiffness) are almost maintained but other properties can intentionally be changed. Thus, by incorporation of small amounts of vinyl acetate into poly(vinyl chloride), the glass transition temperature is slightly lowered and an internal plasticization is achieved. The ability of synthetic fibers to take up dyes can be improved by incorporation of small amounts of comonomers with functional groups that confer a greater affinity towards organic dyestuffs. Polar groups also improve the printability of films and the stability of aqueous copolymer lattices. Significant differences in solubility between copolymers and the corresponding homopolymers are usually observed. The incorporation of larger amounts of comonomers leads then to larger changes in the mechanical properties. Thus, while polyethylene and isotactic polypropylene are crystalline polymers with the characteristic properties of a thermoplastic material, copolymers of ethylene and propylene are over a wide range of composition amorphous, rubber-elastic products.

Alternating copolymerization is a rare event. But when it occurs, the resulting copolymers exhibit unusual properties provided a 100% alternation was achieved (see Sect. 2.4)

Crosslinking copolymerization is also of great practical importance. Such copolymerization is achieved by taking compounds with two or more polymerizable double bonds and copolymerizing them with simple unsaturated monomers to form three-dimensional network materials. For example, crosslinked polystyrene is prepared by copolymerizing styrene with small amounts of divinylbenzene (Example 3.41). These crosslinked polymers are insoluble and nonfusible; however, depending on the degree of crosslinking, they swell to a limited extent in organic

solvents and find application, for example, in the preparation of ion-exchange resins (see Sect. 5.2). The copolymerization of unsaturated polyesters (made from maleic or fumaric acid) with styrene is also a crosslinking copolymerization. Some non-conjugated dienes can polymerize radically via a cyclization propagation step to yield linear chains containing cyclic repeat units (so-called cyclopolymerization). Thus, in the polymerization of acrylic anhydride this tendency to ring formation is so great that the intramolecular reaction occurs almost to the exclusion of the intermolecular crosslinking reaction:

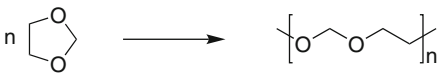


The rates and degrees of polymerizations in radical copolymerizations conform essentially to the same laws as for radical homopolymerization (see Sect. 3.1). Raising the initiator concentration causes an increase in the rate of polymerization and at the same time a decrease in the molecular weight; a temperature rise has the same effect. However, these assertions are valid only for a given monomer composition; in many cases the copolymerization rate depends very much on monomer composition and can pass through a pronounced minimum or maximum.

As already discussed for homopolymerization, radical copolymerizations can be carried out in bulk, in solution, and in dispersion. The composition of the copolymer obtained in suspension or emulsion may be different from that obtained by polymerization in bulk or solution if one of the monomers is more soluble in water than the other. In such a case the composition of the monomer mixture in the organic phase, or in the micelles where the copolymerization takes place, is not the same as the original composition.

There are no essential differences in experimental technique required for ionic copolymerizations, as compared with ionic homopolymerizations. However, the type of initiator and the solvent have a potential influence on the course of ionic copolymerizations as well as on the composition of the copolymers so that the optimum conditions for each monomer pair must be individually determined.

Finally, it should be mentioned that there exist two other routes for the synthesis of copolymers. First the partial chemical conversion of homopolymers (see Sect. 5.1), for example, the partial hydrolysis of poly(vinyl acetate). Secondly, by homopolymerization of correspondingly built monomers. An example for these macromolecular compounds, sometimes called pseudo-copolymers, is the alternating copolymer of formaldehyde and ethylene oxide synthesized by ring-opening polymerization of 1,3-dioxolane.



It should be pointed out that in both cases the copolymers cannot be obtained via "normal" copolymerization of the corresponding monomers.

Example 3.35 Copolymerization of Styrene with Methyl Methacrylate (Dependence on Type of Initiation)

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.

Styrene and methyl methacrylate are destabilized and dried. A mixture of 8.00 g (76.8 mmol) of styrene and 7.68 g (76.8 mmol) of methyl methacrylate is then prepared in a dry receiver (see Sect. 2.2.5.3) under nitrogen and kept in a refrigerator until required.

(a) Radical Copolymerization

16 mg (0.1 mmol) of AIBN are weighed into a 50 ml flask and the air is displaced by evacuation and filling with nitrogen, using a suitable adapter (see Sect. 2.2.5.3). 5 ml of the prepared monomer mixture are then pipetted in, the flask removed under a slight positive pressure of nitrogen and immediately closed with a ground glass stopper secured with springs. The flask is now placed in a thermostat at 60°C, after 4 h it is cooled quickly in ice, and the reaction mixture is diluted with 25 ml of toluene. The solution is added dropwise to 200–250 ml of petroleum ether; the copolymer precipitates in the form of small flakes that tend to stick together somewhat (for this reason methanol is less suitable as precipitant). The copolymer is filtered off into a sintered glass crucible, washed with petroleum ether, and dried to constant weight in vacuum at 50°C. Yield: 10–20% with respect to the monomer mixture.

(b) Anionic Copolymerization

The initiator solution is prepared as follows. Phenylmagnesium bromide is prepared from 12 g (76.5 mmol) of bromobenzene and 1.86 g of magnesium in 30 ml of pure dry THF (see Example 3.19). The apparatus must be carefully dried (all openings being protected by drying tubes); exclusion of atmospheric oxygen is not absolutely necessary. The magnesium should be converted as completely as possible by gentle warming towards the end of the reaction.

The copolymerization is carried out as follows: 5 ml of the monomer mixture (preparation see above) are pipetted into a 50 ml round-bottomed flask that has previously been flamed under vacuum and filled with nitrogen using an adapter. The flask is closed with a self-sealing closure (see Sect. 2.2.5.3) and, after cooling to −50°C, 2 ml of freshly prepared phenylmagnesium bromide solution are injected by means of a hypodermic syringe. After 90 min at −50°C the mixture is diluted with 25 ml of toluene and the copolymer precipitated by dropping the solution into 200 ml of methanol containing about 10 ml of 2 M hydrochloric acid or sulfuric acid. Further treatment is as described under (a). Yield: 10–20% with respect to the monomer mixture.

The anionic polymerization can only be carried out at low temperature, since at higher temperature the Grignard compound can also react with the ester group of methyl methacrylate.

(c) Cationic Copolymerization

A 100 ml flask is fitted with an adapter (see Sect. 2.2.5.3), flamed under vacuum using an oil pump, and filled with nitrogen. 5 ml of the prepared monomer mixture

(see above) are pipetted in, followed by 40 ml of an initiator solution prepared from 50 ml of pure dry nitrobenzene (see Example 3.40) and 300 mg (2.25 mmol) of anhydrous aluminum trichloride. The flask is now removed from the adapter under a slight positive pressure of nitrogen and immediately closed with a ground glass stopper. The flask is briefly shaken and allowed to stand at room temperature for 1 h. The solution is then dropped into methanol and the copolymer worked up as described above. Yield: 40–50% with respect to the monomer mixture.

Cationic copolymerization precedes under the above conditions at such a rate that even at much lower initiator concentration almost half the monomer mixture is polymerized in less than 1 h. The reaction comes to an end after 50% conversion since with cationic initiators, the copolymer consists almost entirely of styrene units.

(d) Characterization of the Copolymers

From the behavior on precipitation of the copolymers prepared by the three different methods, it may already be suspected that, in spite of the common starting mixture, one is dealing with different kinds of polymer. In order to prove this the following solubility tests are carried out.

