Methods and Techniques for Synthesis, Characterization, Processing, and Modification of Polymers

2

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

2.1 Methods for Synthesis of Polymers

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

2.1.1 Chain Growth Polymerizations

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

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

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

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

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

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

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

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

S: chain-terminating agent (stopper)

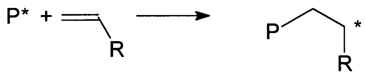
T: chain-transfer agent (solvent, monomer, initiator, polymer, regulator, . . .)

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

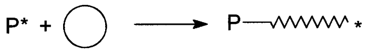
$$\mathrm{I}\left[\mathrm{M}\right]_x\mathrm{M}\left[\mathrm{M}\right]_y\mathrm{M} \underset{-\,\mathrm{Z}}{\xrightarrow{+\,\mathrm{Z^*}}} \mathrm{I}\left[\mathrm{M}\right]_x\mathrm{M^*}\left[\mathrm{M}\right]_y\mathrm{M} \xrightarrow{+\,n\,\mathrm{M}} \mathrm{I}\left[\mathrm{M}\right]_x\underset{\left|\right.}{\mathrm{M}}\left[\mathrm{M}\right]_y\mathrm{M} \quad\text{with}\quad \left[\mathrm{M}\right]_{n-1}\mathrm{M^*} \text{ on the branch} \tag{2.6}$$

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

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



(2.7)

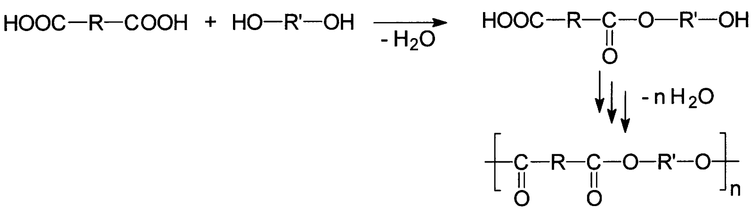


(2.8)

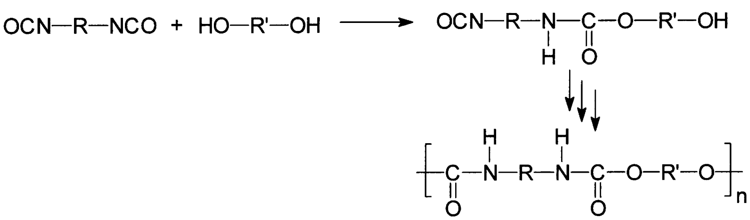
Depending on the nature of the active center, chain-growth reactions are subdivided into radicalic, ionic (anionic, cationic), or transition-metal mediated (coordinative, insertion) polymerizations. Accordingly, they can be induced by different initiators or catalysts. Whether a monomer polymerizes via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

2.1.2 Step Growth Polymerizations

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



(2.9)



(2.10)

Table 2.1 Criteria for chain and stepwise reactions in polymer synthesis

Chain growth reactions	Step growth reactions
Start of the reaction (chain initiation) generally requires initiators or catalysts	Reaction often proceeds without the need for catalysts
Only active species (e.g., macro radicals or macro ions) can add further monomer molecules in the propagation process	Both monomer and polymer molecules with suitable functional end groups can react
Activation energy for chain initiation is higher than that for propagation	Activation energy is about the same for each reaction step
Monomer concentration decreases with reaction time	Monomer molecules disappear very quickly; more than 99% of monomer molecules have already reacted when the degree of polymerization is 10
Macromolecules are formed from the very beginning of the reaction	Monomer molecules first give oligomers; high polymer is formed only towards the end of the reaction
The average molecular weight of the poly-mer normally changes little with reaction time (exception: living polymerization)	The average molecular weight increases steadily with reaction time; long reaction times are usually necessary to produce high molecular weights

Evidently, monofunctional molecules cannot result in polymer chains via step growth polymerizations. Instead, each monomer molecule as well as all inter-mediates must possess two functional groups. When more than two reactive groups are present in a monomer, branched or crosslinked products will result. Moreover, step growth polymerizations are categorized according to how the functional groups are assigned to the monomers. When each monomer bears two identical functional units, the process is called AABB-type polycondensation/polyaddition. Here, mixtures of at least two different types of monomers are required, bearing the complementary functional groups (see Eqs. 2.9 and 2.10). If, on the other hand, each monomer molecule bears the two complementary functional groups required for step growth polymerization, the process is called AB-type polycondensation/polyaddition (see Eqs. 2.11 and 2.12).

$$n\ \mathrm{HO{-}R{-}COOH} \xrightarrow[-\,n\,\mathrm{H_2O}]{} \left[\mathrm{O{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}} \right]_n \qquad (2.11)$$

$$n\ \mathrm{H_2N{-}R{-}COOH} \xrightarrow[-\,n\,\mathrm{H_2O}]{} \left[\mathrm{\overset{\displaystyle H}{\overset{|}{N}}{-}R{-}\overset{\displaystyle O}{\overset{\|}{C}}} \right]_n \qquad (2.12)$$

As a consequence of the lack of special active centers, the chain formation in step growth polymerizations occurs via a sequence of accidental and independent reaction events. It proceeds via dimers, short and longer oligomers until, finally, at conversions higher than 99% long chains are formed which are called condensation polymers (polycondensates) or addition polymers, respectively. Apart from high degrees of conversion also a very precise 1:1 equivalence of the complementary functional groups is essential to achieve very high molar masses. A summary of the most significant differences between step-growth and chain-growth polymerizations are given in Table 2.1.

