

Copolymerization

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If two different monomers, M_1 and M_2 , are polymerized together, the structures shown in Fig. 13.1 result.

In the case of copolymers, we are not dealing with mixtures of the individual homopolymers but instead with products in which both monomers are covalently incorporated in the individual molecules. Although alternating and statistical copolymers can indeed be produced by polymerizing two different monomers together (simultaneously), the syntheses of block and graft copolymers require special methods. To differentiate the products, the following nomenclature has emerged:

- Statistical copolymer: Poly(M_1 -stat- M_2)
- Alternating copolymer: Poly(M_1 -alt- M_2)
- Block copolymer: Poly(M_1 -block- M_2)
- Graft copolymer: Poly(M_1 -graft- M_2)

If it is not intended to distinguish the specific copolymer architecture, the general term is poly(M_1 -co- M_2).

Copolymerization allows us to synthesize a virtually infinite number of different products. If one assumes the existence of 50 technically interesting vinyl monomers, there are $(50 \cdot 49)/2 = 1225$ possible combinations of two different monomers. This number increases further by a large multiple if we vary the mixtures between 1 mol% and 99 mol% and take into account that for each monomer combination there are various possible copolymer architec-

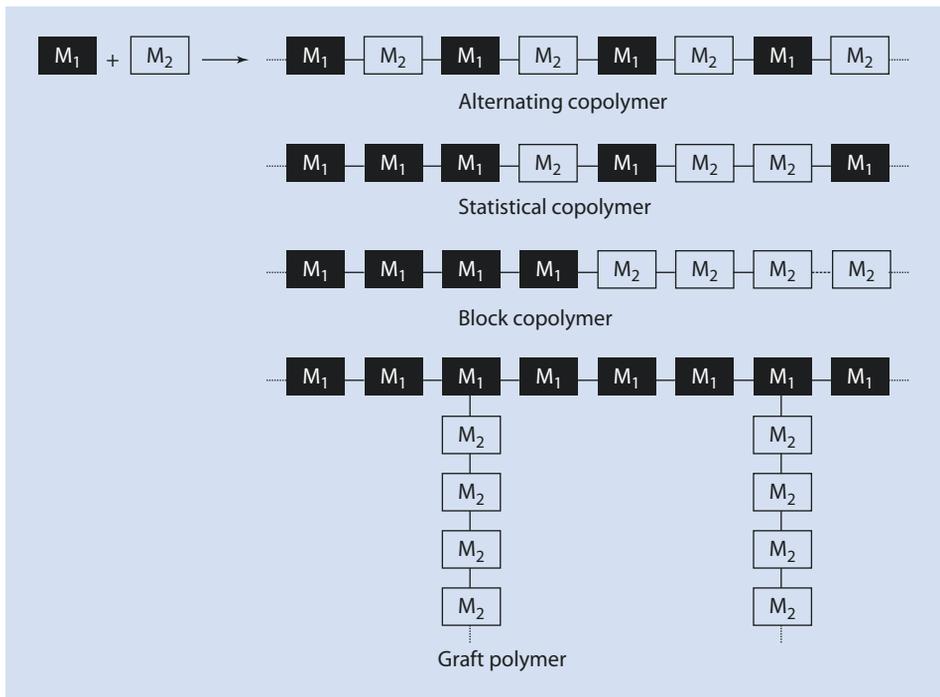


Fig. 13.1 Structures of alternating, statistical, block, and graft copolymers

tures. When copolymers are formed of more than two building blocks,¹ the number of combinations reaches vast proportions. An example of a group of copolymers that have become industrially very important is ABS—terpolymers of acrylonitrile, butadiene, and styrene.

Copolymerization has the great advantage that the attributes of the homopolymers can be deliberately combined. Taking the example of polystyrene, which is brittle and hard and has only moderate solvent resistance, it can be seen how, by introducing comonomers into the polymer, the service range of polymers based on styrene can be expanded. Copolymers with styrene as comonomer can be *thermoplasts* [e.g., poly(styrene-*co*-acrylonitrile), SAN] or *elastomers* [poly(styrene-*co*-butadiene) SBR,² and poly(styrene-*block*-butadiene-*block*-styrene), SBS] (► Sect. 14.5.3). For example, by incorporating acrylonitrile, the strength and ductility of SAN-polymers is improved and the resistance against aliphatic hydrocarbons and mineral oils is enhanced compared with polystyrene. SAN polymers with a wide variation in composition are available commercially.

13.1 Mayo-Lewis Equation of Copolymerization

The compositions of statistical copolymers are determined by the monomer composition and the relative reactivity of the comonomers. In the following, the corresponding rules are derived using the example of radical copolymerization.

13.1.1 Deduction of the Mayo–Lewis Equation of Copolymerization

If the radical polymerization is initiated in the presence of two different monomers, M_1 and M_2 , the polymerization goes through all the individual phases of a radical polymerization; that is, the polymerization is initiated by the disintegration of the initiator, the primary radical reacts with the monomer (M_1 or M_2), and the chains grow until they terminate (► Sect. 9.2.1). Other than in the polymerization with only one monomer M_1 , in the case of copolymerization, four different phases of growth, rather than one, need to be distinguished. A growing chain end derived from M_1 can react with either M_1 or M_2 . Two further possibilities of growth emerge when the growing chain ends are derived from M_2 (■ Fig. 13.2).

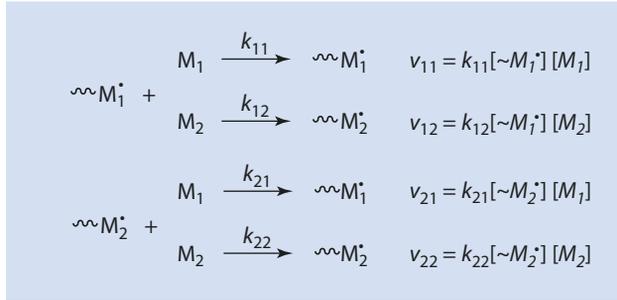
As the monomers are only consumed by chain growth, the following equations can be formulated for monomer consumption:

$$-\frac{d[M_1]}{dt} = k_{11} [\sim M_1^\bullet] [M_1] + k_{21} [\sim M_2^\bullet] [M_1] \quad (13.1)$$

$$-\frac{d[M_2]}{dt} = k_{22} [\sim M_2^\bullet] [M_2] + k_{12} [\sim M_1^\bullet] [M_2] \quad (13.2)$$

- 1 Polymers resulting from the copolymerization of more than two monomers are called *terpolymers*.
- 2 The abbreviation SBR derives from “styrene–butadiene rubber” reflecting the elastomeric properties of the copolymers.

■ Fig. 13.2 Chain growth during a radical polymerization of two monomers M_1 and M_2



Furthermore, assuming a stationary state with respect to the number of radicals (as described in ► Chap. 9), it follows that

$$k_{12}[\sim M_1^\bullet][M_2] = k_{21}[\sim M_2^\bullet][M_1] \quad (13.3)$$

and

$$[\sim M_1^\bullet] = \frac{k_{21}[\sim M_2^\bullet][M_1]}{k_{12}[M_2]} t \quad (13.4)$$

The division of (13.1) by (13.2) yields

$$\begin{aligned}
 \frac{d[M_1]}{d[M_2]} &= \frac{k_{11}[\sim M_1^\bullet][M_1] + k_{21}[\sim M_2^\bullet][M_1]}{k_{22}[\sim M_2^\bullet][M_2] + k_{12}[\sim M_1^\bullet][M_2]} \\
 &= \frac{[M_1]}{[M_2]} \cdot \frac{k_{11}[\sim M_1^\bullet] + k_{21}[\sim M_2^\bullet]}{k_{22}[\sim M_2^\bullet] + k_{12}[\sim M_1^\bullet]} \quad (13.5)
 \end{aligned}$$

The expression $d[M_1]/d[M_2]$ is a measure of the rate at which the monomers M_1 and M_2 are incorporated into the growing polymer chains at any moment during the polymerization. Thus, this expression describes the chemical composition of the copolymers formed at any one moment in time. Introducing (13.4) into (13.5) gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{k_{11} \cdot \frac{k_{21}[\sim M_2^\bullet][M_1]}{k_{12}[M_2]} + k_{21}[\sim M_2^\bullet]}{k_{22}[\sim M_2^\bullet] + k_{12} \cdot \frac{k_{21}[\sim M_2^\bullet][M_1]}{k_{12}[M_2]}} \quad (13.6)$$

which can be simplified to

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{k_{11} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{[M_1]}{[M_2]} + k_{21}}{k_{22} + k_{21} \cdot \frac{[M_1]}{[M_2]}} \quad (13.7)$$

By multiplying the second quotient in (13.7) by $[M_2]/k_{21}$ and simplifying one obtains

$$\begin{aligned} \frac{d[M_1]}{d[M_2]} &= \frac{[M_1]}{[M_2]} \cdot \frac{k_{11} \cdot \frac{[M_1]}{k_{12} [M_2]} \cdot \frac{[M_2]}{k_{21}} + k_{21} \frac{[M_2]}{k_{21}}}{k_{22} \frac{[M_2]}{k_{21}} + k_{21} \cdot \frac{[M_1]}{[M_2]} \cdot \frac{[M_2]}{k_{21}}} = \\ &= \frac{[M_1]}{[M_2]} \cdot \frac{\frac{k_{11}}{k_{12}} \cdot [M_1] + [M_2]}{\frac{k_{22}}{k_{21}} [M_2] + [M_1]} \end{aligned} \quad (13.8)$$

Equation (13.8) can be further simplified by introducing the so-called *copolymerization parameters* r_1 and r_2 . These are defined as follows:

$$r_1 = \frac{k_{11}}{k_{12}} \quad (13.9)$$

$$r_2 = \frac{k_{22}}{k_{21}} \quad (13.10)$$

The copolymerization parameters, the reactivity ratios r_1 and r_2 , are very important parameters. They describe the relative reactivity of the radicals towards the monomers M_1 and M_2 . If $r_1 > 1$, then a polymer radical derived from M_1 preferably reacts with the monomer M_1 . In this case, homopolymerization is favored over heteropolymerization. Moreover, only these two parameters are necessary to describe the copolymerization instead of the four rate constants.