50 mg of each of the three copolymers, as well as a mixture of equal parts polystyrene and poly(methyl methacrylate), are warmed with about 5 ml of the following solvents:

1. Mixture of acetone and methanol (volume ratio 2:1),
2. Acetonitrile,
3. Mixture of cyclohexane and toluene (volume ratio 4:1).

If any material remains undissolved, the supernatant liquid is decanted and dropped into methanol in order to precipitate the dissolved portion.

Solvents 1 and 2 are known to be good solvents for poly(methyl methacrylate); solvent 3 readily dissolves polystyrene. The solubility tests show that the radically polymerized sample is insoluble in all three solvents. The solubility is thus different from that of both poly(methyl methacrylate) and polystyrene. The anionically polymerized product dissolves on warming in the acetone/methanol mixture and also in acetonitrile; it is insoluble in cyclohexane/toluene. The solubility is thus similar to that of poly(methyl methacrylate). For the cationically initiated polymerization the product is only slightly soluble in acetone/methanol, insoluble in acetonitrile, but very readily soluble in cyclohexane/toluene. The solubility thus resembles that of polystyrene.

In addition to the solubility tests, the structures of the polymers can be determined easily from the IR and ^{1}H-NMR spectra.

Example 3.36 Radical Copolymerization of Styrene with 4-Chlorostyrene (Determination of the Reactivity Ratios)

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.

20 mg (0.12 mmol) of AIBN are placed in each of nine test tubes fitted with joints, together with the approximate amounts of destabilized styrene and

Table 3.11 Test series for Example 3.36

Batch	Styrene		*p*-Chlorostyrene	
#	[g]	[mmol]	[g]	[mmol]
1	3.0	29	0	0
2	2.6	25	0.4	3
3	2.3	22	0.7	5
4	1.6	15	1.4	10
5	1.1	11	1.9	14
6	0.7	7	2.3	17
7	0.3	3	2,7	19
8	0.1	1	2.9	21
9	0	0	3.0	22

4-chlorostyrene indicated in Table 3.11, weighed accurately to three decimal places. If the samples cannot be polymerized on the same day they must be stored in a refrigerator.

The vessels are cooled in a methanol/dry ice bath, evacuated through an adapter (see Sect. 2.2.5.2) and, after thawing, filled with nitrogen; this procedure is repeated twice more. The tubes are now withdrawn from the adapter under a slight positive pressure of nitrogen, immediately closed with ground glass stoppers (secured with springs), and brought to 50°C in a thermostat. After 8 h the tubes are quickly cooled, the contents diluted with 5 ml of toluene and dropped into about 80 ml of stirred methanol. The copolymers are filtered off, reprecipitated twice and dried to constant weight in vacuum at 50°C. The yield under these conditions is about 300 mg (10%).

The chlorine content of the dried copolymers can be determined gravimetrically according to the method of Wurtzschmitt, and their composition derived. The copolymerization diagram is drawn and the reactivity ratios are calculated.

Example 3.37 Radical Copolymerization of Styrene with Acrylonitrile (Azeotropic Copolymerization)

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 following experiment is designed to show the independence of the composition of a copolymer on the yield in the copolymerization of an "azeotropic" mixture. 3.23 g (31 mmol) of styrene, 1.01 g (19.0 mmol) of acrylonitrile, and 12.1 mg (0.05 mmol) of BPO are weighed into each of five tubes with joints, degassed, and polymerized under nitrogen at 60°C. The tubes are removed successively from the thermostat after 2, 4, 6, 8, and 10 h, and immediately quenched in a cold bath. The contents are dissolved in DMF. This can best be done as follows: The samples that are still fluid are washed out with 20 ml of DMF to which a little hydroquinone has been added; where the samples have solidified the tubes are broken open and the polymer is dissolved in 500 ml of DMF with vigorous stirring.

The copolymers are precipitated by dropping into 500 ml or 1 l of methanol, respectively, filtered and dried. The yield in wt% is plotted against polymerization time; the reasons for the deviation from linearity should be considered. The copolymers are reprecipitated once more from DMF into methanol, washed several times with methanol and dried. The compositions are determined by nitrogen analysis or spectroscopically.

Example 3.38 Radical Copolymerization of Styrene with Maleic Anhydride (Alternating Copolymerization)

300 ml of distilled toluene, 10.4 g (0.1 mol) of destabilized styrene (see Example 3.1), 9.8 g (0.1 mol) of pure maleic anhydride, and 0.1 g (0.4 mmol) of dibenzoyl peroxide are placed in a 500 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) and stirred at room temperature until a clear solution is obtained. The reaction mixture is continuously stirred and heated to boiling on a water bath; the copolymer gradually precipitates. After 1 h the mixture is cooled, the solid polymer filtered off, and dried to constant weight in vacuum at 60°C. Yield: 19–20 g.

The 1:1 copolymer so obtained has alternating monomeric units of styrene and maleic anhydride. This can be verified by NMR spectroscopy. It is insoluble in carbon tetrachloride, chloroform, toluene, and methanol, but soluble in THF, 1,4-dioxane, and DMF. It can be hydrolyzed to a polymeric acid (see Example 5.3)

Example 3.39 Radical Copolymerization of Methacrylic Acid with n*-Butyl Acrylate in Emulsion (Continous Monomer Addition)*

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.

200 ml of distilled water are filled into a 500 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) three-necked flask equipped with dropping funnel, stirrer, thermometer, and nitrogen inlet tube. Then, 400 mg potassium peroxodisulfate (1 wt%) and 400 mg dodecyl sulfate are added. Oxygen is removed by passing nitrogen through the solution and heating to 80°C. Under a slight flow of nitrogen, 40 ml of a mixture made from 16 g methacrylic acid and 24 g *n*-butyl acrylate are added dropwise over a period of 1 h. A slight increase of temperature is observed. The contents of the flask appear milky turbid. Looking from the side, a pale blue color, induced by daylight scattering, is observed. On the other hand, a reddish color is observed by direct view from a high intensity, colorless background illumination. The copolymer can be isolated by adding dropwise the emulsion to sodium chloride solution or to dilute hydrochloric acid. Additionally, the emulsion should become almost clear with a strong increase of viscosity in alkaline medium. From this aqueous solution, the copolymer can be precipitated by the addition of Ca salts. Yield: quantitative.

Please note: due to differences in the copolymerization parameters of *n*-butyl acrylate and methacrylic acid a continuous addition of the monomer mixture is necessary in order to achieve a homogeneous composition of the copolymer product.

Copolymer emulsions with free carboxylic acid groups are useful, for example, for paper refinement as well as for coating of polar particles like pigments, fillers, or fibers. For this purpose, the particles to be coated are added under stirring to the weakly alkaline emulsion. Then, polyvalent salts or acids are added to separate out the copolymer dispersion which deposits almost quantitatively on the surface of the particles.

Example 3.40 Cationic Copolymerization of 1,3,5-Trioxane with 1,3-Dioxolane (Ring-Opening Copolymerization)

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.

1,3,5-Trioxane and 1,3-dioxolane are purified as in Example 3.24 or by refluxing for a day over calcium hydride followed by fractional distillation. Nitrobenzene is refluxed over P_4O_{10} and distilled.