2.1.3 Modification of Polymers

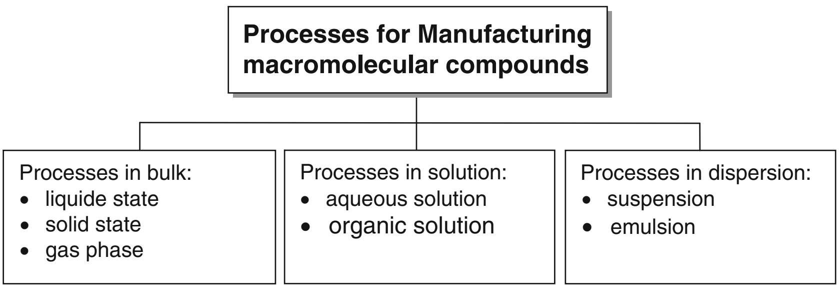
The third possibility for synthesizing polymeric substances is the modification of existant natural or synthetic macromolecules (see Chap. 5). These processes can either be chemical or physical. Chemical modifications are reactions on macromolecules without degradation of the main chain (macromolecular substitution routes, "polymer-analogous reactions") like, for example, hydrolysis, esterification, and etherification of side groups. Physical modifications include addition of stabilizers as well as the addition of (inorganic) reinforcing agents and also the mixing of different polymers (polymer blends).

2.1.4 Polymer Recipes Reference List

The present book contains about 110 detailed polymer recipes. Yet, for quite a number of common polymers recipes are missing. The following Tables 2.2, 2.3, 2.4, and 2.5 attempt to fill this gap. The information provided includes the name of the monomer, the formula of the basic unit of the polymer, and references for detailed recipes. Table 2.2 lists polymers prepared by chain growth polymerization, Tables 2.3 and 2.4 those prepared by step growth polymerization, and Table 2.5 contains polymers obtained by chemical modifications of (natural) macromolecules.

2.2 Techniques for Manufacturing of Polymers

The processes for manufacturing macromolecules can be divided into three different categories (Scheme 2.1).



Scheme 2.1

Table 2.2 Synthesis of macromolecules by chain growth polymerization. *Note:* The citation of literature in the right-hand column of the following tables should be understood as follows: the number(s) in the first line(s) refer(s) to this book. For example, 3.2 means experiment number 2 in Chap. 3. The following line refers to: Houben Weyl, Methoden der Organischen Chemie, Vol. E20, Makromolekulare Stoffe Teil 1–3, Thieme Verlag, Stuttgart, New York, 1987 (abbreviated: HW). For example, the citation HW:135 refers to an experimental procedure described on page 135 thereof. The bottom line refers to H. R. Kricheldorf, Handbook of Polymer Synthesis, Vols. 1 and 2, Dekker, New York, 1992 (abbreviated: K). For example, K:34 refers to further references given on page 34 of that book

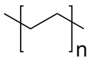
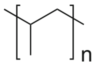
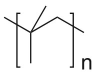
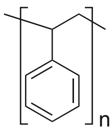
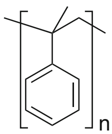
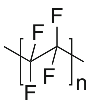
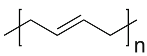
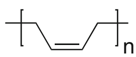
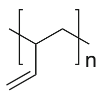
Monomer[a]	Basic unit of the polymer	Preparation examples, literature
1. Olefins		
Ethylene (r, c, Z/N)		(Z/N) 3–28 (r+c) HW: 689 K: 3
Propylene (c, Z/N)		(Z/N) 3–29/3–32 (c) HW: 769 K: 26
Isobutylene (c)		(c) 3–16 HW: 769 K: 53
Styrene (r, c, a, Z/N)		(r) 3–1/3–2/3–6/3–7 (Z/N) 3–30 HW: 762 K: 77
α-Methylstyrene (r, c, a) (r only copolymerization)		(c) 3–18 (a) 3–19 HW: 1012 K: 90
Tetrafluoroethylene (r)		HW: 1028 K: 197
2. Diolefins		
Butadiene (r, c, a, Z/N)	 1,4E (trans)  1,4Z (cis)  1,2	(Z/N) 3–31 HW: 798 K: 386

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Table 2.2 (continued)