By inserting the parameters r_1 and r_2 into (13.8) one obtains the Mayo–Lewis copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]} \quad (13.11)$$

m_1	Concentration of M_1 in the newly formed polymer ³
m_2	Concentration of M_2 in the newly formed polymer
$[M_1]$	Concentration of M_1 in the reaction mixture
$[M_2]$	Concentration of M_2 in the reaction mixture
r_1, r_2	Copolymerization parameters

Equation (13.11) describes the composition of the polymer formed at any one time as a function of the monomer composition at that time. During most copolymerizations, as the reaction progresses, and depending on the reactivity of the individual comonomers,

3 The proportion of M_1 and M_2 incorporated into the polymer at any one time cannot be determined simply from the composition of the polymer. However, if the copolymerization is prematurely stopped at conversions $p < 5\%$, the difference between the composition at the time of stopping the reaction and the integral, experimentally obtained, copolymer is negligible. It should be noted that all the concentrations mentioned here are molar concentrations.

a more or less dramatic change in the proportion of the comonomers in the reaction mixture occurs. Thus, the copolymers produced after different reaction times, i.e., at different conversions, may be chemically different. Only at extremely low conversions of less than 5% can the relative monomer concentrations be assumed to be approximately constant; at this stage, (13.11) gives a good first approximation of the copolymer composition.

If a copolymerization is allowed to continue to complete conversion, the average composition of all the polymer chains naturally corresponds to the initial monomer composition. However, in this case the product also contains a large number of chemically different macromolecules.

13.1.2 Example: Statistical Copolymerization of Styrene and Acrylonitrile

To copolymerize styrene with acrylonitrile, both monomers are mixed in different mole fractions (here: $0.1 \leq x_1 \leq 0.9$) and polymerized up to a conversion of max. 5%. The polymer is separated from the residual monomer by precipitation and its chemical composition analyzed. The method of analysis of the copolymers is determined by the nature of the components. In the case of styrene and acrylonitrile, $^1\text{H-NMR}$ -spectroscopy, IR-spectroscopy (typical CN- and phenyl bands), UV-spectroscopy (absorption of the phenyl ring), and elementary analysis (acrylonitrile concentration via nitrogen analysis) are all appropriate.

A typical copolymerization of styrene (M_1) and acrylonitrile (M_2), conducted without a solvent, delivers the following data (■ Table 13.1).

A plot of the mole fraction of the monomer (M_1) in the polymer $m_1/(m_1 + m_2)$ against the mole fraction of the monomer (M_1) in the initial monomer mixture shows clearly that rather than a simple linear relationship between $m_1/(m_1 + m_2)$ and $[M_1]/([M_1] + [M_2])$, their interdependence is more complicated (■ Fig. 13.3). This is discussed in more detail in the next section.

13.2 Copolymerization Diagrams and Copolymerization Parameters

A graph plotting the monomer composition in the polymer as a function of the initial⁴ concentration of the monomers in the reaction mixture shown in ■ Fig. 13.3 is referred to as a *copolymerization diagram*.

The intersection of the curve in ■ Fig. 13.3 with the diagonal dotted line is referred to as the *azeotrope*. At this point the copolymer composition and the composition of the monomer mixture are identical. This is the only point at which the composition of the original monomer mixture does not change despite further conversion, i.e., chemically identical polymers are produced throughout the entire polymerization process. The mixture with this basic composition can therefore be fully polymerized without altering the

4 At very low conversion the actual monomer composition hardly differs from that of the initial composition so the initial mole fraction is used.

Table 13.1 Mole fractions of the monomers in the initial reaction mixture and in the polymer formed via a radical polymerization of styrene (M_1) and acrylonitrile (M_2), initiated with AIBN, $T=48\text{ }^\circ\text{C}^a$

$\frac{[M_1]}{[M_1]+[M_2]}$	$\frac{m_1}{m_1+m_2}$
0.1	0.30
0.2	0.40
0.3	0.43
0.4	0.46
0.5	0.47
0.6	0.49
0.7	0.54
0.8	0.60
0.9	0.70

^aAfter a conversion of ca. 5 %, the copolymer is separated from the residual monomers by precipitation. This polymer composition was determined by $^1\text{H-NMR}$ -spectroscopy.

copolymer composition with increasing conversion. For all other monomer compositions, either styrene (in the example given here) is preferentially incorporated into the polymer (below or to the left of the azeotrope) or acrylonitrile (above or to the right of the azeotrope). This leads to the remaining monomer composition moving away from the azeotrope as the polymerization proceeds and a chemically inhomogeneous material is obtained. By making monomer additions of the monomer being preferentially incorporated during the polymerization, this effect can be corrected.

If the copolymerization parameters r_1 and r_2 are known, the azeotrope can be calculated using (13.11):

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \quad (13.11)$$

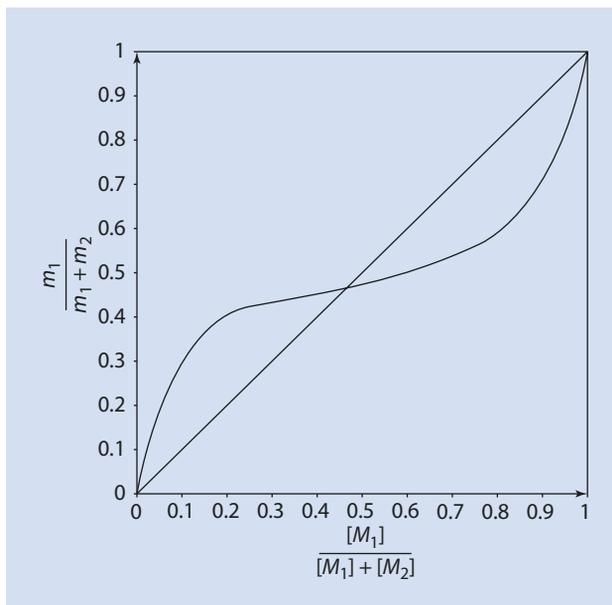
At the azeotrope:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \quad (13.12)$$

Inserting (13.12) into (13.11) gives

$$1 = \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \quad (13.13)$$

■ **Fig. 13.3** Instantaneous copolymer composition as a function of the initial monomer composition using the example of the copolymerization of styrene (M_1) and acrylonitrile (M_2)



This can easily be transformed into

$$\frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1} \quad (13.14)$$

An azeotrope exists if r_1 and r_2 are both smaller than 1 (preferred heteropolymerization). This case is true for the radical copolymerization of styrene/acrylonitrile under the circumstances mentioned here ($r_1 = 0.40$; $r_2 = 0.17$). This is also referred to as a statistical copolymerization. ■ Table 13.2 offers an overview of the combination of copolymerization parameters for each type of copolymerization.

In relation to the copolymerization parameters, we can distinguish between five different types of copolymerization (■ Table 13.2).

Typical curves analogous to ■ Fig. 13.3 for the different cases given above are shown in ■ Fig. 13.4. A detailed discussion of the individual cases can be found in the subsequent sections of this chapter.

In ■ Table 13.3 some examples of copolymerization parameters for selected monomer pairs are compiled.

13.3 Alternating Copolymerization

In some cases it is not possible for a monomer to add a growing radical derived from another molecule of the same monomer. Thus, the parameters r_1 and $r_2 = 0$, as well as k_{11} and $k_{22} = 0$ (■ Fig. 13.5).

■ **Table 13.2** Combination of copolymerization parameters and the resulting class of copolymer

			Copolymerization class
a	$r_1 < 1$	$r_2 < 1$	Statistical (► Sect. 13.1)
b	$r_1 = 1$	$r_2 = 1$	Ideal (► Sect. 13.4)
c	$r_1 > 1$	$r_2 < 1$	Ideal, if $r_1 \cdot r_2 = 1$
	$r_1 < 1$	$r_2 > 1$	
d	$r_1 = 0$	$r_2 = 0$	Alternating (► Sect. 13.3)
e	$r_1 > 1$	$r_2 > 1$	unknown

(a) r_1 and r_2 are both less than 1. In this case, the copolymerization diagram has an azeotrope (► Fig. 13.3).

(b) r_1 and r_2 both equal 1. It follows from the definition of the copolymerization parameters that both monomers are built into the growing polymer chain with the same rate constants and are therefore indistinguishable. In this case, the composition of the copolymers corresponds to that of the original monomer mixture. This copolymerization is referred to as ideal azeotropic copolymerization.

(c) r_1 is less than 1, r_2 is greater than 1 (or reversed). In this case one of the two monomers is always preferentially incorporated. If the product of the copolymerization parameters equals 1, this is referred to as an ideal non-azeotropic copolymerization. In this case the two polymer radicals react with the two monomers with identical ratios, i.e., the reactivity of the two radicals is the same in relation to the two monomers.

(d) r_1 and r_2 both equal 0. This situation implies that one active chain end subsequently always adds the other monomer. As a result, an alternating copolymer is formed.

(e) r_1 and r_2 are both greater than 1. In this case homopolymerization is kinetically favored over heteropolymerization. However, there are no examples of this case.

■ **Fig. 13.4** Typical

copolymerization curves

(a) $r_1 < 1, r_2 < 1$, (b) $r_1 = 1, r_2 = 1$,

(c) $r_1 > 1, r_2 < 1$, (d) $r_1 = r_2 = 0$

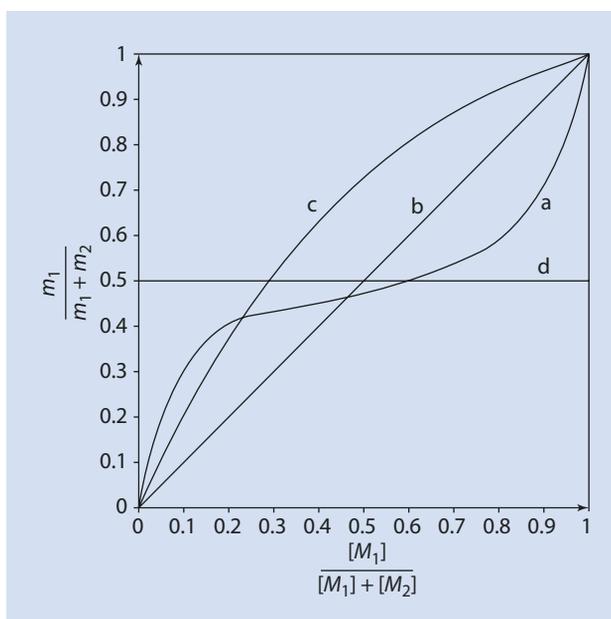
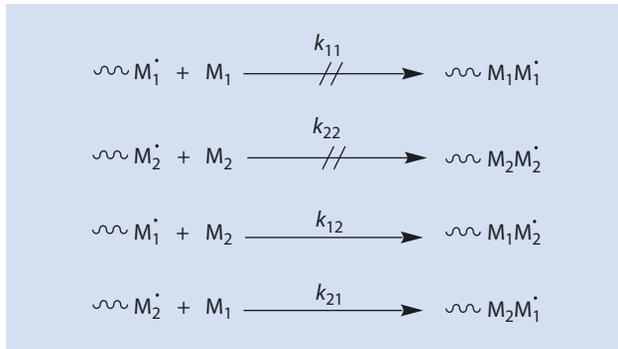


Table 13.3 Examples of copolymerization parameters^a

M_1	r_1	M_2	r_2	Type
Methyl methacrylate	0.84	Vinylidene chloride	0.99	a, ~b
Styrene	0.58	Butadiene	1.35	c
Styrene	56	Vinyl acetate	0.01	c
Styrene	0.05	Maleic acid anhydride	0.005	~d
Acrylonitrile	5.5	Vinyl acetate	0.06	c
Styrene	0.40	Acrylonitrile	0.17	a

^aThe parameters are for radical polymerizations. These parameters are hardly affected by the temperature at which the polymerization takes place and, apart from a few exceptions (cf., for example ► Sect. 13.5), are almost independent of the solvent.