90 g (1 mol) of 1,3,5-trioxane and 9 g (0.12 mol) of 1,3-dioxolane are dissolved in 300 ml of nitrobenzene in a 500 ml flask that has been flamed under vacuum and filled with dry nitrogen or air. 0.18 ml (1.4 mmol) of boron trifluoride etherate (dissolved in 10 ml of nitrobenzene) are injected through a self-sealing closure (see Sect. 2.2.5.2). The mixture is now warmed to 45°C. The copolymer begins to precipitate within a few minutes. After 2 h the product is stirred with acetone, filtered off and washed well with acetone. In order to remove initiator and nitrobenzene residues, the polymer is boiled for 30 min with 1 l of ethanol, containing 1 wt% of tributylamine. It is then filtered off, washed with acetone, and sucked dry. About 90 g of a pure white copolymer are obtained containing about 30 $–O–CH_2–$ units for every $–O–CH_2–CH_2–$ unit. It melts at 156–159°C and has a molecular weight of about 30,000 (corresponding to an hsp/c value of about 0.04 l/g in DMF at 140°C). The thermal stability at 190°C (see Example 5.13) is compared with that of a homopolymer of 1,3,5-trioxane (see Example 3.24).

Example 3.41 Radical Copolymerization of Styrene with 1,4-Divinylbenzene in Aqueous Suspension (Crosslinking Copolymerization)

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.

Styrene and 1,4-divinylbenzene (the latter as 50–60% solution in ethylbenzene) are destabilized and distilled as described in Example 3.1.

A standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) fitted with a stirrer (preferably with revolution counter) is evacuated and filled with nitrogen three

times. 250 mg of poly(vinyl alcohol) are placed in the flask (see Example 5.1) and dissolved in 150 ml of deaerated water at 50°C. A freshly prepared solution of 0.25 g (1.03 mmol) of dibenzoyl peroxide in 25 ml (0.22 mmol) of styrene and 2 ml (7 mmol) of 1,4-divinylbenzene is added with constant stirring in order to produce an emulsion of fine droplets of monomer in water. This mixture is heated to 90°C on a water bath while maintaining a constant rate of stirring and passing a gentle stream of nitrogen through the reaction vessel. After about 1 h (about 5% conversion) the crosslinking becomes noticeable (gelation). Stirring is continued for another 7 h at 90°C, the reaction mixture then being allowed to cool to room temperature with stirring. The supernatant liquid is decanted from the beads which are washed several times with methanol and finally stirred for another 2 h with 200 ml of methanol. The polymer is filtered off and dried overnight in vacuum at 50°C. Yield: practically quantitative. The crosslinked copolymer of styrene and 1,4-divinylbenzene so obtained can be used for the preparation of an ion-exchange resin (see Examples 5.9 and 5.10).

The swellability is determined by placing 1 g of the dried polymer in contact with toluene for 3 days in a closed 250 ml flask. The swollen beads are collected on a sintered glass filter (porosity G1), suction is applied for 5 min and the filter immediately weighed. The percentage increase in the weight of the beads can then be calculated. The size of the swollen and unswollen beads can be compared under the microscope.

Example 3.42 Copolymerization of Styrene with Methyl Acrylate (Internal Plasticization)

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.

16.4 mg (0.1 mmol) AIBN are added to 4 ml of toluene in a thick-walled test tube with ground joint. Then, 0.01 mol of a monomer mixture consisting of styrene and methyl acrylate are added according to Table 3.12. To remove oxygen, the solution is bubbled with nitrogen via a Pasteur pipette for 30 s. The test tubes are sealed and maintained at 65°C for 3 h in a thermostatted water bath. The polymerization is terminated by cooling the test tubes in a cooling bath (ice/water). Then, 5 ml of toluene are added to the content of each test tube.

Samples 1 and 2 are precipitated by adding 50 ml of methanol containing 3 drops of concentrated hydrochloric acid. All other samples are precipitated by the addition of *n*-hexane. All of the precipitants should be cooled with an ice/water mixture. The yields have to be calculated.

To investigate the internal plasticization of polystyrene ($T_g = 105°C$) by insertion of methyl acrylate ($T_g = 4°C$), the samples are run on a DSC. Therefore, approximately 15 mg of each of the well dried polymers are weighed into small aluminum pans and measured by two heat-cool runs in a DSC apparatus. The glass transition is found as a characteristic jump in the heat capacity in the system. The glass transition temperature is evaluated after the second heating from the DSC plot.

Table 3.12 Test series for Example 3.42

Sample#	$\frac{[M_{MA}]}{[M_{MA}]+[M_S]}$	MA [g]	S [g]
1	0.00	0	5.208
2	0.10	0.430	4.687
3	0.25	1.076	3.906
4	0.35	1.507	3.385
5	0.45	1.937	2.864
6	0.55	2.367	2.343
7	0.65	2.798	1.823
8	0.75	3.228	1.302
9	0.85	3.659	0.781
10	0.90	3.874	0.521
11	0.95	4.089	0.260
12	1.00	4.305	0

Example 3.43 Three-Step Synthesis of Core/Double Shell Particles of Methyl Methacrylate/Butyl/Acrylate/Methyl Methacrylate

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 concept of core/shell impact modifiers for thermoplastic polymers (see Sect. 5.51).

(a) PMMA Core Synthesis by Crosslinking Copolymerization

In a reaction vessel equipped with mechanic propeller stirrer, argon inlet, and reflux condenser an emulsion is prepared of distilled water (300 ml), methyl methacrylate (MMA; 9.5 g), allyl methacrylate (ALMA; 0.5 g) and sodium dodecyl sulfate (SDS; 50 mg). The emulsion is heated (75°C), and ammonium peroxodisulfate (APS; 0.6 g) dissolved in water (5 ml) is added. After 50 min a mixture of MMA (28.5 g) and ALMA (1.5 g) is added dropwise (within 1 h). Subsequently, a "monomer emulsion" formed by water (250 ml), SDS (1.1 g), MMA (252 g), ALMA (8 g), and APS (0.5 g) is added continuously (within 225 min) to the reaction mixture. After complete addition, stirring is continued for further 1 h at 75°C and for further 2 h at 85°C. Finally, the emulsion is allowed to cool down to room temperature.

(b) Synthesis of the First (Elastomeric) Shell via Crosslinking Copolymerization

In a reaction vessel, the above PMMA latex (163 g) and water (175 g) are stirred and heated (75°C). A solution of APS (0.5 g) in water (5 ml) is added. Then, a mixture of butyl acrylate (BA) and ALMA (0.4 g) is added continuously (within 30 min). Subsequently, a "monomer emulsion" of water (90 ml), SDS (0.57 g), BA (120.5 g) ALMA (2.5 g), and APS (0.3 g) is added continuously, within 200 min. After complete addition, the polymerization is finished by stirring the mixture for further 1 h at 75°C and for further 2 h at 85°C. Finally, the mixture is allowed to cool down to room temperature.

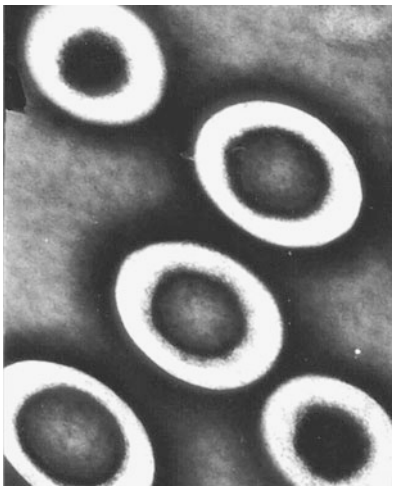


Fig. 3.5 TEM image of a cut through a SAN matrix with incorporated core/double shell particles. dark core: PMMA; bright area: PBA shell; diameter of the particles of the first shell: about 220 nm; the second PMMA shell is compatible with SAN matrix, therefore the contrast is very weak (Details see Bibliography)

(c) Synthesis of the Second (Thermoplastic) Shell by Homopolymerization of MMA

In a reaction vessel, the above PMMA-PBA latex (400 g) and water (75 ml) are stirred and heated to 75°C. A solution of APS (0.35 g) in water (5 ml) is added. Then, MMA (10 g) is added to the reaction mixture slowly, within 45 min. followed by a "monomer emulsion" of water (35 ml), SDS (0.25 g), MMA (50 g) and APS (0.15 g) which is added slowly and continuously as well (within 2 h). After complete addition, stirring is continued for a further 1 h at 75°C and for further 2 h at 85°C. Finally, the emulsion is allowed to cool down to room temperature.