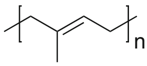
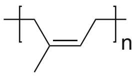
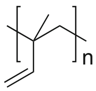
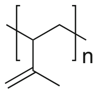
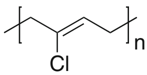
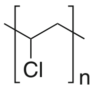
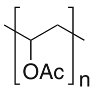
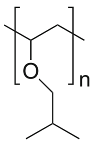
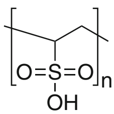
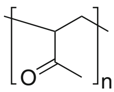
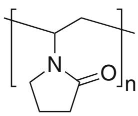
Monomer[a]	Basic unit of the polymer	Preparation examples, literature
2-Methyl-1,3-butadiene (isoprene) (r, c, a, ZN)	 1,4E (trans)  1,4Z (cis)  1,2  3,4	(r) 3–12 (a) 3–21 HW: 822 K: 393
2-Chloro-1,3-butadiene (chloroprene) (r)	 1,4Z (cis)	HW: 842 K: 396
3. Vinyl derivatives		
Vinyl chloride (r, a)		(a) HW: 1042 K: 172
Vinyl acetate (r)		3–3/3–4 HW: 1115 K: 164
Isobutyl vinyl ether (r, c)		(c) 3–17 HW: 1072 K: 145
Vinylsulfonic acid (r)		HW: 1259
Methyl vinyl ketone (r, c)		HW: 1138 K: 360
N-Vinylpyrrolidone (r, c)		HW: 1267 K: 114

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Table 2.2 (continued)

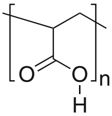
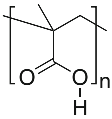
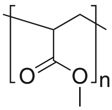
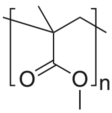
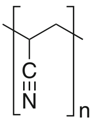
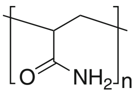
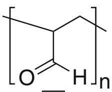
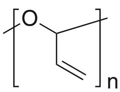
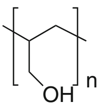
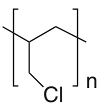
Monomer[a]	Basic unit of the polymer	Preparation examples, literature
4. Acryl compounds		
Acrylic acid (r)		HW: 1148 K: 268
Methacrylic acid (r)		3–5 HW: 1148 K: 268
Methyl acrylate (r, a)		HW: 1144 K: 223
Methyl methacrylate (r, a)		(r) 3–8 (a) 3–20 HW: 1144 K: 223
Acrylonitrile (r, a)		(r) 3–11 (a) HW: 1192 K: 280
Acrylamide (r, a)		(r) 3–9 (a) HW: 1176 K: 256
Acrolein (1: r, c; 2: a)	 1  2	HW: 1127 K: 337
5. Allyl compounds		
Allyl alcohol (r)		HW: 2013
Allyl chloride (r, c)		HW: 1013

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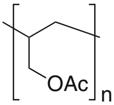
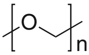
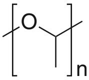
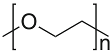
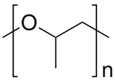
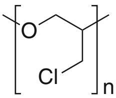
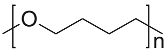
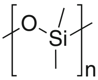
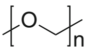
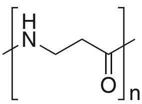
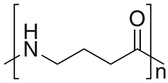
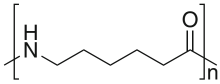
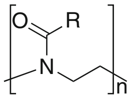
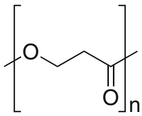
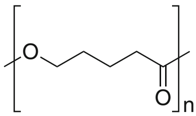
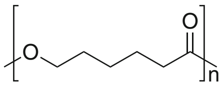
Table 2.2 (continued)

Monomer[a]	Basic unit of the polymer	Preparation examples, literature
Allyl acetate (r)		HW: 1013
6. Monomers with C=O bonds		
Formaldehyde (c, a)		(a) 3–22 (c) HW: 1388 K: 618
Acetaldehyde (c, a)		HW: 1380 K: 632
7. Ring-opening polymerization		
(a) Cyclic ethers		K: 481
Ethylene oxide (c, a)		HW: 1367 K: 484
Propylene oxide (c, a)		HW: 1367 K: 501
Epichlorohydrin (c, a)		HW: 1367 K: 503
Tetrahydrofuran (c)		3–23 HW: 1367 K: 521
Cyclosiloxanes (e.g., 2,4,6-hexamethyl-cyclotrisiloxane) (c, a)		4–21/4–22 HW: 2219 K: 1144
(b) Cyclic acetals		K: 630
1,3,5-Trioxane (c)		3–24 HW: 1388 K: 633
(c) Cyclic amides, oxazolines		K: 807, 876
β-Propiolactam (a)		HW: 1505 K: 890

(continued)

Table 2.2 (continued)

Monomer[a]	Basic unit of the polymer	Preparation examples, literature
γ-Butyrolactam (a)		HW: 1505 K: 891
ε-Caprolactam (c, a)		(a) 3–26 HW: 1505 K: 892
2-Alkyloxazolines (c)		3–27 K: 747
(d) Cyclic esters		K: 652
β-Propiolactone (c, a)		HW: 448 K: 653
δ-Valerolactone (c, a)		HW: 448 K: 660
ε-Caprolactone (c, a)		HW: 448 K: 661

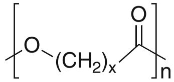
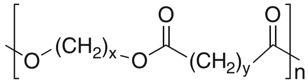
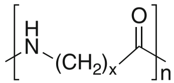
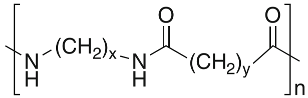
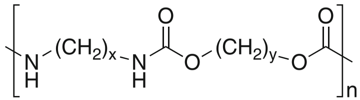
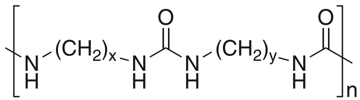
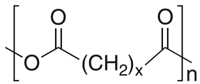
[a]Polymerizability: radical (r), cationic (c), anionic (a), Ziegler/Natta (Z/N)

The basic characteristics as well as some advantages and disadvantages are illustrated in Sects. 2.2.2 (polyreactions in bulk), 2.2.3 (polyreactions in solution), and 2.2.4 (polyreactions in dispersion). Prior to this some special features that must be considered in the preparation of polymers (Sect. 2.2.1) and some suitable techniques for the preparation in the laboratory (Sect. 2.2.5) are described.