Fig. 13.5 Formation of an alternating copolymer from the exclusive addition of the growing chain end to a monomer different from the monomer from which it was derived



This means that the corresponding homopolymerization steps do not take place and the monomer sequence is alternating. Independent of the monomer composition, a polymer of the molar composition

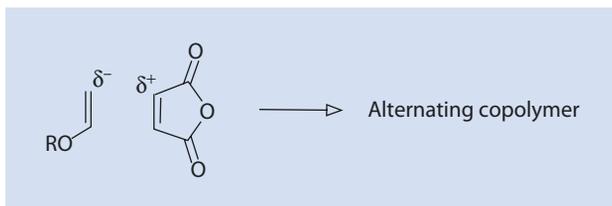
$$\frac{m_1}{m_1 + m_2} = 0.5 \quad (13.15)$$

$$\frac{m_2}{m_1 + m_2} = 0.5 \quad (13.16)$$

with an alternating succession of the monomers M_1 and M_2 is produced.

Alternating copolymers are often the result if donor–acceptor complexes are formed from polar interactions between M_1 and M_2 and these polymerize in pairs (► Fig. 13.6).

■ **Fig. 13.6** Donor–acceptor complex from vinyl ether and maleic acid anhydride



13.4 Ideal Copolymerization

A copolymerization with $r_1 \cdot r_2 = 1$ is often referred to as an *ideal copolymerization*. If both parameters r_1 and $r_2 = 1$, this makes sense as it follows from (13.11) that for this case:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \quad (13.17)$$

Such systems are rare but these monomer pairs can be quantitatively copolymerized to give copolymers having the same composition as that of the original monomer mixture. Such copolymerizations are thus easy to conduct—as opposed to statistical copolymerization, in which the disproportionately incorporated comonomer has to be continually replaced to obtain a homogeneous product.

Systems with the values $r_1 > 1$, $r_2 < 1$ (■ Table 13.2, Case c) can also meet the condition $r_1 \cdot r_2 = 1$. In this case, by inserting (13.9) and (13.10) and rearranging one obtains

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}} \quad (13.18)$$

According to the above, the relative rates at which M_1 and M_2 (second numeral of the subscript) react with the active chains ends $\sim M_1^*$ and $\sim M_2^*$ (first numeral of the subscript) are the same and independent of the nature of the active chain end. As a result, Eq. (13.11) can be simplified to

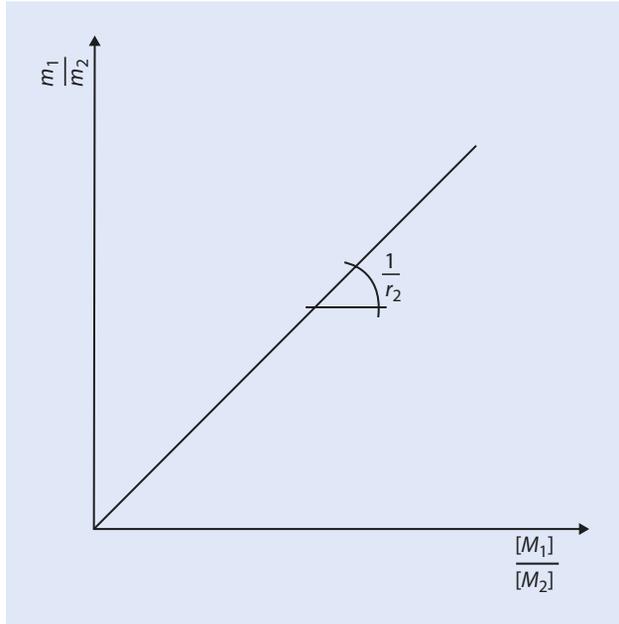
$$\frac{m_1}{m_2} = \frac{1}{r_2} \cdot \frac{[M_1]}{[M_2]} \quad (13.19)$$

For the experimental determination of r_2 , various mixtures $[M_1]/[M_2]$ are polymerized up to a conversion of max. 5%. Thereafter, the copolymers are separated from the residual monomer, for example, by precipitation, and then analyzed. From a graph of $m_1/m_2 = f([M_1]/[M_2])$, $1/r_2$ or r_1 is given by the gradient of the straight line (■ Fig. 13.7).

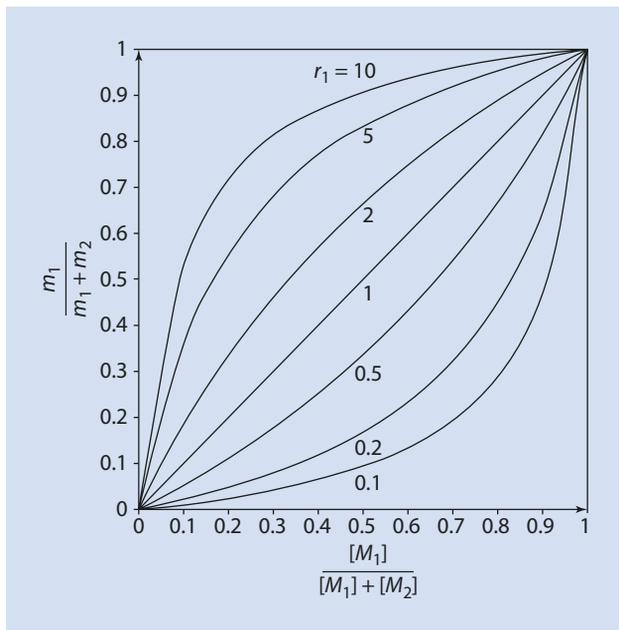
The validity of the assumption $r_1 \cdot r_2 = 1$ should always be verified. To this end, the parameters should also be analyzed using the Mayo–Lewis and/or the Fineman–Ross equations (► Sect. 13.6).

The copolymerization diagrams of systems with $r_1 \cdot r_2 = 1$ can nevertheless assume extremely varied forms (■ Fig. 13.8).

▣ Fig. 13.7 Determination of the copolymerization parameter r_2 for an ideal copolymerization ($r_1 \cdot r_2 = 1$)



▣ Fig. 13.8 Copolymerization diagrams for ideal copolymerizations with $r_1 = 0, 1, \dots, 10$ ($r_1 \cdot r_2 = 1$)



■ **Table 13.4** Copolymerization parameters for the radical copolymerization of acrylic acid (M_1) and MMA (M_2) in different solvents at 50 °C

Solvent	r_1	r_2
<i>N,N</i> -Dimethyl formamide	0.24	2.89
Tetrahydrofuran	0.25	2.46
Dioxan	0.30	2.32
Acetonitrile	0.33	2.17
Bulk (without solvent)	0.24	1.89

Polar solvents interfere to varying degrees with the formation of the hydrogen bonded dimers of acrylic acid.

13.5 Influencing the Inclusion Ratio of the Monomers

An influence of the solvent on the reactivity of the monomers can generally be neglected. Nevertheless, a systematic variation of the copolymerization parameters for the radical copolymerization of acrylic acid with methyl methacrylate (MMA) has been observed which depends on the propensity of the solvent to form hydrogen bonds (■ Table 13.4) (Glamann 1969).

Furthermore, the copolymerization behavior of monomers can be influenced by a change in the electron density of the C-C double bond. For example, if acrylic acid methyl ester is copolymerized instead of acrylic acid:

Styrene (M_1)/acrylic acid (M_2): $r_1 = 0.15$; $r_2 = 0.25$

Styrene (M_1)/acrylic acid methyl ester (M_2): $r_1 = 0.75$; $r_2 = 0.18$

The rate of propagation can also be drastically altered by complexation. Thus, the reactivity of acrylonitrile is changed considerably, e.g., by ZnCl_2 or $\text{Al}(\text{CH}_3)_3$ and is forced into an alternating copolymerization with ethylene. A change in mechanism from a radical to a cationic or anionic copolymerization has equally drastic consequences. For example, although the copolymerization of styrene and MMA results in statistical copolymers via a radical mechanism, homo-polystyrene is the sole product from a cationic initiation because MMA does not polymerize cationically. Via an anionic polymerization almost pure PMMA is produced initially before styrene is also incorporated in the polymer, i.e., in the ideal case poly(MMA-*block*-styrene) is produced.

13.6 Experimental Determination of the Copolymerization Parameters

As previously discussed in ► Sect. 13.1.2, the composition of the copolymers $m_1/(m_1 + m_2)$ is determined for various $[M_1]/([M_1] + [M_2])$ at a conversion of less than 5% and, from the results, the copolymerization diagram drawn (■ Fig. 13.3).