Isolation of the polymer particals see Example 3.2 and 3.3.

Figure 3.5 shows a TEM picture of the core/double shell latex particles incorporated into an styrene/acrylonitrile (SAN) copolymer matrix (thin cut through the particle-filled matrix). The particles are very homogeneous in size and can also be used to prepare artifical opals.

Example 3.44 Radical Copolymerization of Butadien with Styrene in Emulsion

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: All work is to be undertaken behind a protective screen; hands should also be protected with safety gloves in order to avoid cuts should one of the flasks explode (internal pressure 3 bar).

Monomeric styrene is destabilized (see Example 3.1) and distilled into a suitable receiver (see Sect. 2.2.5.3) under nitrogen. Butadiene from a cylinder is condensed under nitrogen atmosphere into a trap cooled in a methanol/dry ice bath. A 500-ml pressure bottle is evacuated and filled with nitrogen. A solution of 5 g of sodium oleate (or sodium dodecyl sulfate) is then made up in 200 ml of deaerated water, and 0.25 g (0.93 mmol) of potassium peroxodisulfate is added; the mixture is shaken until everything has dissolved. The pH is adjusted to a value of 10–10.5 with dilute sodium hydroxide, 30 g (0.29 mol) of styrene containing 0.5 g of dodecylmercaptane as regulator, and 70 g (1.30 mol) of butadiene are added under nitrogen, and the bottle is sealed. The best procedure is to cool the pressure bottle in an ice/salt mixture, place it on a balance scale and then, under a hood, pour in a small excess of butadiene from the cold trap; the excess butadiene is allowed to evaporate on the balance until the correct weight is reached. The sealed bottle is allowed to warm to room temperature behind a safety screen, wrapped with a towel and vigorously shaken to emulsify the contents. It is then placed in a bath at 50°C and should be shaken or rotated continuously. (If a suitable apparatus is not available, the bottle can be shaken again vigorously after 1 h). The bottle is held at 50°C for 15 h behind a safety screen, then allowed to cool to room temperature and finally cooled in ice. It is weighed again to check whether any butadiene has escaped. The latex is then slowly poured into about 500 ml of stirred ethanol contained in a beaker under a hood; to the ethanol has previously been added 2 g *N*-phenyl-β-naphthylamine, this being the amount required to protect the copolymer against oxidation. Most of the unconverted butadiene evaporates and the copolymer is obtained as loosely coherent crumbs that are dried for 1–2 days in vacuum at 50–70°C. The composition of the copolymer can be calculated from the analytically determined double bond content or from the spectroscopically determined content of styrene units (see Sect. 2.3.2); the arrangement of the butadiene monomeric units can be found from the IR spectrum (see Example 3.21). By vulcanization (see Example 5.8) the copolymer can be converted into an insoluble, highly elastic product. It finds application in tires.

Example 3.45 Radical Copolymerization of Butadiene with Acrylonitrile in Emulsion

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.

Monomeric acrylonitrile is distilled under nitrogen into a suitable receiver (see Sect. 2.2.5.3). Butadiene from a cylinder is condensed under nitrogen atmosphere into a trap cooled in a methanol/dry ice bath.

As described in Example 3.44, a mixture of 10 g (0.19 mol) of acrylonitrile containing 0.1 g dodecylmercaptane as regulator and 25 g (0.46 mol) of butadiene is polymerized in 50 ml of a 5% aqueous solution of sodium oleate (or sodium dodecyl sulfate) containing 0.25 g (0.93 mmol) of potassium peroxodisulfate as initiator. After 18 h the pressure bottle is allowed to cool to room temperature and is finally cooled in ice. It is now weighed again to confirm that no butadiene has been lost by leakage. The bottle is carefully opened, the latex poured into a beaker and

Table 3.13 Test series for Example 3.46

	Batch 1	Batch 2	Batch 3	Batch 4
Distilled water	23 ml	23 ml	23 ml	23 ml
Emulsifier[a]	684 mg	450 mg	684 mg	594 mg
Methacrylic acid	756 mg (8.8 mmol)	756 mg (8.8 mmol)	756 mg (8.8 mmol)	1.26 g (14.6 mmol)
Styrene	31.5 g (0.30 mol)	31.5 g (0.30 mol)	40.95 g (0.39 mol)	31.5 g (0.30 mol)
Butyl acrylate	31.5 g (0.27 mol)	31.5 g (0.27 mol)	22.05 g (0.17 mol)	31.5 g (0.27 mol)

[a]Commercial alkylbenzene sulfonic acid sodium salt (linear C10–C13 alkyl chains, 70% in water), (e.g., from Sasol)

0.5 g of *N*-phenyl- β-naphthylamine stirred in as antioxidant. A solution of 5 wt% of sodium chloride in 2% sulfuric acid is now added dropwise with stirring until the copolymer flocculates. It is filtered off, stirred vigorously with water several times in a beaker, filtered again and dried in vacuum at 65–70°C. The composition of the copolymer is determined from the nitrogen content determined according to the Kjeldahl method or from the double bond content. The arrangement of the butadiene monomeric units is found by IR spectroscopy (see Example 3.21).

Copolymers of butadiene and acrylonitrile are soluble in aromatic or chlorinated hydrocarbons but insoluble in aliphatic hydrocarbons. Therefore they find use in oil-resistant rubber articles (hoses, sealings etc.)

Example 3.46 Preparation of a Styrene/Butyl Acrylate/Methacrylic Acid Terpolymer Dispersion (Influence of Emulsifier)

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 following experiment should demonstrate the influence of particle size and minimal film-formation temperature (which is connected with the glass transition temperature and therefore with the chemical structure of the polymers) on the properties of films, prepared from aqueous dispersions.

Four 250 ml standard apparatus (round bottom flask, several inlets for stirrer, reflux condenser, nitrogen flux or vaccum, thermometer, heating bath) are filled each with 38 ml of distilled water and 405 mg (1.8 mmol) ammonium peroxodisulfate. To the fourth flask, additionally 90 mg of an alkylbenzene sulfonic acid sodium salt emulsifier (linear C10–C13 alkyl chains, 70% in water) are added. After reaching an internal temperature of 80°C, 3 g of a monomer emulsion (prepared according to Table 3.13) are added to each of the four batches. Within an induction phase of 15 min the reactions start. This is visualized by the pale blue coloration of the content of the flasks. Then the remaining monomer emulsion is added over a period of 3 h. The internal temperature has to be maintained at 80°C during the whole reaction. After all monomer emulsion has been added, the batches are heated at 80°C for another 30 min. Then, the flasks are allowed to cool to room temperature. Now the reaction mixtures are adjusted to pH 8.5 by addition of 5% NaOH solution.

The contents of batch 2 and batch 4 are spread on a glass plate and dried at 35°C for 24 h. Then, the glass plates with the dried films are placed into water. Run 2 (particle size approx. 270 nm) becomes turbid very rapidly, whereas run 4 (particle size approx. 150 nm) stays clear.