2.2.1 Particularities in the Preparation of Polymers

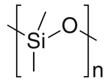
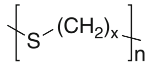
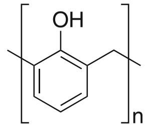
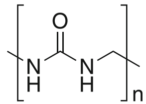
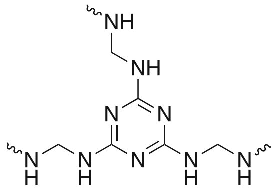
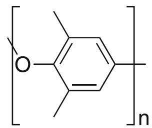
Especially in the case of macromolecular materials, not only the method of synthesis, but also the manufacturing process has a large influence on size and structure of the molecules, and consequently on the physical properties. For example, poly(vinyl chloride), produced by radical polymerization in suspension, differs in some practical properties from PVC obtained by radical polymerization in bulk. Changes in the

Table 2.3 Synthesis of macromolecules by step growth polymerization (polycondensation)

Monomer 1	Monomer 2	Polymer	Basic unit of the polymer	Preparation examples, literature
ω-Hydroxy-carboxylic acids		Linear polyesters		HW: 555 K: 646
Diols	Dicarboxylic acids or derivatives	Linear polyesters		4–1 to 4–7 HW: 555 K: 649
Tri- or polyols	Di- or poly-carboxylic acids or their derivatives	Branched or crosslinked polyesters		HW: 555 K: 674, 677
ω-Amino carboxylic acids		Linear polyamides		4–9 HW: 1497 K: 810
Diamines	Dicarboxylic acids or derivatives	Linear polyamides		4–10 to 4–13 HW: 1497 K: 818, 829
Diamines	Bis-chloro-carboxylic acid esters	Linear polyurethanes		HW: 1561 K: 687
Diamines	Phosgene	Linear polyureas		HW: 1721 K: 715
Dicarboxylic acids		Poly-anhydrides		HW: 1400 K: 1668

(continued)

Table 2.3 (continued)

Monomer 1	Monomer 2	Polymer	Basic unit of the polymer	Preparation examples, literature
Dimethyl-silane-Diol		Polysiloxanes		HW: 2219 K: 1149
α,ω-Dihalo-alkanes	Sodium polysulfide	Polyalkylene sulfides		HW: 1458 K: 992
Phenols	Formaldehyde	Phenol/formaldehyde condensate		4–14 HW: 1764 K: 1484
Urea	Formaldehyde	Urea/formaldehyde condensate		4–15 HW: 1811 K: 1489
Melamine	Formaldehyde	Melamine/formaldehyde condensate		4–16 HW: 1811
2,6-Dimethyl-phenol		Poly(dimethyl phenylene ether)		4–17 HW: 1380 K: 546

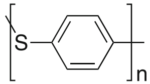
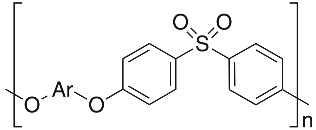
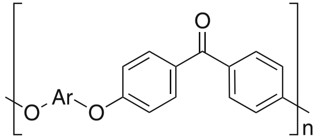
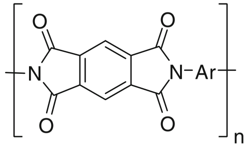
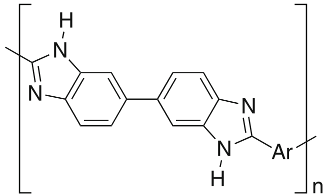
Dichloro-benzene	Sodium sulfide	Poly(pheny-lene sulfide)		HW: 1463 K: 1397
Bisphenol	4,4′-Dichloro-diphenyl sulfone	Poly(arylene ether sulfone)		4–18 HW: 1475 K: 1038
Bisphenol	4,4′-Difluorobenzo-phenone	Poly(arylene ether ether ketone)		4–19
Bisanhydride	Aromatic diamines	Polyimides		4–20 HW: 2182 K: 943
Aromatic diphenyl carboxylate	Biphenyl-tetramine	Poly(benzimid azoles)		HW: 2186 K: 1247

Table 2.4 Synthesis of macromolecules by step growth addition polymerization (polyaddition)