Mathematically, according to Mayo and Lewis, (13.11) is transformed to give $r_2 = f(r_1, [M_1], [M_2], m_1, m_2)$:

$$r_2 = \frac{[M_1]^2}{[M_2]^2} \cdot \frac{m_2}{m_1} \cdot r_1 + \frac{[M_1]}{[M_2]} \cdot \frac{m_2}{m_1} - \frac{[M_1]}{[M_2]} \quad (13.20)$$

With

$$a = \frac{[M_1]}{[M_2]} \quad (13.21)$$

and

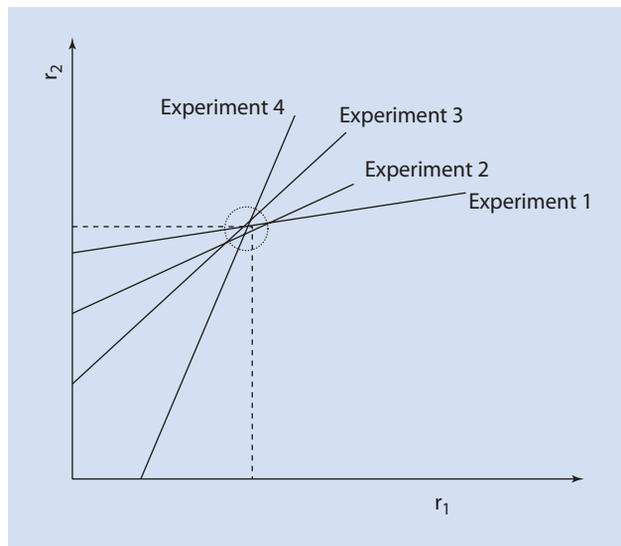
$$b = \frac{m_2}{m_1} \quad (13.22)$$

it follows from (13.20) that

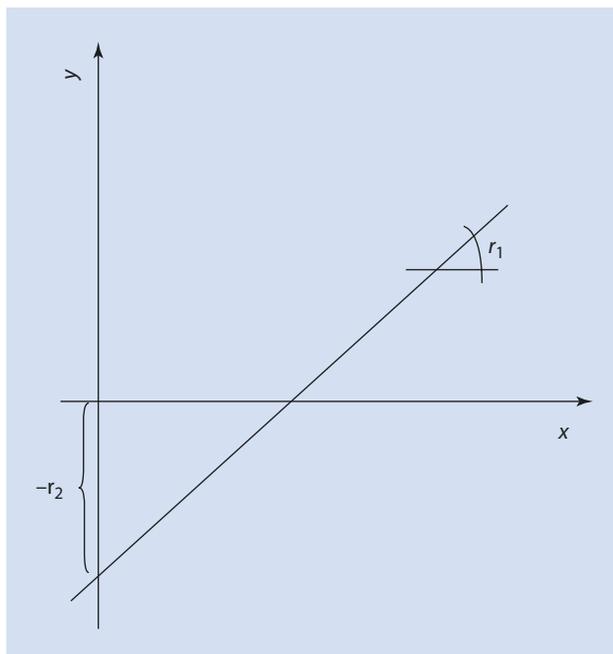
$$r_2 = r_1 \cdot a^2 \cdot b + a \cdot b - a \quad (13.23)$$

As $[M_1]$ and $[M_2]$ are given and m_1 and m_2 can be determined experimentally, an equation is obtained with two unknowns, r_1 and r_2 . A second experiment with altered $[M_1]$ and $[M_2]$ and thus alternative values for m_1 and m_2 provides a second conditional equation. A graph of $r_2 = f(r_1)$ results in straight lines for both experiments, the intersection of which yields the values for the required parameters r_1 and r_2 . The reliability of the values determined increases with the number of experiments (■ Fig. 13.9).

■ Fig. 13.9 Determining the copolymerization parameters using the method of Mayo and Lewis



■ **Fig. 13.10** Determining the copolymerization parameters using the method of Fineman and Ross



Depending on the accuracy with which m_1 and m_2 can be determined, there is often a larger or smaller deviation from the theoretically expected, common intersection. Alternatively, r_1 and r_2 can be determined from the gradient and the intercept of a graph of the so-called Fineman and Ross copolymerization equation (13.24); ► see Fig. 13.10.

$$y = r_1 x - r_2 \quad (13.24)$$

By extending the term on both sides of (13.11) with +1, the mole fraction variant of the Mayo–Lewis equation is obtained. Using definitions (13.25) to (13.30) and several transformations, the conditional equation for r_1 and r_2 in the form of equation (13.24) can be obtained.

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad (13.25)$$

$$f_2 = \frac{[M_2]}{[M_1] + [M_2]} \quad (13.26)$$

$$F_1 = \frac{m_1}{m_1 + m_2} \quad (13.27)$$

$$F_2 = \frac{m_2}{m_1 + m_2} \quad (13.28)$$

and by combining $f_1, f_2, F_1,$ and F_2 into x and y :

$$y = \frac{f_1(2F_1 - 1)}{f_2 \cdot F_1} \quad (13.29)$$

$$x = \frac{(1 - F_1) \cdot f_1^2}{F_1 \cdot f_2^2} \quad (13.30)$$

From a series of experiments with different $[M_1]/([M_1] + [M_2])$ a set of x, y pairs is obtained, which can be plotted to give a straight line. The gradient of the straight line is r_1 and r_2 the y -intercept (■ Fig. 13.10).

By introducing the auxiliary variable $H = F_{\min}/F_{\max}$ from (13.27) or (13.28), extreme monomer ratios can be given greater statistical weight (Kelen et al. 1980) and the influence of those measurements particularly prone to error can be reduced so that the reliability of the values of r_1 and r_2 is improved. By dividing (13.24) by $H + x$ one obtains

$$\frac{y}{H + x} = \frac{-r_2 + r_1 x}{H + x} = -\frac{r_2}{H} + \left(r_1 + \frac{r_2}{H}\right) \cdot \frac{x}{H + x} \quad (13.31)$$

The r_1 -, r_2 -parameters compiled in tables (Kelen et al. 1980) have often been optimized using this method.

13.7 The Q, e Schema of Alfrey and Price

The copolymerization parameters are specific to a particular monomer pair. As stated in the introduction to this chapter, n monomers produce $(n \cdot (n - 1))/2$ combinations in binary systems ($1/2$, as $a \cdot b = b \cdot a$). For 100 technically interesting monomers, this leads to $(100 \cdot 99)/2 = 4950$ parameter combinations of which many are compiled in reference works such as the *Polymer Handbook* by J. Brandrup and E.H. Immergut (Brandrup and Immergut 1989).

Alfrey and Price developed a method to determine monomer rather than pair specific parameters using an empirical approach. In this method they describe the r -parameters in terms of four parameters for the reactivity and polarity of each individual monomer:

$$k_{12} = P_1 \cdot Q_2 \cdot e^{-e_1 e_2} \quad (13.32)$$

P_1	Reactivity of $\sim M_1^\cdot$
Q_2	Reactivity of M_2
e_1	Measurement for the polarity of $\sim M_1^\cdot$ and M_1
e_2	Measurement for the polarity of $\sim M_2^\cdot$ and M_2

By analogy:

$$k_{11} = P_1 \cdot Q_1 \cdot e^{-e_1 e_1} \quad (13.33)$$

Thus, for r_1 from Eq. (13.10):

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_1 \cdot Q_1 \cdot e^{-e_1 e_1}}{P_1 \cdot Q_2 \cdot e^{-e_1 e_2}} = \frac{Q_1}{Q_2} \cdot e^{-e_1(e_1 - e_2)} \quad (13.34)$$

Again, by analogy, for r_2 from Eq. (13.11):

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{P_2 \cdot Q_2 \cdot e^{-e_2 e_2}}{P_2 \cdot Q_1 \cdot e^{-e_2 e_1}} = \frac{Q_2}{Q_1} \cdot e^{-e_2(e_2 - e_1)} \quad (13.35)$$

If r_1 and r_2 have been determined experimentally, only two conditional equations are available to provide values for the four unknowns Q_1 , Q_2 , e_1 , and e_2 .

To solve the problem, the reactivity Q and the polarity e of the monomer styrene are arbitrarily defined: $Q_{\text{styrene}} = 1.00$, $e_{\text{styrene}} = -0.80$.

With these numbers, the values for Q and e of other comonomers can be calculated. High values of Q represent high reactivity of the corresponding monomer. Strongly negative values of e indicate an electron-rich double bond.

The values of Q and e for selected monomers are compiled in [Table 13.5](#).

In [Fig. 13.11](#), the Q, e scheme is visualized as a “map”.

This map should be interpreted as follows:

1. Copolymerization of monomers with extremely different values of Q is difficult (e.g., vinyl chloride/styrene)
2. Monomers with similar Q values (e.g., styrene/butadiene) can be copolymerized more easily
3. Systems with similar Q and extremely different e values tend to yield alternating copolymers

Table 13.5 Q - and e -values for a selection of monomers (Brandrup and Immergut 1989)

Monomer	Q	e
Styrene	1.00	-0.80
Acrylonitrile	0.48	$\ll 23$
1,3-Butadiene	1.70	-0.50
Isobutylene	0.023	-1.20
Ethylene	0.016	0.05
Isoprene	1.99	-0.55
Maleic acid anhydride	0.86	3.69
Methyl methacrylate	0.78	0.40
α -Methyl styrene	0.79	-0.81
Propylene	0.009	0.88
Vinyl acetate	0.026	0.88
Vinyl chloride	0.056	0.16

With these data, the copolymerization parameters for monomer pairs which haven't been experimentally determined can be predicted. However, although the Q, e scheme is a very useful, it is no more than an empirical concept so that a more thorough, theoretical interpretation is not worthwhile; these parameters should be regarded simply as semi-quantitative indicators for the corresponding monomer.

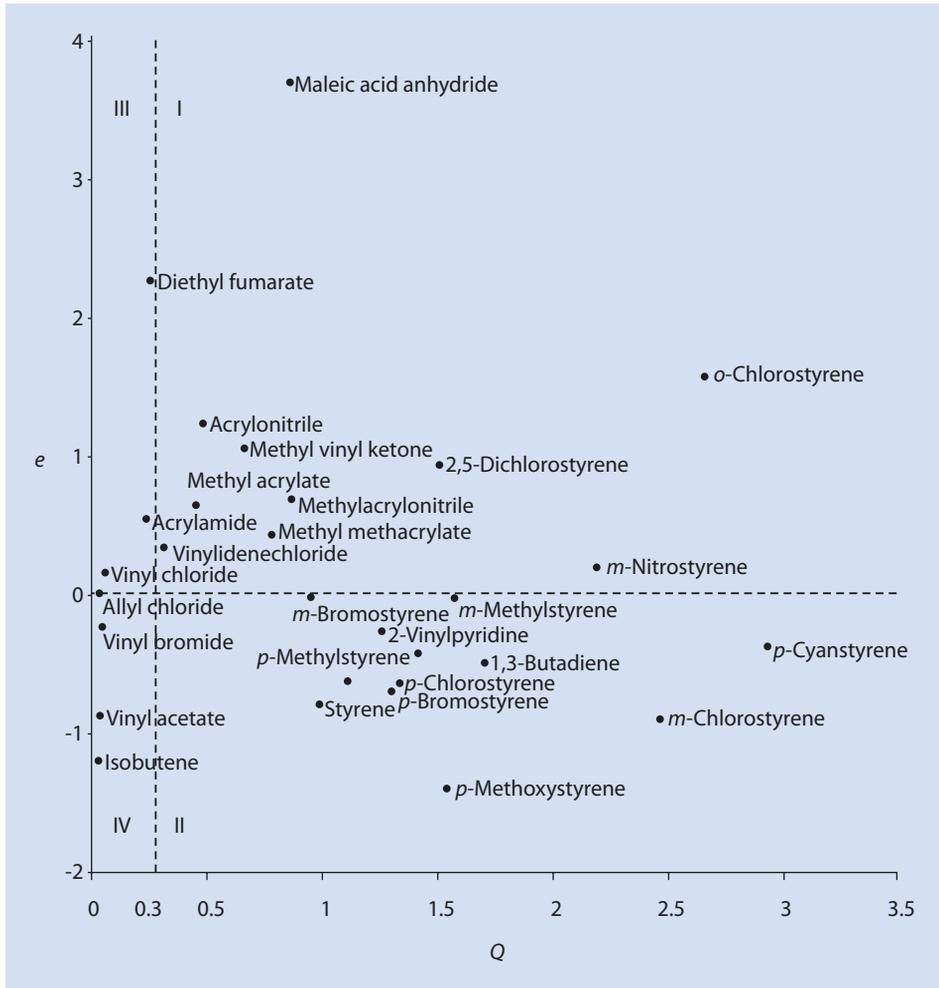


Fig. 13.11 Q, e scheme developed by Alfrey and Price

Copolymerization of monomers with different reactivity from quadrants III or IV with monomers from quadrants I or II is not favorable, whereas monomers from the same quadrant usually copolymerize very well. Copolymerization of monomers from quadrant I with monomers from quadrant II tends to yield alternating copolymers.