Batch 1 and batch 3 are spread on a glass plate and dried at room temperature. Batch 1 gives a clear film without cracks (minimal film-forming temperature below room temperature) whereas batch 3 gives no coherent, crack-free film (minimal film-forming temperature above room temperature).

3.4.2 Block and Graft Copolymerization

Conventional copolymerizations yield macromolecules mostly with random distribution and only very seldom with alternating distribution of the monomer units. In order to synthesize block or graft polymers, special methods must be used, of which some are described in the following sections.

3.4.2.1 Block Copolymers

In the simplest case, block copolymers consist of successive series (blocks or segments) of A and B units. Depending on the number of linked blocks, one distinguishes diblock, triblock and multiblock copolymers:

diblock (A-A-A) – (B-B-B)

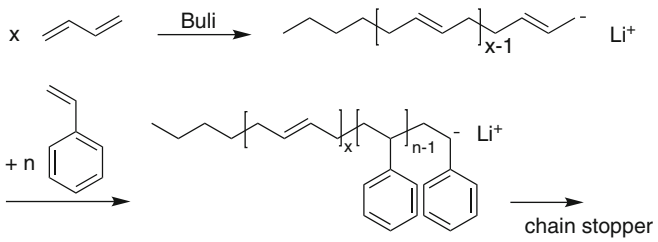
triblock (A-A-A) – (B-B-B) – (A-A-A)

multiblock (-A-A-A) – (B-B-B) – (A-A-A) – (B-B-B-). . .

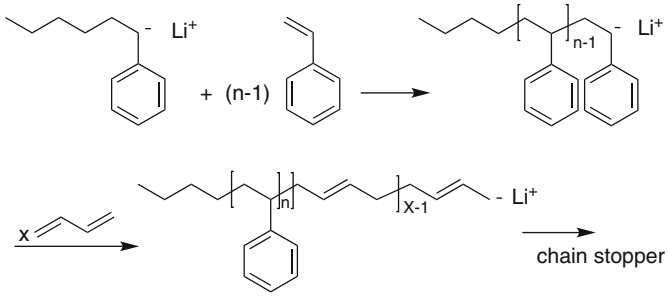
For the synthesis of block copolymers chain addition polymerization (ionic or radical) as well as condensation polymerization and stepwise addition polymerization can be used.

Well developed is the *anionic polymerization* for the preparation of olefin/diolefin – block copolymers using the techniques of "living polymerization" (see Sect. 3.2.1.2). One route makes use of the different reactivities of the two monomers in anionic polymerization with butyllithium as initiator. Thus, when butyllithium is added to a mixture of butadiene and styrene, the butadiene is first polymerized almost completely. After its consumption stryrene adds on to the living chain ends, which can be recognized by a color change from almost colorless to yellow to brown (depending on the initiator concentration). Thus, after the styrene has been used up and the chains are finally terminated, one obtains a two-block copolymer of butadiene and styrene:

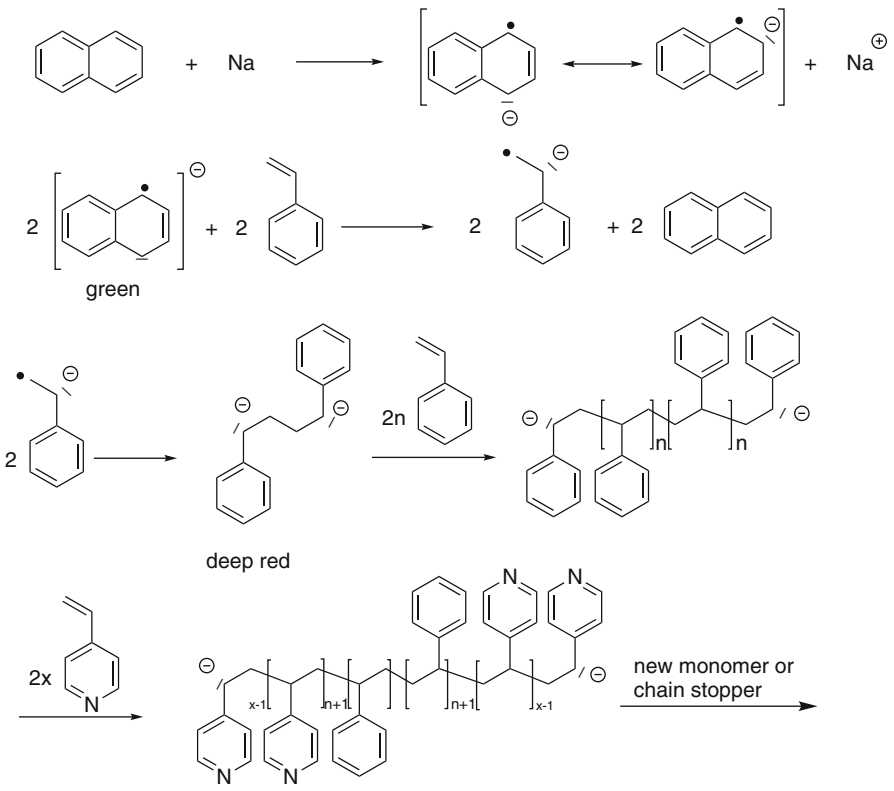
Oxidative degradation by splitting off the double bonds in the butadiene blocks allows the styrene blocks to be isolated. The degradation of the chains can be followed by molecular weight determinations or viscosity measurements (see Examples 3.47, 5.12, 5.14, and 5.15).



A second route is termed sequential anionic polymerization. More recently, also controlled radical techniques can be applied successfully for the sequential preparation of block copolymers but still with a less narrow molar mass distribution of the segments and the final product. In both cases, one starts with the polymerization of monomer A. After it is finished, monomer B is added and after this monomer is polymerized completely again monomer A is fed into the reaction mixture. This procedure is applied for the production of styrene/butadiene/styrene and styrene/isoprene/styrene triblock copolymers on industrial scale. It can also be used for the preparation of multiblock copolymers.

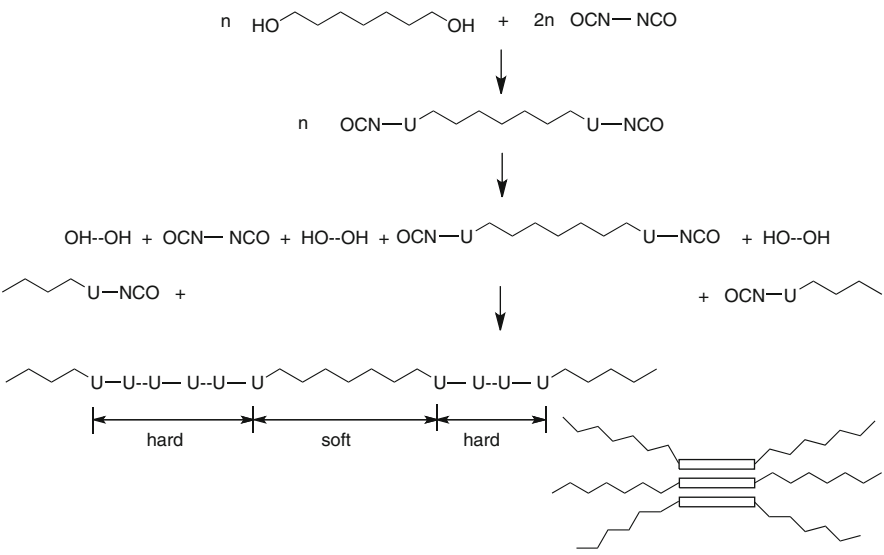


A variation of the sequential anionic polymerization is the use of dianions as initiator, like sodium naphthalene. One starts with the polymerization of monomer A. Then monomer B is fed to the reaction mixture which adds immediately to the "living" anions at each end of block A and thus leads to a triblock copolymer with an A-middle block and two B-outer blocks. This triblock copolymer is still "alive" and repetition of the above procedure results in a multiblock copolymer (see Example 3.49).