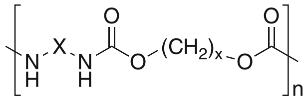
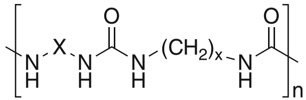
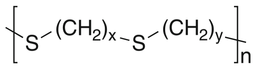
Monomer 1	Monomer 2	Polymer	Basic unit of the polymer	Preparation examples, literature
Diols, e.g. polyether diols	Diisocyanates (X = arylene or alkylene)	Polyurethanes		4–23
				HW: 1561
				K: 685
Diamines	Diisocyanates (X = arylene or alkylene)	Polyureas		HW: 1721
				K: 713
Di- or poly-epoxides	Amines or anhydrides	Epoxide resins		4–24
				HW: 1891
				K: 1496
Non-conjugated dienes	Dithioles	Polythioethers		HW: 1458
				K: 1011

Table 2.5 Modification of macromolecules via polymer analogous reactions

Educt	Chemical reaction	Product	Preparation examples, literature
Cellulose	Esterification	Cellulose esters	5–5/5–7
			HW: 2042
			K: 1528
Cellulose	Etherification	Cellulose ethers	5–6
			HW: 2042
			K: 1518
Cellulose	Etherification with chloroacetic acid (carboxymethylation)	Carboxymethyl cellulose	5–6
			HW: 2042
			K: 1521
Poly(vinyl acetate)	Saponification	Poly(vinyl alcohol)	5–1
			HW: 2042
			K: 1504
Poly(vinyl alcohol)	Acetalization	Poly(vinyl butyral)	5–2
			HW: 2042
			K: 1506
Crosslinked polystyrene	Sulfonation	Cation exchanger	5–9
			HW: 1944
Polysulfone	Sulfonation	Sulfonated polysulfone	HW: 1944

properties of the products can be realized even within the same manufacturing process by changing the reaction conditions. Thus, in radical polymerization of styrene in bulk, polymers with the same molecular weight, but different distributions of molecular weight can be obtained solely by use of different reaction conditions. This is noticeable in the rheological characteristics of the molten polymer (processability) and in some properties of the solid material.

The reaction kinetics of polyreactions have their own characteristics. *Radical* and *ionic polymerizations* proceed as chain reactions, whereby the stationary concentration of the active ends of the chain, i.e., of the growing macro radicals or macro ions, is very small. In radical polymerizations, this concentration is about 10^{-8} mol/l. For this reason, chain polymerizations are remarkably sensitive towards impurities that can react with radicals or ions. Reactions of such impurities with the growing ends of the chains can cause a deceleration or interruption of the polymerization or a decrease of the molecular weight by chain transfer. A reaction with the initiator or catalyst can cause inhibition as well as acceleration (redox catalysis, co-catalysis). In addition, the steric arrangement of the monomers (*cis-trans* isomerism, tacticity) is strongly influenced by small amounts of certain substances. In *condensation polymerizations* and *stepwise addition polymerizations* of bifunctional monomers, conversion rates of more than 99% must be reached in order to obtain high molecular weights; this is only possible when monofunctional compounds are largely excluded. Therefore, the requirements in purity of the monomers and auxiliary materials are very high. In many cases, the tolerance limit for certain impurities is in the range of a few ppm. Methods for laboratory use which meet these requirements are described in Sect. 2.2.5.

One more feature is that polymer melts as well as polymer solutions have a very high viscosity due to the size and shape of the macromolecules. Thus, in polymerizations in the melt or in homogeneous solution, the viscosity of the reaction mixture increases, often by many orders of magnitude. Beside an impairment of mass transfer, high viscosity also causes difficulties in pumping, stirring, and mixing. In principle, the increase of the viscosity can be compensated by increasing the temperature, but this is strictly limited by the thermal stability of some polymers and, especially, by kinetic factors. An increase of the temperature in particular causes a strong decrease in molecular mass and an increase in side reactions (chain transfer, crosslinking) in many polymerizations. Finally, the high viscosity of the reaction mixture also substantially hinders heat transfer. Due to the fact that nearly all chain growth polymerizations and step growth polymerizations are strongly exothermic, the rapid removal of large amounts of heat creates severe difficulties, especially if one works in bulk or solution. Furthermore, polymers are poor heat conductors, thus the heat transfer coefficient decreases with increasing concentration of polymer. In addition, the heat transfer is reduced by the laminar boundary layer at the inner wall of the reactor, which is enlarged with increasing viscosity. In this respect, polymerizations in dispersion are distinctly more favorable because the reaction mixture retains a low viscosity and therefore turbulent stirring is possible and relatively high heat transfer coefficients can be reached. If the polyreaction is performed in aqueous medium, the high specific heat capacity of water additionally contributes to the heat dissipation. One more characteristic difference in comparison to the preparation of low-molecular-weight substances is the limitation in subsequent purification of the polymers. Thus, the complete removal of low-molecular-weight substances, such as solvents, oligomers, initiator residues, catalysts, and monomers can be very difficult. Because of this, purification is time- and cost-intensive in the laboratory and especially on an industrial scale. Special apparatus is often required (for laboratory techniques, see Sect. 2.2.5). Industrially, it is nearly impossible to separate the resulting polymer mixture into macromolecules of the same molecular size, structure, and composition, but for analytical use, some methods are available (see Sect. 2.3.3.4).