13.8 Copolymerization Rate

As for homopolymerization, chain initiation, growth, and termination are identified as the copolymerization steps. Here, too, the monomer is also consumed almost exclusively by the copolymer chain growth.

$$-\frac{d[M_1]+d[M_2]}{dt} = k_{11}[\sim M_1^\bullet][M_1] + k_{12}[\sim M_1^\bullet][M_2] + k_{22}[\sim M_2^\bullet][M_2] + k_{21}[\sim M_2^\bullet][M_1] \quad (13.36)$$

With the termination reactions⁵ given in **Fig. 13.12** ($k_{ab12} \equiv k_{ab21}$) and assuming a quasi-stationary state for the radical concentration

$$k_{21}[\sim M_2^\bullet][M_1] = k_{12}[\sim M_1^\bullet][M_2] \quad (13.3)$$

If the rate of initiation is introduced using $v_i = v_{ab}$ (stationary state \Rightarrow the rate of initiation \sim rate of termination):

$$v_i = 2k_{ab11}[\sim M_1^\bullet]^2 + 2k_{ab12}[\sim M_1^\bullet][\sim M_2^\bullet] + 2k_{ab22}[\sim M_2^\bullet]^2 \quad (13.37)$$

The radical concentration in Eq. (13.16) can now be eliminated to give an equation for the overall rate of polymerization v_{br} ⁶:

$$v_{br} = -\frac{d[M_1]+d[M_2]}{dt} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2) \cdot \sqrt{v_i}}{\sqrt{r_1^2 \delta_1^2 [M_1]^2 + 2 \cdot \Phi \cdot r_1 r_2 \cdot \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2}} \quad (13.38)$$

In Eq. (13.8):

$$\delta_1 = \sqrt{\frac{2k_{ab11}}{k_{11}^2}} \quad (13.39)$$

$$\delta_2 = \sqrt{\frac{2k_{ab22}}{k_{22}^2}} \quad (13.40)$$

$$\Phi = \frac{k_{ab12}}{2 \cdot \sqrt{k_{ab11} \cdot k_{ab22}}} \quad (13.41)$$

The δ -values are the reciprocals of the $k_w / \sqrt{k_{ab}}$ values known from the corresponding radical homopolymerizations (**► Sect. 9.3.1**).

The result of an evaluation using (13.38) is given in **Fig. 13.13**.

At $\Phi > 1$, cross-termination is more important than homo-termination ($v_{ab11} + v_{ab22} \ll v_{ab12} + v_{ab21}$) and with $\Phi = 6$ the experimental curve can be best described. It can be

5 As well as the terminations involving radical combination given in **Fig. 13.12**, termination via disproportionation or indeed other mechanisms is possible but, however, does not influence the kinetic analysis.

6 The symbol for the overall rate of the polymerization v_{br} has not been changed from the original text. The subscript "br" is derived from the German Brutto.

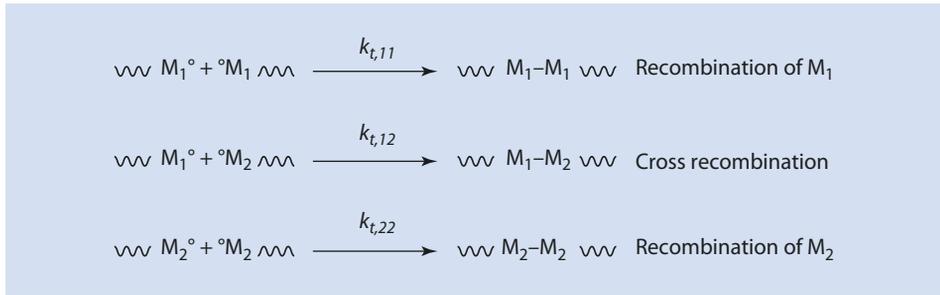


Fig. 13.12 Termination reactions during a copolymerization

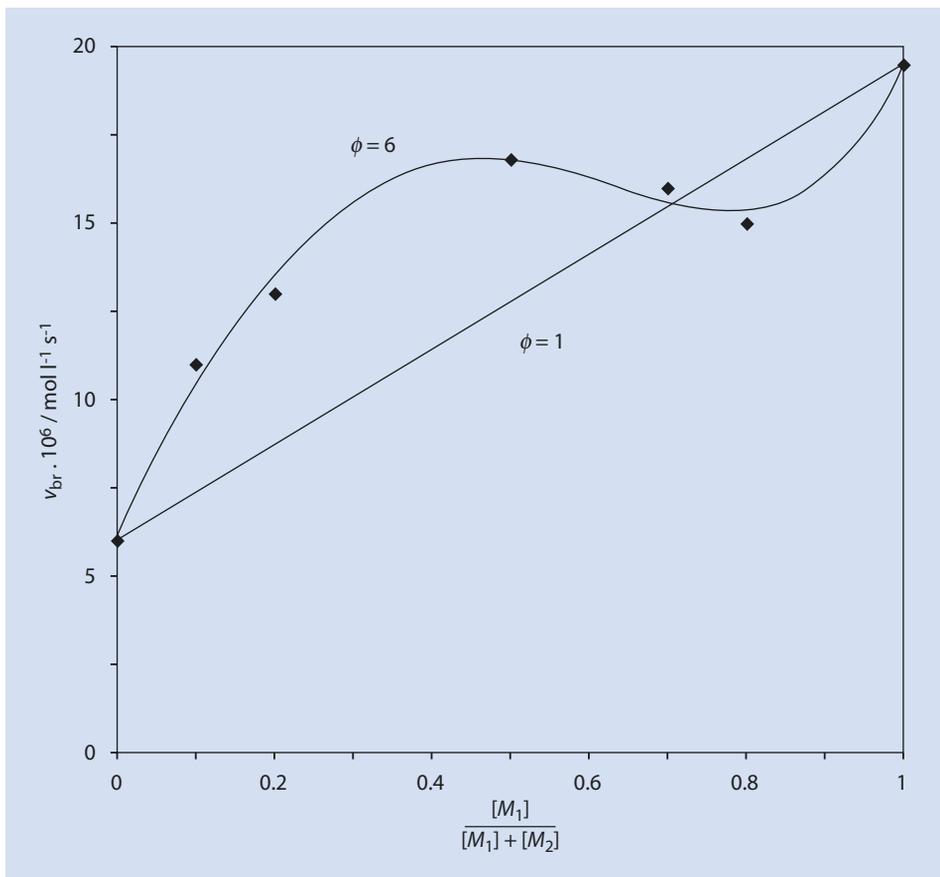


Fig. 13.13 Radical copolymerization of styrene (M_1) and methacrylonitrile (M_2) at 60 °C (Ito 1978)

concluded from the experimental data that an average rate for a copolymerization cannot, or at least can very rarely, be derived from the average rate of polymerization of the two homopolymerizations (Table 13.6).

■ **Table 13.6** Φ -Values for a selection of monomer pairs

Monomer pair	Φ
Styrene–butyl acrylate	150
Styrene–methyl acrylate	50
Styrene–methyl methacrylate	13
Styrene–methacrylonitrile	6
Styrene– <i>p</i> -methoxy styrene	1

It is surprising that the fairly complex experimental curve in ■ Fig. 13.13 can be described rather well by only five parameters $r_1, r_2, \delta_1, \delta_2$ and Φ

13.9 Block and Graft Copolymers

The main focus of this section is on methods of radical polymerization which lead to block and graft copolymers. Both polymer classes are not accessible via simultaneous radical polymerization of two or more monomers. Special methods are needed for such syntheses. Alternative methods for synthesizing block or graft polymers are described in ► Chaps. 9 and 10.

13.9.1 Block Copolymers

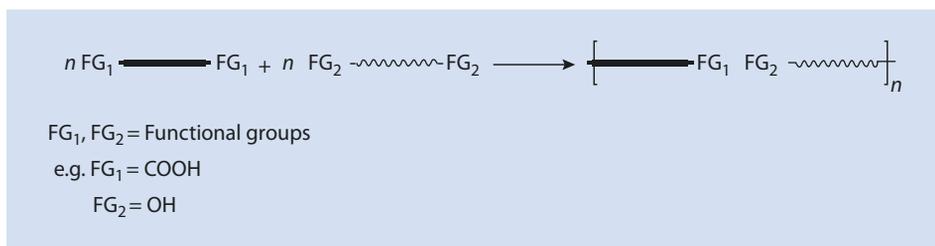
Block copolymers are distinguished from statistical copolymers by the monomer distribution. In the simplest block polymers, a longer sequence of repeating units ($-M_1M_1M_1-$) is joined with that of a sequence of different repeating units ($-M_2M_2M_2-$). Such products are also referred to as AB block copolymers (■ Fig. 13.1). If the sequences are repeated multiple times, they are called $(AB)_n$ -block copolymers. An ABA block copolymer is shown in ■ Fig. 10.58. In contrast to statistical copolymers, whose attributes, to a reasonable approximation, are averages of the corresponding homopolymer properties, block copolymers often have multi-phase morphologies and thus have the attributes of all elements from which they are formed. This makes them very interesting materials.

13.9.1.1 Block Copolymers by Controlled Radical Polymerization (CRP)

Methods such as ATRP, NMP, RAFT, and polymerization in the presence of 1,1 diphenyl ethylene have given strong impulses to the synthesis of block copolymers with radicals as chain transfer agents. These methods have already been discussed in ► Sect. 9.5 and therefore are not discussed here.