Condensation polymerization and stepwise addition polymerization are, for example, applied for the preparation of block polyesters. The synthesis concepts are different from those of chain polymerization in that at least one "monomer" is an oligomer with one or two functional end groups, for example polytetrahydrofurane with a molecular weight of several hundred and OH–end groups (see Example 3.23). If this oligomer partially replaces butandiol in the condensation polymerization with terephthalic acid (compare Examples 4.1 and 4.2), a poly(ether ester) is obtained with hard polyester segments and soft polyether segments and with the properties of a thermoplastic elastomer.

Stepwise addition polymerization is used in the preparation of segmented polyurethanes (compare Sect. 4.2.1), e.g., poly(ester ether) urethanes which also find applications in thermoplastic elastomers. Here, both blocks are preformed separately and are linked together by reaction with isocyanates:



In segmented polyurethanes as well as in many other block copolymers incompatible polymer segments are combined. This incompatibility of different CRUs means that block copolymers often form multiphase systems (see TEM-picture in Sect. 2.3.5.14) that are distinguished by special properties. They are already used in so-called thermoplastic elastomers (TPE). They consist of thermoplastic hard segments and of rubber-elastic soft segments, for example, styrene/butadiene/styrene block copolymers or segmented polyurethanes. They are not crosslinked via covalent bonds, but by formation of domains by the hard segments. On the other hand, they fulfill the requirements for rubber-elastic properties. This physical crosslinking is thermally reversible, so that these elastomers – in contrast covalently crosslinked elastomers – can be thermally processed. It must be stressed that in case of styrene/butadiene/styrene, the triblock composition is absolutely mandatory for obtaining TPE properties. Both styrene blocks must be terminal.

Example 3.47 Preparation of a Butadiene/Styrene Diblock Copolymer

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

A 500 ml two-necked flask, fitted with ground glass stopper and tap, is dried for 2 h at 110°C. Into the still warm flask are distilled 200 ml of toluene under nitrogen, a moderate stream of nitrogen (3 l/min) is then being passed through the solvent for 3 min, using a delivery tube with a sintered glass disk. The flask is immediately closed with a self-sealing rubber cap and the pressure reduced to 0.3–0.5 bar nitrogen. With the aid of a dry hypodermic syringe, 6 g (6.7 ml) of dry, stabilizer-free styrene are added, together with 14 g (23 ml) of dry, stabilizer-free butadiene from a vessel provided with an injection needle (the materials must be cooled to a suitable temperature). The flask is well shaken and placed in a suitable

wire basket. Finally, as initiator, 8–10 ml of a 0.1 M solution of butyllithium in hexane are injected with a hypodermic syringe. The necessary initiator concentration depends on the water content of the reaction mixture and must be determined by trial and error.

The flask in its wire basket is placed in a water bath at 50°C. After 5 h the polymerization has finished and the color of the solution is then yellow. After cooling to room temperature, 1 ml of 2-propanol is injected and the excess pressure released by insertion of an injection needle. The flask is opened, 0.5 g of 2,6-di-*tert*-butyl-4-methylphenol added as stabilizer, and the polymer precipitated in a three-fold volume of methanol. The viscous product is dried in vacuum at 50°C. The yield is quantitative. The limiting viscosity number is determined in toluene at 25°C.

(b) Oxidative Degradation of the Diblock Copolymer of Butadiene and Styrene

6.0 g of the polymer are swollen or dissolved in 600 ml of 1,2-dichlorobenzene at room temperature, heated for 10 min at 120°C and then cooled to 95°C. 90 ml of *tert*-butyl hydroperoxide (80%) are added, the temperature brought back to 95°C, and 15 ml of a solution of 0.08 wt% of osmium tetroxide in distilled toluene is then added. The temperature rises a few degrees. After 20 min the reaction mixture is cooled to room temperature and shaken three times in a separating funnel with 600 ml of a mixture of 1,500 ml of methanol and 500 ml of water. The lower phase is the 1,2-dichlorobenzene solution. The 1,2-dichlorobenzene is distilled off under vacuum at 60°C (oil pump) and the residue weighed. About 2.4 g of a deep yellow, highly viscous mass are obtained. This can be decolorized by taking it up in toluene and warming with activated charcoal. The polymer then precipitates well in methanol. The reaction products of the degraded butadiene sequences, and also the styrene sequences having a molecular weight less than 500, are removed by this treatment. The limiting viscosity number of the residue is now determined in toluene at 25°C and the molecular weight of the styrene sequences determined. The IR spectrum of the residue from degradation corresponds very closely to that of polystyrene. The amount of styrene sequences is only slightly less than the amount of styrene in the block copolymer since only a small proportion of the styrene is present within short chain lengths containing both monomeric units, which form the junction points of the two-block sequences.

Example 3.48 Preparation of a t*-Butyl Methacrylate/Styrene/*t*-Butyl Methacrylate (→ Acrylic Acid/Styrene/Acrylic Acid) Triblock Copolymer*

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

General: The triblock copolymer is prepared by anionic polymerization. As in Example 3.19, the greatest care must be taken to exclude air and moisture. Also all transfers have to be carried out under rigorous exclusion of air, either in a glove box or using Schlenck techniques. Tetrahydrofurane is dried as described in Example 3.19.

The monomers are dried for 24 h over calcium hydride and then distilled under vacuum at room temperature. 1,1-Diphenyl ethylene (DPE) is dried by dropwise addition of *n*-butyl lithium until a stable dark-red color appears. The DPE is then distilled in vacuo at 120°C. Naphthalene (best purity) can be used as obtained.

Lithium naphthalene is prepared by adding, under argon, lithium metal to a solution of naphthalene (3 wt%) in THF (1 equiv. Li with respect to naphthalene). The mixture is stirred for 7 h at room temperature until all lithium has disappeared and an intensively green solution is obtained. The true concentration of the thus obtained solution of lithium naphthalene can be determined by carrying out a model styrene polymerization and determining the resulting degree of polymerization. When carefully sealed and put under an atmosphere of argon, this solution is stable for several months at −30°C.

Lithium naphthalene (0.5 mmol) in THF is added quickly to a cooled (−78°C) solution of styrene (5 g) in THF (50 ml). The mixture immediately turns orange. Stirring at −78°C is continued for 30 min. A small sample may be taken from the mixture with a syringe and quenched in degassed methanol. This sample can be used to measure the molar mass of the styrene block (by GPC). The mixture is allowed to warm to −18°C, then a solution of 1,1-diphenylethylene (108 mg, 0.6 mmol) in THF (1 ml) is added whereupon the color immediately changes to an intensive red. Now *tert*-butylmeth-acrylate (*t*-BMA; 5 g) is added quickly. The color disappears, and stirring is continued at −18°C for further 60 min. Degassed methanol (1 ml) is added to terminate the reaction. After allowing the mixture to warm to room temperature, the obtained polymer is precipitated by pouring the whole mixture into methanol (500 ml). The precipitate is filtered off, washed with methanol, and dried in vacuo to constant weight. The molar mass of this triblock copolymer may again be measured by GPC.