2.2.2 Polyreactions in Bulk

Polyreactions in bulk are carried out without solvents or diluents. In this way, high molecular weights can be obtained frequently with high rates of reaction. The resulting products are very pure, because only monomers and, if necessary, initiators and catalysts are added. Polyreactions in bulk are also advantageous for economical and ecological reasons because recycling and purification of solvents or dispersants as well as the disposal of liquid waste (as in the case of aqueous suspension or emulsion polymerizations) are not necessary. On the other hand, considerable difficulties in running the process are often caused by the removal of the heat of polymerization and the handling of the viscous reaction mixtures. Furthermore, polyreactions in highly viscous media show intensified side reactions such as chain transfer, thus influencing the properties of the resulting product.

Polyreactions in bulk are divided into homogeneous and heterogeneous reactions, depending on whether the polymer remains dissolved in its monomer or not or, respectively, whether the polyreaction is performed above or below the softening temperature of the polymer.

2.2.2.1 Homogeneous Polyreactions in Bulk

In homogeneous polyreactions in bulk, the polymer remains dissolved in the monomer. In some cases, this can only be achieved by carrying out the polyreaction above the softening temperature of the polymer. Chain polymerizations, condensation polymerizations, and stepwise addition polymerizations can be performed homogeneously in bulk. The number of *chain polymerizations* that can be performed in a homogeneous phase is very limited. On the one hand, only a few monomers are able to dissolve their own polymers (e.g., styrene and methyl methacrylate), on the other hand, temperatures above the softening point often cannot be used for kinetic and thermodynamic reasons (ceiling temperature, low molecular weights, increase of side reactions).

In contrast, *condensation polymerizations* and *stepwise addition polymerizations* in the homogeneous phase are the most frequently performed processes on an industrial scale. Because the resulting polymers usually have high softening points and the fact that the molecular weight – and therefore the melt viscosity – increases with progressing reaction, temperatures of above 250°C are often necessary, at least at the end of the reaction. Even so, the removal of the highly volatile reaction products (water, alcohol), which is necessary in order to obtain high molecular masses, is difficult. Therefore, evacuation and intensive mixing, which create larger surfaces and short diffusion paths, are necessary. Similarly, the conditions for high conversion rates and the equivalency of end groups in condensation polymerization and stepwise addition polymerization must be adjusted by suitable technical measures. Moreover, high thermal stabilities of the starting materials and the resultant polymers are necessary on account of the long reaction times at high temperatures. Thus, many high-melting polyamides are not accessible by this process. Hence, they must be prepared in solution or by interfacial condensation polymerization.

2.2.2.2 Heterogeneous Polyreactions in Bulk

In heterogeneous polymerizations in bulk, the formed polymer is insoluble in its monomer and the polyreaction is performed below the softening point of the polymer. On an industrial scale, this type of process is especially utilized for chain polymerizations, for example, the radical polymerization of liquid vinyl chloride, the polymerization of liquid propylene with Ziegler-Natta or with metallocene catalysts, and the polymerization of molten trioxane.

Besides in the liquid phase, some polyreactions are also performed in the *solid state*, for example, the polymerization of acrylamide or trioxane (see Example 3.24). The so-called post condensation, for example, in the case of polyesters (see Example 4.3), also proceeds in the solid phase. Finally, ring closure reactions on polymers with reactive heterocyclic rings in the main chain (e.g., polyimides, see Example 4.20) are also performed in the solid state.

A third possible variation of heterogeneous polyreactions in bulk is the polymerization in the *gaseous phase* or *gas phase*. The term gaseous phase is used when the reaction is performed with gaseous monomers. The polymerization itself does not occur in the gaseous phase, rather the gaseous monomer is adsorbed on the solid catalyst particles and polymerized in that state. With proceeding polymerization, the catalyst particles are encapsulated by the solid polymer layer. From there on, the monomer must diffuse from the gaseous phase through the polymer cover to the catalytically active centers. The reaction medium is now a gas/solid dispersion of a solid polymer in its gaseous monomer. Heterogeneous bulk polymerizations often show deviations in their kinetics in comparison to polymerizations in a homogeneous phase. Similar considerations hold true for processes on a technical scale due to lower viscosities and differences in material transport.

2.2.3 Polyreactions in Solution

There are two different ways for carrying out polyreactions in a solvent. When both the monomer and the resulting polymer are soluble in the solvent, one speaks of a homogeneous solution polymerization; on the other hand, if the polymer precipitates during the course of the reaction, it is called precipitation polymerization. By addition of a solvent, different effects are obtained: Basically, the viscosity of the reaction mixture is decreased in comparison to a bulk polyreaction; this facilitates heat transfer, mass transport, and handling.

In *chain polymerizations*, some additional aspects have to be considered. For example, the undesired Trommsdorff effect (gel effect, see Sect. 3.1) in radical polymerization can be completely or partially prevented by choosing the appropriate concentration and solvent. Furthermore, if solvents with a high chain transfer constant are used, the solvent molecules can undergo transfer reactions with the growing macroradicals; this reduces the degree of polymerization. In addition, terminal groups can be introduced which influence the thermal and chemical stability of the polymer. In ionic polymerizations, the influence of the solvent on the course of the reaction is even more pronounced. Besides transfer reactions, reactions with the initiator or solvation of the growing macroion may also occur. In certain cases, the solvent also influences the configurational sequence of the constitutional repeating units, as in the polymerization of dienes. Thus, the solvent for polymerization must be chosen very carefully and certain solvents must be avoided. If there are no side reactions, the same kinetic rules as in homogeneous polymerization in bulk can be applied to homogeneous polymerization in solution. On the other hand, if the polymer precipitates during the course of the reaction, abnormal kinetics are observed. This is because the typical chain termination via bimolecular reaction of macroradicals is hindered, whereas chain propagation is not affected. The solid concentrations obtainable in polymerizations in solution are mostly below 20% and therefore distinctly lower in comparison to polymerizations in suspension or emulsion.