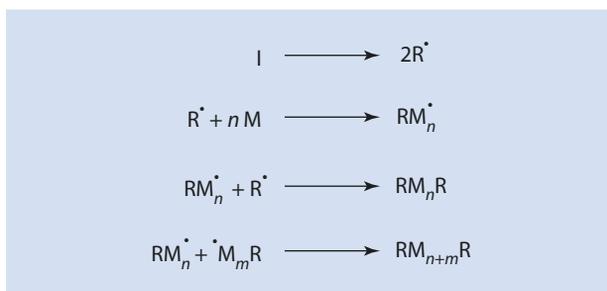
13.9.1.2 End Group Functionalized Polymers (Telechelics)

Oligomers or polymers with well-defined end groups (functional groups, subsequently denoted FG) can be joined together via these groups to build block copolymers (■ Fig. 13.14). This is why methods of radical synthesis which result in such components are presented here. The joining of the components is obviously a step-growth reaction (► Chap. 8).

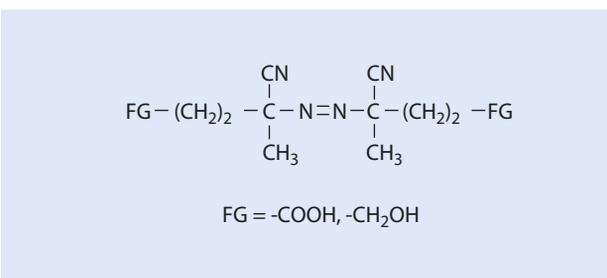


■ Fig. 13.14 Coupling oligomers or polymers with functional end groups to form block copolymers

■ Fig. 13.15 Synthesis of telechelics by *dead-end*-polymerization



■ Fig. 13.16 Functionalized AIBN derivatives



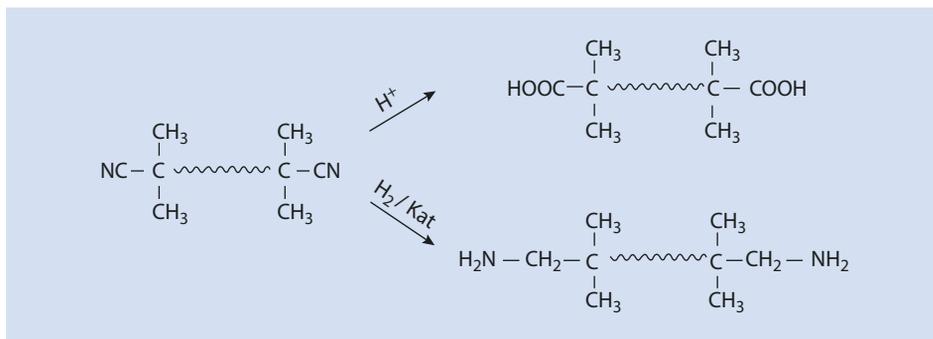
Functionalized Initiators

Radical polymerization in the presence of high initiator concentrations leads to the so-called *dead-end* polymerization and products which carry the functional group of the initiator fragment at their head and tail ends (■ Fig. 13.15).

The primary radicals R^\bullet add to the monomer, but they can also terminate a growing chain. If no transfer occurs and, additionally, termination only involves primary radicals or two growing chains, polymer chains form with an R -group at each chain end. If a functional group is part of the R moiety, products are formed that can be coupled together to form block copolymers, as shown in ■ Fig. 13.14.

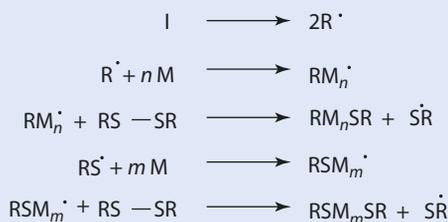
■ Figure 13.16 shows typical functionalized initiators.

AIBN itself can also be seen as a functionalized initiator. However, the CN group is rather a potential functional group and needs to be transformed into more reactive groups after polymerization (■ Fig. 13.17).



■ Fig. 13.17 Synthesis of acid- and amino-group terminated polymers starting from a nitrile group

■ Fig. 13.18 Introducing functional end groups employing a transfer reagent. R includes a functional group, e.g., COOH, CH₂OH, NH₂



Functionalized Transfer Reagents

In ■ Fig. 9.22 the reaction scheme leading to end group functionalized polymers from the reaction of the growing chain ends with a transfer reagent (CCl₄) is shown. An alternative route to such polymers is to carry out the polymerization in the presence of a disulfide derivative (■ Fig. 13.18).

The use of disulfides as chain transfer agents leads to bifunctional oligomers. These can then be converted into block copolymers of the type (AB)_{*n*}. Alternatively, if we use mercaptans for the chain transfer, monofunctional polymer segments result which can be transformed into AB-block copolymers.

13.9.1.3 Polymer Initiators

The concept of the synthesis of block copolymers from polymeric initiators (*macro initiators*) is shown in ■ Fig. 13.19.

Depending on the type of chain termination, block copolymers of type AB or ABA are the result. Multi block copolymers are formed if initiators are used that contain multiple azo functionality as part of the polymer backbone. However, in most cases a mixture of AB, ABA, and (AB)_{*n*} block copolymers is produced.

■ Figure 13.20 gives a typical synthesis of a polymeric initiator with N=N functionality as part of the polymer backbone.

Fig. 13.19 Block copolymers from polymeric initiators

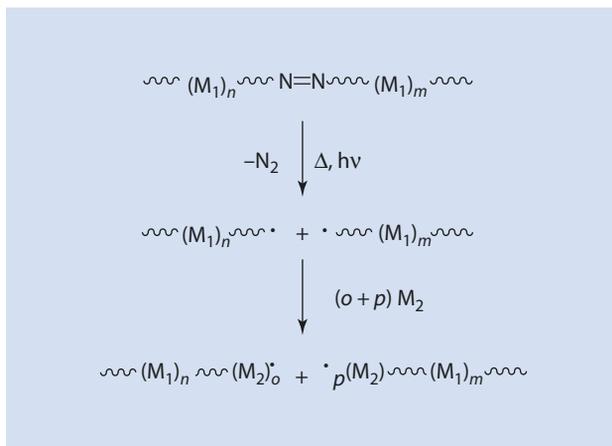
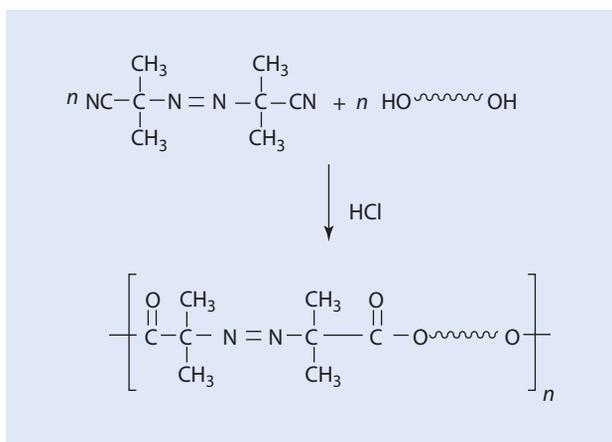


Fig. 13.20 Synthesis of a polymeric initiator



The nitrile groups of the AIBN are converted to acid groups via an acid catalyzed hydrolysis which in turn are esterified with a diol to give the polymeric initiator.

13.9.1.4 Change of Mechanism

A variant of the synthesis of block copolymers which, until now, has remained solely of academic interest involves changing the polymerization mechanism.

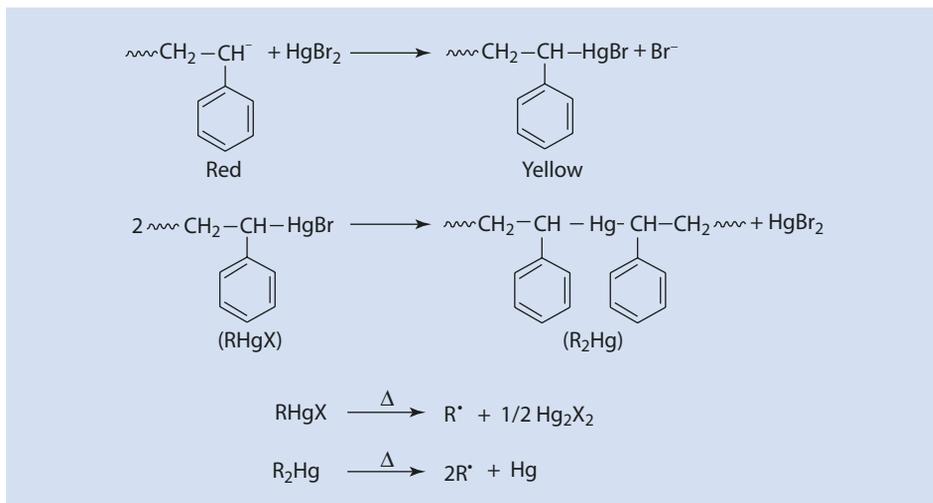
The reaction of HgBr_2 with a carbanion leads initially to an —HgBr -terminated polymer (Fig. 13.21).

If $r_2\text{Hg}$ and RHgX (R =polystyrene) are heated in the presence of another monomer, for example in a solution of MMA in benzene at 80°C , poly(styrene-*block*-methyl methacrylate) can be made.

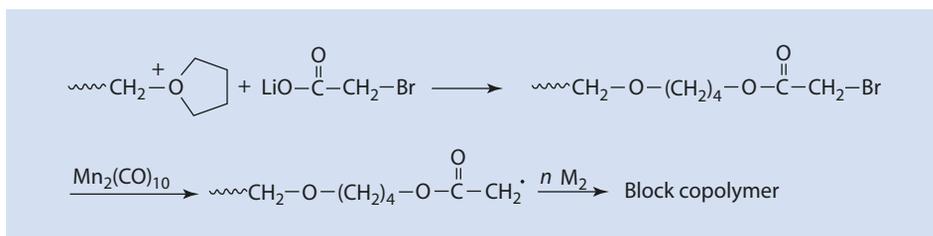
Carbocations can also be transformed into radicals (Fig. 13.22).

13.9.2 Graft Polymers

Graft copolymers are branched polymers in which the main and side chains are chemically different (Fig. 13.1). As with block copolymers, they generally have a



■ Fig. 13.21 Conversion of an anion into a radical



■ Fig. 13.22 Conversion of a cation into a radical

multi-phase morphology and thus exhibit the typical attributes of the homopolymers of the components from which they are made rather than average property values. This makes them interesting raw materials. They have considerable potential as compatibilizers to improve the mixing of incompatible homopolymers. Even small amounts of poly(M_1 -graft- M_2) reduce the interfacial tension between homopoly(M_1) and homopoly(M_2).