Hydrolysis of the poly(*t*-BMA) blocks is achieved by dissolving the triblock copolymer (1 g) in dioxane (100 ml) at room temperature. Conc. hydrochloric acid (1.5 ml) is added, and the resulting mixture is heated (100°C) and stirred for 18 h. After cooling to room temperature the solution is concentrated down to approx. 10 ml which are poured into cold (0°C) diethylether (100 ml). The precipitate is filtered off, washed with methanol and dried in vacuo to constant weight. The result is an acrylic acid-*b*-styrene-*b*-acrylic acid triblock copolymer.

The parent triblock copolymer t-BMA-*b*-S-*b*-t-BMA and the hydrolyzed triblock copolymer acrylic acid–*b*-styrene-*b*-acrylic acid should be analyzed by IR spectroscopy. The ester and acid carbonyl peaks indicate the saponification (see Sect. 2.3.2.2)

The two products differ in polarity and thus in hydrophilicity. The acrylic acid-*b*-styrene-*b*-acrylic acid triblock copolymer exhibits amphiphilic properties and forms an emulsion in dilute sodium hydroxide solution where the acid groups are neutralized.

Example 3.49 Preparation of a Multiblock Copolymer of 4-Vinylpyridine and Styrene by Anionic Polymerization

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 block copolymer is prepared by anionic polymerization. As in Example 3.19, the greatest care must be taken to exclude air and moisture.

Monomeric styrene is destabilized as in Example 3.1 and pre-dried with calcium chloride. The monomer is now allowed to stand over calcium hydride for 24 h and then distilled under reduced pressure of nitrogen into a previously flamed out

Schlenk tube. Pure 4-vinylpyridine is distilled twice over KOH pellets in vacuum. It is then vacuum distilled under nitrogen through a column packed with Raschig rings into a previously flamed out Schlenk tube (bp 62°C/12 Torr). The closed Schlenk tubes containing the monomers are stored in a refrigerator until required. The preparation of the initiator solution (sodium naphthalene) is described in Example 3.19.

The polymerization is carried out as follows: a Schlenk tube that has been flamed out and filled with nitrogen, is charged with 50 ml of pure THF and 1 ml of sodium naphthalene (see Example 3.19). Using a nitrogen-filled syringe, 4.6 ml (40 mmol) of styrene are added to this solution at room temperature with vigorous agitation, while nitrogen is passed through the tube. The closed tube containing the red polymerizing mixture is allowed to stand for 15 min at room temperature.

To 5.3 g of 4-vinylpyridine is added to THF up to a volume of 50 ml; 5 ml of this solution (containing 5 mmol 4-vinyl pyridine) are added in the same way to the above solution containing the "living" polystyrene, with vigorous agitation. After 15 min another 40 mmol of styrene are added, followed 15 min later by another 5 mmol of 4-vinylpyridine; this operation is repeated once more. 15 min after the last addition of monomer the block copolymer is precipitated by dropping the solution into a mixture of 300 ml of diethyl ether and 300 ml of petroleum ether. The polymer is filtered, washed with ether, filtered again, and dried in vacuum at room temperature.

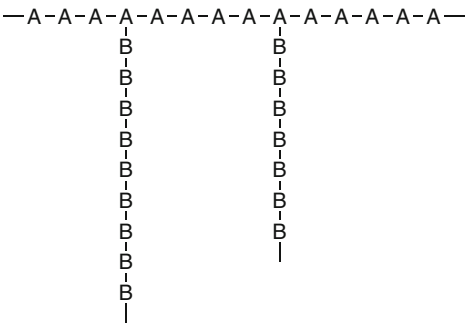
The blocks of 4-vinylpyridine must not be too long, otherwise the polymer is no longer completely soluble in THF. This can easily be observed when 20 ml lots of 4-vinylpyridine are used instead of 5 ml; the solution then becomes cloudy, but after fresh addition of styrene it turns clear again.

For comparison, polystyrene and poly(4-vinylpyridine) are prepared by anionic polymerization with sodium naphthalene as initiator. Poly(4-vinylpyridine) precipitates from THF; the mixture is poured into 200 ml of diethyl ether and the polymer filtered off. The polymer is then reprecipitated from pyridine solution into a tenfold amount of diethyl ether and dried in vacuum.

The IR spectra of all three polymers are recorded and compared with one another. The incorporation of monomeric units of 4-vinylpyridine can also be demonstrated by nitrogen analysis of the block copolymer. The solubility behavior is also determined. Poly(4-vinylpyridine) is soluble in pyridine, methanol, and chloroform, but insoluble in toluene and diethyl ether; it swells considerably in water. On the other hand, the block copolymer, like polystyrene, is soluble in pyridine, chloroform, and toluene; but unlike polystyrene, it swells significantly in methanol.

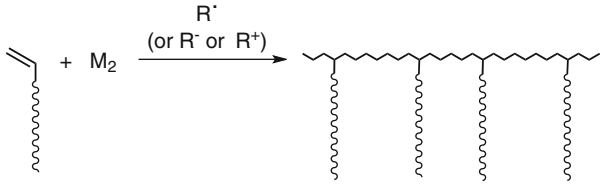
3.4.2.2 Graft Copolymers

Block copolymers are linear, but *graft* copolymers are branched, with the main chain generally consisting of a homopolymer or a random copolymer, while the grafted side chains are composed of either the same or another monomer or several monomers:

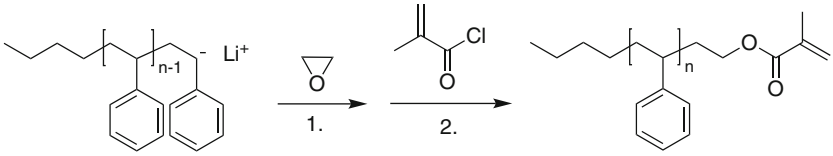


The numerous ways for the synthesis of *graft* copolymers can be divided into three categories.

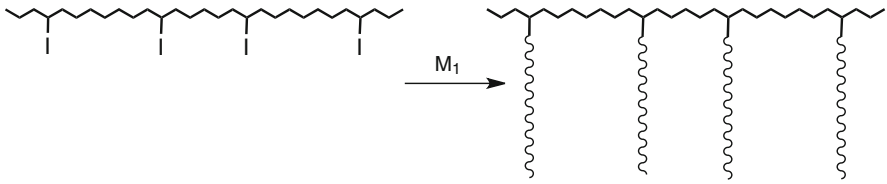
To the first category belong the homo- and copolymerization of macromonomers. For this purpose, macromolecules with only one polymerizable end group are needed. Such macromonomers are made, for example, by anionic polymerization where the reactive chain end is modified with a reactive vinyl monomer. Also methacrylic acid esters of long-chain aliphatic alcohols or monofunctional polyethylene oxides or polytetrahydrofurane belong to the class of macromonomers.



An example for polystyrene macromonomer synthesis:



The second possible route is called "grafting from". This means that active sites are generated at the polymer backbone A which initiate the polymerization of monomer B, thus leading to long-chain branches:

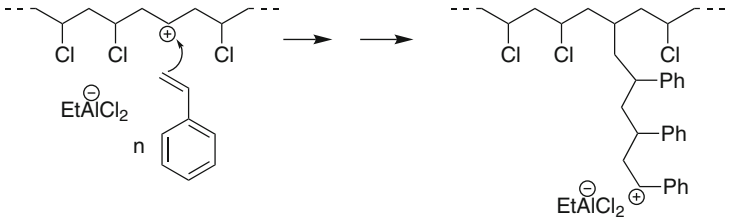


I = azo or peroxo group (free radical polymerization),
CH_2Cl or nitroxy group (controlled radical polymerization),

CH_2Cl (cationic polymerization, e.g., of oxazolines),
halogens + Li (anionic polymerization).