Polycondensation and *polyaddition* reactions can also be conducted in solution. Condensation of diols with dicarboxylic acids in solution is advantageous for the preparation of polyesters that do not withstand the high temperatures necessary for melt polycondensations, or when molecular weights above 30,000 g/mol are required (see Example 4.2). For this purpose, the polycondensation is carried out with an approximately 20% solution of reactants in an inert solvent. Especially preferred are hydrophobic solvents, such as toluene, xylene, or chlorobenzene, which not only form an azeotrope with the liberated water, but also prevent a back reaction by providing a protective solvation shell for the ester linkages already formed. The low viscosity of the solution compared to that resulting from melt condensation allows the water formed to be removed much more easily; hence, solution condensation can be carried out at a relatively low temperature, controlled by the boiling point of the solvent. However, in order to obtain a sufficiently high esterification rate, a catalyst, usually an acidic compound such as *p*-toluenesulfonic acid, is necessary. If one of the starting components (diol or dicarboxylic acid) is insoluble in the desired solvent, it is possible first to carry out a pre-condensation in the melt at about 120–150°C and then to subject the resulting low-molecular-weight polyester to further condensation in solution.

Condensation polymers, especially polyamides, can also be prepared in solution by the Schotten-Baumann reaction at low temperature (see Example 4.11). For this purpose, two rapidly reacting monomers, for example, diamine and dicarboxylic acid dichloride, are mixed together with stirring in an inert solvent; the eliminated hydrogen chloride is trapped with an acid acceptor.

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

The Schotten-Baumann reaction between dicarboxylic acid dichlorides and diamines can be performed not only in organic solvents, but also, by means of a special experimental technique known as interfacial polycondensation (see Examples 4.5 and 4.11). Both variants have the advantage of short reaction times at low temperature with simple equipment.

2.2.4 Polyreactions in Dispersion

Many polyreactions, especially chain polymerizations, can also be carried out under heterogeneous conditions. In this case, the liquid monomer is dispersed by stirring to small droplets in a liquid in which it is insoluble, and polymerized in that state. During the reaction, there is a change in the aggregation state of the dispersed phase, since the macromolecules formed are solids. Thus, the original liquid/liquid dispersion (emulsion) becomes a solid/liquid dispersion (suspension). If the polymer is insoluble in the monomer, e.g., polyacrylonitrile, this transition occurs early in the reaction; if, on the other hand, it is soluble in or swollen by the monomer, e.g., polystyrene, the state of the emulsion changes only at high conversion. The term "suspension polymerization" was chosen with respect to the final state, while the term "emulsion polymerization" refers to the initial state of the system. Despite this formal similarity, the two processes differ in some essential respects, for example, in the size of the resulting polymer particles (0.1–0.5 μm in emulsion polymerization, 0.5 μm–2 mm in suspension polymerization) and in the reaction kinetics. These methods offer the following advantages: The heat of polymerization is readily dissipated because of the segmentation of the monomer in small droplets and the high heat capacity of water. The reaction mixture remains very mobile even at high conversion, because the viscosity is strongly increased only in the monomer/polymer droplets, without larger changes in the overall viscosity. Therefore, solid contents of 50% are easy to handle. Polyreactions in dispersions can be conducted relatively simply in the laboratory. In some cases, they are also used in polycondensation and polyaddition reactions (e.g., interfacial polycondensation, see Example 4.11).

Suspension and emulsion techniques provide additional means for modifying the properties of the resulting polymers, for example:

- Variation of particle size and particle size distribution.
  This influences the rheology of the latex as well as the properties of the solid film (see Example 3.46).
- Incorporation of small amounts of ionic groups.
  This has an influence on the pigment load capacity and on the stability of high solid-containing latices (see Example 3.39).
- Preparation of polymer particles with core/shell-structure.
  Crosslinked rubbery polymers that are used as impact modifiers often do not have sufficient compatibility with the hard matrix of the surrounding thermoplast. One elegant method is to cover the rubbery modifier particle with a thin layer of a polymer that is compatible with both, the rubbery core and the thermoplastic matrix.