13.9.2.1 Grafting Onto

Reactions which follow the scheme shown in ■ Fig. 13.23 are referred to as *grafting onto*.

An actual example, is the radical grafting of polybutadiene with polystyrene (■ Fig. 13.24).

In this example polystyryl radicals are *grafted onto* the polybutadiene chain. Thus, polybutadiene is dissolved in a toluene/styrene mixture or in pure styrene and a radical polymerization of the styrene is initiated, e.g., with a peroxide or AIBN. The growing polystyrene chains can abstract H-radicals, from the polybutadiene chain in a transfer step to form allylic polybutadiene radicals. If other polystyrene radicals

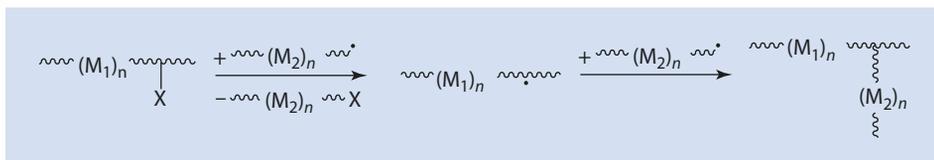


Fig. 13.23 Individual reaction steps for *grafting onto*

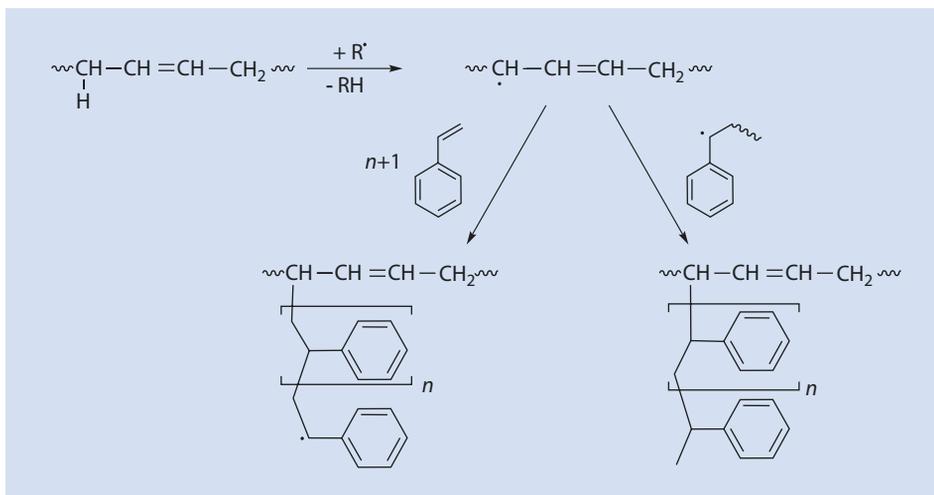


Fig. 13.24 Grafting polybutadiene with polystyrene

combine with these allyl radicals *grafting onto* occurs and the desired poly (butadiene-*graft*-styrene) is formed (Fig. 13.24, right). Alternatively, the allyl radicals can initiate a new polystyrene side chain (Fig. 13.24, left). This would be a *grafting from* reaction.

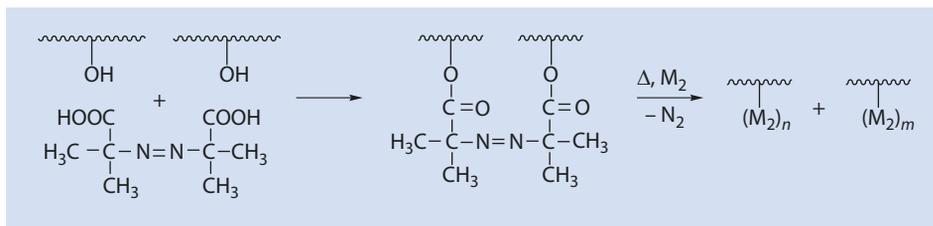
13.9.2.2 Grafting From

More elegant and efficient than *grafting onto* is the *grafting from* strategy. With this strategy polymers with initiator functions as side chains are used for the polymerization (grafting) (Figs. 13.25, 13.26 and 13.27). Such polymers are referred to as *polymeric initiators*, just as are those with initiator groups as part of the polymer backbone (Sect. 13.9.1.3).

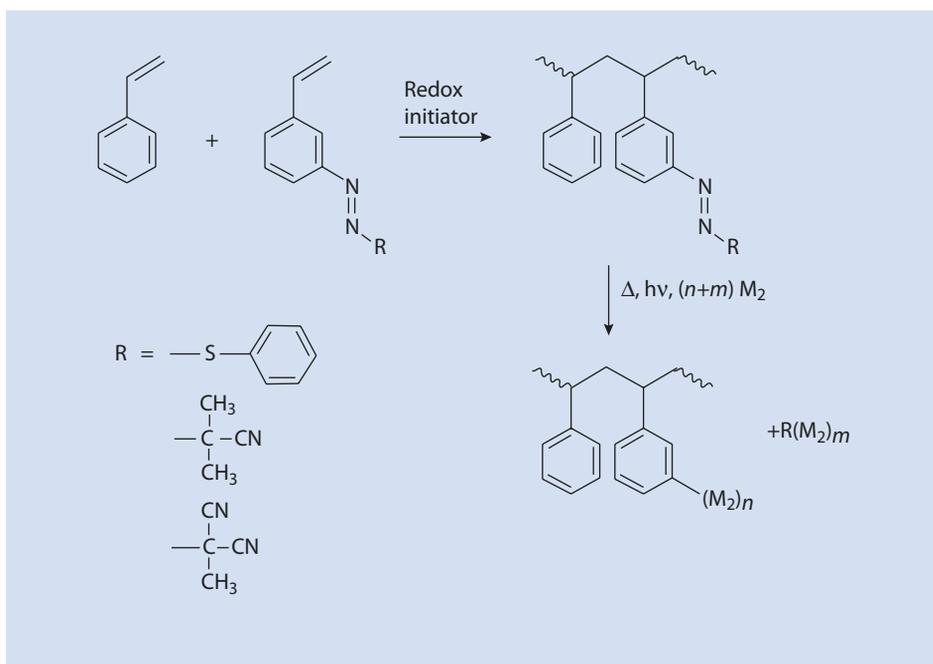
The polymeric initiators can be obtained from simple copolymerization (Fig. 13.26).

Furthermore, such polymeric initiators are also accessible via step-polymerization (Fig. 13.27).

As opposed to the polymeric initiators introduced in Sect. 13.9.1.3, which carry the initiating group as part of the polymer backbone and thus, following initiation yield block copolymers, the initiating groups of these polymeric initiators are side groups along the chain so that initiation leads to the growth of side chains from monomer M_2 , graft copolymers.



■ Fig. 13.25 Polymeric initiator for *grafting from* via polymer analog reaction



■ Fig. 13.26 Copolymerization to yield a polymeric initiator for *grafting from*

Using such polymeric initiators to synthesize graft copolymers results in several products: ungrafted backbone (A) (originally polymeric initiator), ungrafted side chain polymers (C) (initiated by R'), and the target graft copolymer (B) (■ Fig. 13.28).

If, for example, methacrylonitrile is grafted from polystyrene, the products A, B, and C can be separated by selective extraction (■ Fig. 13.29).

During grafting, A and C are undesirable by-products and are avoided as much as possible. A can be minimized if the initiator has multiple initiator molecules per chain, since because every additional initiator function increases the probability of grafting. As soon as A has at least one side chain, it qualifies as grafted and thus becomes B. C can be minimized if R' is less reactive than the polymer radical so that, in the best case, it is not capable of initiating the polymerization.