In order to create a radical center on the backbone one may irradiate with ultraviolet radiation (see Sect. 3.1.4) or with high energy radiation. Autoxidation leads to hydroperoxide groups whose decomposition can also lead to suitable radical centers.

Of particular interest are certain ionic graft copolymerizations in which the polymerization reaction is initiated only on the macromolecular framework and no homopolymer is formed. An example is provided by the formation of polymeric carbonium ions from chloride-containing polymers, such as poly(vinylchloride), in the presence of diethylaluminum chloride:

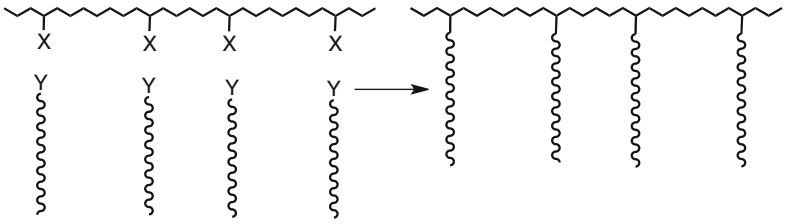


The polymer cations can then initiate the polymerization of cationically polymerizable monomers such as styrene or isobutylene.

The third possibility to prepare graft copolymers is termed "grafting onto". This means that a growing chain B attacks the polymer backbone A with formation of a long branch. This attack can be a chain-transfer reaction or a "copolymerization" with unsaturated groups, for example, in polydienes.

These reactions play an important role in the preparation of high impact polystyrene (see Example 5.23) and of ABS-polymers (made from acrylonitrile, butadiene, and styrene), whereby grafting occurs in situ at the beginning of the polymerization process. The formed graft copolymers act in two ways: As emulsifiers during the polymerization process and, secondly, in the solid end product as compatibilizer between the thermoplastic hard phase and the rubber-elastic dispersed phase (already in concentrations below 3%).

Last but not least, "grafting onto" can also be achieved by reaction of monofunctional oligomers with the reactive side groups of a polymer backbone. The esterification of (co)polymers of methacrylic acid chloride with polyethylene oxides or polytetrahydrofuranes bearing only one OH-group belongs to this category.



It has to be kept in mind that in most of the recipes for the preparation of graft copolymers, mentioned above, larger amounts of homopolymers B are formed.

In general, graft copolymers play often a role as compatibilizer in polymer blends (see Sect. 5.5).

The characterization of block or graft copolymers is generally much more difficult than that of random copolymers (see Sect. 2.3.2.7). Especially, DSC measurements are useful for the characterization of the different segments (determination of T_g). Also dynamic-mechanical measurements are used to distinguish statistical copolymers from those with block or graft structure.

The properties of these types of copolymer depend markedly on the number and length of the blocks and side chains, as well as on the structure of the monomeric units and their molar ratio. In general, graft and block copolymers combine additively the properties of the corresponding homopolymers, while random copolymers normally exhibit the average of the properties of the two homopolymers. This can be recognized very well from the glass transition temperatures: Statistical copolymers show only one T_g which is often found in the region between the T_g values of the two corresponding homopolymers. In contrast to this, block and graft copolymers show, because of the microphase-separation, two T_g values that correspond to the individual homopolymers.

There is, therefore, the possibility of preparing copolymers with desired combinations of properties. This can generally not be achieved by blending the corresponding homopolymers, since chemically different polymers are rarely compatible with one another.

Example 3.50 Graft Copolymerization of Styrene on Polyethylene

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 dry, weighed polyethylene film (length 50 mm, breadth 25 mm, thickness 0.1–0.2 mm) is placed in a tube (about 70 ml capacity) fitted with a ground glass joint and stopcock. After addition of some crystals of benzophenone (as sensitizer) the sample is heated for 1 h on a water bath at 60°C. The outside of the tube is dried, the stopcock closed, and the tube exposed to 15 min irradiation from a mercury lamp (maximum of emission in the region of $\lambda = 253$–254 nm).

While the sample is being irradiated a second tube is filled with 50 ml of destabilized styrene (see Example 3.1) and 0.1 ml of tetraethylenepentamine, the tube then being evacuated and filled with nitrogen. With the aid of a large syringe 40 ml of this solution are injected through the bore of the stopcock into the tube containing the film. The tube is now evacuated, filled with nitrogen, and the closed vessel maintained at 60°C in a thermostat for 2 h. The grafted polyethylene foil is then extracted in a Soxhlet apparatus for 1 h with ethyl acetate, dried to constant weight in vacuum at 50°C and weighed. The extract is added dropwise to about 400 ml of methanol; the precipitated homopolymer of styrene is filtered off through a sintered glass filter, dried in vacuum at 50°C, and weighed.

The amount of grafted styrene is given by the increase in weight of the film. It may also be calculated quite well from the densities of polyethylene (d_1), polystyrene (d_2), and the graft copolymer (d_3) according to the following Eq. 3.31:

$$\frac{100 - x}{d_1} + \frac{x}{d_2} = \frac{100}{d_3} \tag{3.31}$$

where x is the weight percentage of grafted polystyrene, relative to the weight of the grafted film. The density of polystyrene (d_2) may be taken as 1.05 g/cm^3; the densities d_1 and d_3 can be determined on small pieces (0.2–0.5 cm^2) of the polyethylene and grafted films by the flotation method using ethanol/water mixtures (see Sect. 2.3.5.1). In addition, the ratio of grafted polystyrene and homopolymer of styrene is determined.

Example 3.51 Radical Graft Copolymerization of Vinylpyrrolidone onto Poly(vinylalcohol)

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.

An initiator solution is prepared by dissolving 0.625 g of 2,2-azobis (2-aminopropene) dihydrochloride in 6 ml water. The solution is transferred under argon into a syringe.

A standard apparatus (250 ml, three-neck round-bottom flask, thermometer, heating bath) is equipped with magnetic stirrer, reflux condenser, dropping funnel with pressure release, and one neck is sealed with a septum which can be used for thermometer inlet but also addition of initiator solution using a syringe; the apparatus is flushed with argon. Under argon atmosphere one adds 8.3 g of a 30-wt% polyvinylalcohol aqueous solution (2.5 g of PVA, molar mass about 30,000 g/mol), 1/5 of the vinylpyrrolidone amount (4.5 g), and about 3 drops of the initiator.

Under slow argon stream (inlet via dropping funnel, outlet via condensor) the mixture in the flask is heated to 80°C. Within 3 h the remaining portion of vinylpyrrolidone (18.5 g) is added through the dropping funnel, and within 4 h, half of the remaining initiator solution (about 3 g water solution) is added through the septum using the syringe. The mixture is stirred for 1 h at 80°C and then the remaining initiator solution is added within 45 min. The mixture is polymerized to full conversion by keeping it for additional 3.5 h at 80°C. After cooling to room temperature one obtains a light yellow, viscous polymer solution in water (about 30 wt%).

Characterization of the Graft Copolymer

Two solutions have to be prepared:

– Polymer solution A: 3 g of the obtained graft polymer solution + 6 ml water (=10 wt% solution)

– Polymer solution B: 9 g 10 wt% aqueous polyvinylpyrolidone (M_n about 50,000 g/mol, e.g., Luviskol K30 from BASF AG) solution + 1 g 10 wt% aqueous polyvinylalcohol solution (M_n about 30,000 g/mol).

About 10 drops of solution A and B, respectively, are added dropwise to 30 ml of an acetone/ethanol mixture (2:1). While the ungrafted mixture causes a visible clouding, the graft product is fully soluble.

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