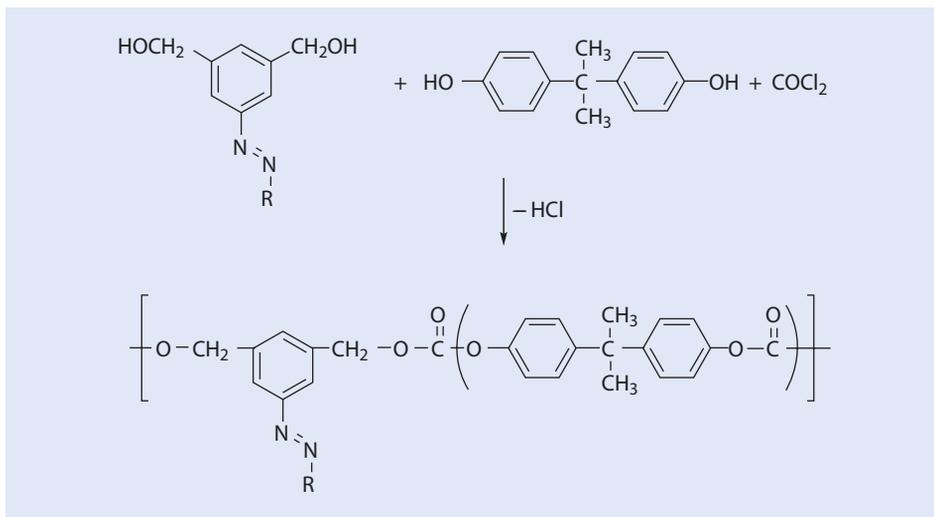


Fig. 13.27 Step-polymerization to yield a polymeric initiator

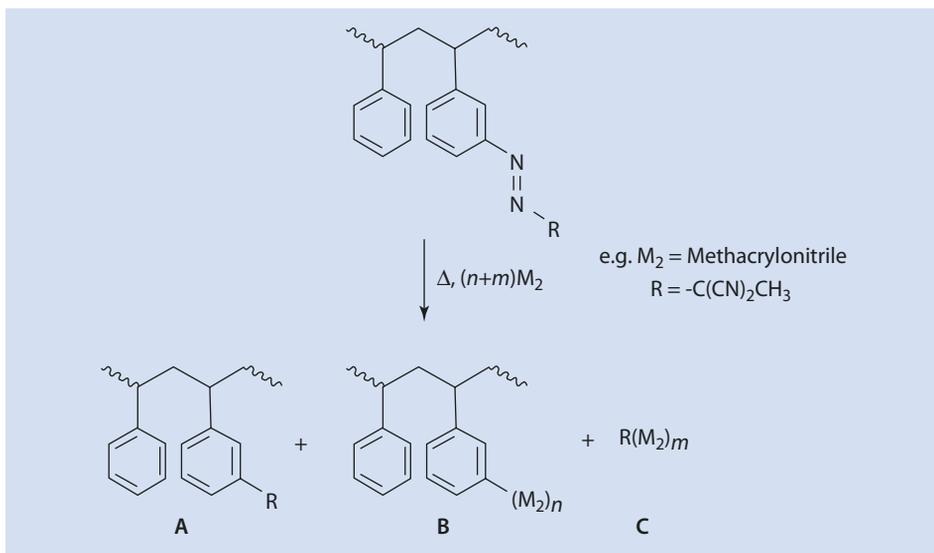
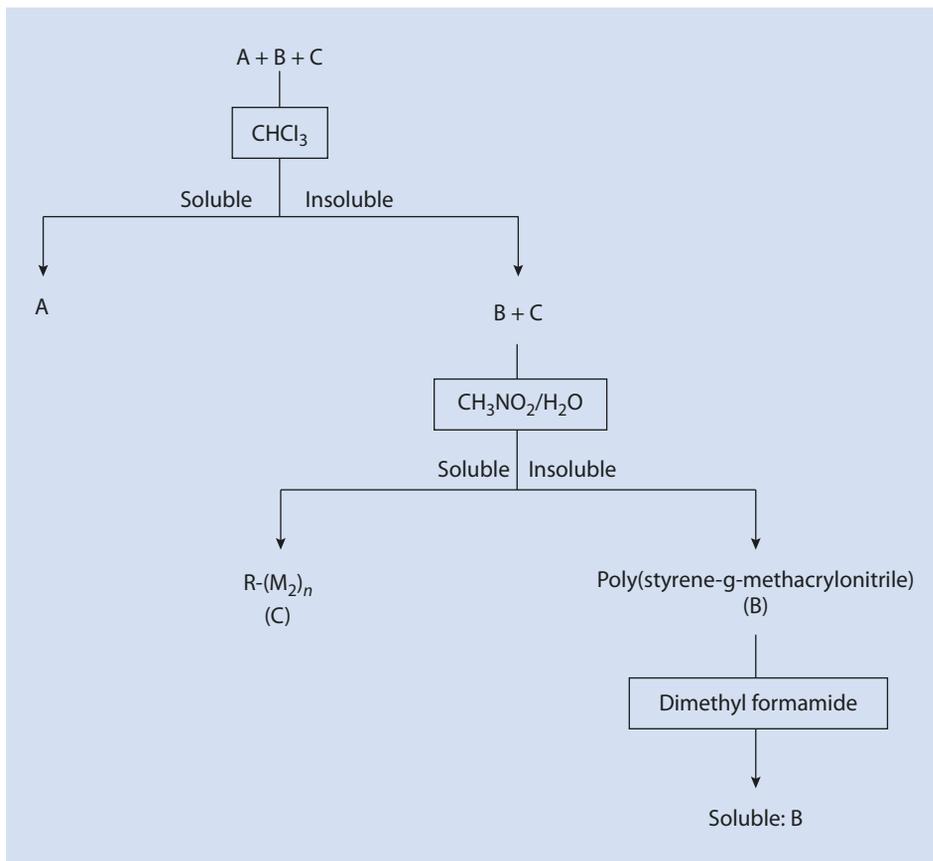


Fig. 13.28 The products from a graft polymerization



■ Fig. 13.29 Separating the products from grafting polystyrene with methacrylonitrile

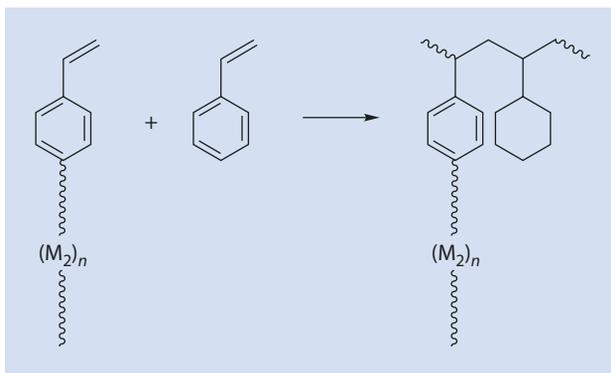
13.9.2.3 Macromonomer Method

Macromonomers (also called macromers) are polymers (oligomers) with a polymerizable terminal functionality and thus are also suitable for copolymerization (■ Fig. 13.30). This is undoubtedly the most elegant synthesis route to graft copolymers.

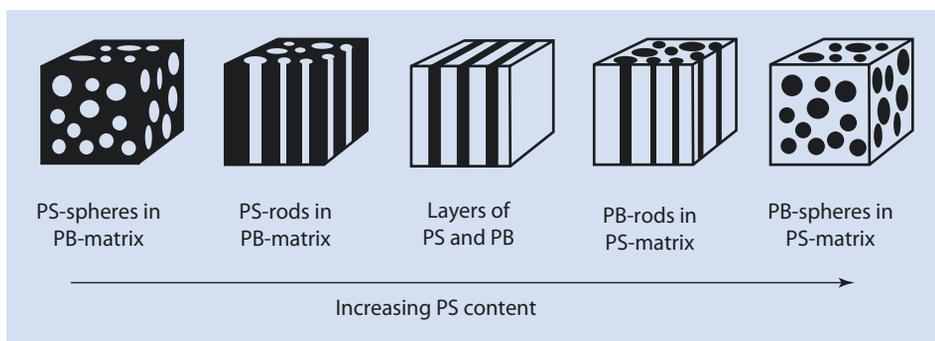
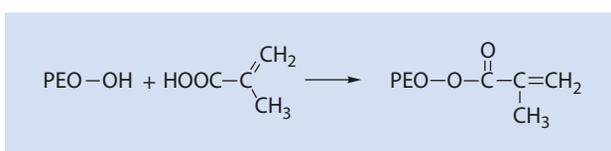
The great advantage of this method is that unwanted homopolymers are almost completely avoided. There are a great many ways to synthesize macromonomers. The basic polymers can be prepared radically, anionically or cationically. The terminal functionality can be attached to the base polymer via the initiator, transfer reagent or the termination reagent. Alternatively, an end group can be reacted to yield the desired functionality. An example of the latter is the conversion of the terminal $-OH$ of polyethylene oxide (PEO) into an acrylate macromonomer via esterification given in

■ Fig. 13.31.

■ Fig. 13.30 Graft copolymers via the macromonomer method



■ Fig. 13.31 Synthesis of a PEO-macromonomer



■ Fig. 13.32 Five basic morphologies for block- and graft-copolymers. PS polystyrene, PB polybutadiene

13.10 Technically Important Copolymers⁷

As mentioned above, statistical copolymers generally have properties reflecting the average values of the homopolymers, whereas block and graft copolymers usually have the attributes of both components. Poly(styrene-*block*-butadiene-*block*-styrene) is a typical and commercially very important example of these special polymers. The cause of this dualism of attributes is a microphase separation of the two distinct, incompatible polymers whereby the two phases are covalently bound together. The covalent bonding also inhibits a macroscopic phase separation. Taking the example of poly(styrene-*block*-butadiene-*block*-styrene) phases of polybutadiene coexist with phases of pure polystyrene. Depending on the ratio of the two polymers the morphologies shown in (■ Fig. 13.32) can be observed. These morphologies are described in more detail in ► Chap. 7.

⁷ The technically most important copolymers are described in ► Chap. 14 in subsections of the relevant homopolymers.

13.11 Structural Elucidation of Statistical Copolymers, Block and Graft Copolymers

To characterize statistical copolymers, the same methods can be used as those applied to homopolymers. As well as elementary analysis, $^1\text{H-NMR}$ -, $^{13}\text{C-NMR}$ -, UV-, and IR-spectroscopy, GPC (► Sect. 3.3.2) and DSC are used. One should not neglect simple solubility tests, by which, assuming a knowledge of the homopolymer solubilities, simple mixtures of the homopolymers can be ruled out. If the method used to synthesize the polymer is known, using the aforementioned analytical methods should allow a reliable determination of the total composition and indeed the monomer sequences. If the glass transition temperatures of the homopolymers are sufficiently different, the difference between a simple mixture of two homopolymers and a statistical copolymer is clear from a DSC; a mixture of two homopolymers has two glass transition temperatures, whereas a statistical copolymer exhibits only a single value.

To distinguish reliably between a homopolymer mixture and a block or graft copolymer, a selective extraction is essential. Mixtures are often easily separated with this method. Of course, the composition of the separate phases should always be analyzed. In this case, a DSC measurement is less appropriate, as a mixture of two homopolymers as well as block or graft copolymers all exhibit two glass transition temperatures.

The following methods of analysis have also proved suitable:

1. Solubility (see above)
2. Film transparency: block copolymers produce transparent films despite phase separation if the diameter of the microphases is less than $\lambda/20$ (λ = wave length of daylight)
3. Compatibility of polymer solutions (a solution of 10 % block copolymer usually remains transparent, whereas a mixture becomes turbid)
4. GPC: a block copolymer is generally monomodal whereas a mixture of two polymers with different molar masses is bimodal
5. Block copolymers tend to have high melt viscosities
6. Information about the morphology of the polymers can be obtained from REM, TEM, and staining, e.g., with OsO_4

The average sequence length and the order of the segments remain difficult questions as far as the complete structural description is concerned and require a knowledge of the synthetic method.

^1H - and ^{13}C -NMR spectroscopic measurements on statistical copolymers on the one hand and block and graft copolymers on the other are easily distinguishable because of the different sequences of the building blocks. Electron microscopy and small-angle scattering provide visual evidence for the presence of phase separation for block- and graft-copolymers whereas for statistical copolymers no special signals are observed. An increased melt viscosity can suggest that the material is a block- or graft-copolymer. If there is evidence of crystallization, then the sample is more likely to be a block- or graft-copolymer than a simple statistical copolymer.

Several methods for characterizing block- and graft-copolymers are summarized in

■ Table 13.7.

Table 13.7 Methods for characterizing block- and graft-copolymers

Block- and graft-copolymers vs. homopolymer mixtures	
1.	Solubility, fractional extraction
2.	Film appearance
3.	Compatibility of polymer solutions
4.	Molar mass distribution, GPC
5.	Rheology
Block- and graft-copolymers vs. statistical copolymers	
1.	^1H - and ^{13}C -NMR spectroscopy
2.	IR spectroscopy
3.	DSC, glass transition temperature(s)
4.	Electron microscopy
5.	Small-angle scattering (SAS)
6.	Rheology
7.	Crystallization

As part of the structure analysis, all methods suitable for measuring mass are worthwhile. Additionally, selective polymer degradation can provide valuable information.

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