2.2.4.1 Polyreactions in Suspension

In radical polymerizations in aqueous suspension, the liquid monomer, usually containing a dissolved water-insoluble initiator (e.g., dibenzoyl peroxide), is finely dispersed by vigorous stirring and polymerized at increased temperature. Polymerization takes place in the monomer droplets, and hence it follows the kinetic laws of bulk polymerization. Normally, suspension aids (dispersants) must be added in order to facilitate the dispersion and, even more importantly, to prevent the coagulation of the polymer particles swollen by monomer in the later stage of polymerization. Therefore, either water-soluble macromolecules (so-called protective colloids) or fine-grained and insoluble inorganic compounds, the so-called Pickering emulsifiers (e.g., calcium carbonate) need to be added in amounts of 0.1–0.5%. Combinations of both types of dispersants are also used. The volume ratio of monomer to water phase is mostly between 25:75 and 50:50. If the size of the droplets is homogeneous, the ratio of 74:26 cannot be exceeded for steric reasons. In order to obtain high conversion, initiators with different decay constants are used and the temperature is increased towards the end of the polymerization.

The polymer particles accumulating in suspension polymerization of liquid monomers show almost the same size as the original monomer droplets when no secondary aggregation occurs, as for example, with PVC. When the resulting polymer is insoluble in the monomer, the polymer precipitates in the form of irregularly shaped particles, e.g., polyacrylonitrile. On the other hand, if the polymer is soluble in the monomer, the polymer is produced in the form of regular beads, e.g., polystyrene. This particular case of suspension polymerization is referred to as bead polymerization. In many technical suspension polymerizations (for example, expandable polystyrene or PVC), one is interested in definite particle size distributions and particle morphology. Both are influenced in a complex way by many factors, for example, by the volume ratio of the phases monomer/water, the type and concentration of the dispersant, the geometry of the reactor, the shape of the stirrer, and the intensity of stirring.

On the industrial scale, suspension polymerizations are not only carried out in the aqueous phase, but also in aliphatic hydrocarbons using Ziegler-Natta catalysts, as for example, in the polymerization of ethylene and propylene (see also Sect. 3.3.1).

2.2.4.2 Polyreactions in Emulsion

Working in emulsion is essentially limited to radical polymerization in water. Similar to suspension polymerization, the basic principle is to disperse a sparingly water-soluble monomer in water and bring about polymerization in this state. There are, however, some essential differences between the two procedures:

- At least a very low water solubility of the monomer is required. Extremely hydrophobic monomers, e.g., stearyl acrylate, do not polymerize under emulsion conditions.
- The emulsification of the monomer takes place in the presence of water-soluble emulsifiers that can form micelles. At the beginning of the polymerization, the monomer is present in form of monomer droplets as well as in the micelles.
- Water-soluble initiators (potassium peroxodisulfate; redox systems) are used except for a few special cases.
- The initiation step takes place preferentially in the aqueous phase.
- Polymerization does not occur in the monomer droplets but in the micelles which thereby slowly swell to latex particles.

- The rate of polymerization (at constant initiator concentration) depends on the number of micelles and therefore on the emulsifier concentration. The rate and degree of polymerization can be increased simultaneously.
- The size of the resulting polymer particles is much smaller than in suspension polymerization.

The ingredients for an emulsion polymerization consist essentially of four components:

- Water (demineralized),
- A monomer, sparingly soluble in water,
- A water-soluble, radical-generating initiator, and
- An emulsifier.

The course of an emulsion polymerization and the properties of the resulting polymer latex are strongly affected by the emulsifier. Emulsifier molecules consist of a hydrophilic and a hydrophobic moiety. According to the electrical charge on the hydrophilic part, one distinguishes between anionic, cationic, and nonionic emulsifiers. Examples of anionic emulsifiers are the K, Na, and NH_4 salts of fatty acids, sodium dodecyl sulfate, as well as salts of alkyl-substituted benzene- or naphthalenesulfonic acids. Examples of cationic emulsifiers are quaternary ammonium salts that possess at least one hydrophobic substituent. Typical non-ionic emulsifiers are ethoxylated phenols and *block* copolymers of ethylene oxide and propylene oxide. In very dilute aqueous solution, emulsifiers behave as isolated molecules or as electrolytes. With increasing emulsifier concentration, however, an abrupt change in some physical properties of the solution occurs, e.g., surface tension, viscosity, electrical conductance, and osmotic pressure. The concentration at which these abrupt changes are observed, is called the critical micelle concentration (CMC). It has a characteristic value for each emulsifier. Below the critical micelle concentration, the emulsifier is dissolved as individual molecule, but above the CMC, the emulsifier molecules cluster to form ordered molecular aggregates, the so-called micelles, in which the hydrophobic residues are turned inwards and the hydrophilic residues are turned outwards towards the aqueous phase. These micelles have a diameter of about 3.5 nm.

The size of the micelles is significantly increased by the addition of monomer up to a diameter of 4.5–5 nm. However, the size of the monomer droplets is still very much larger than that of the micelles (diameters up to 1 μm). In emulsion polymerization, one generally uses 0.5–5 wt.% of emulsifier relative to monomer. With the usual oil-in-water emulsions, the water content varies from half to four times the amount of monomer.

The micelles are present at a concentration of about 10^{18} per ml of liquor and each micelle contains around 100 monomer molecules. In contrast, the number of monomer droplets is only about 10^{10} per ml. Thus, despite the larger volume of monomer droplets, the micelles offer a very much larger surface area. A radical formed in the aqueous phase will thus encounter a monomer-filled micelle much more often than a monomer droplet. Therefore, the polymerization takes place practically only in the micelles and not in the monomer droplets. The monomer

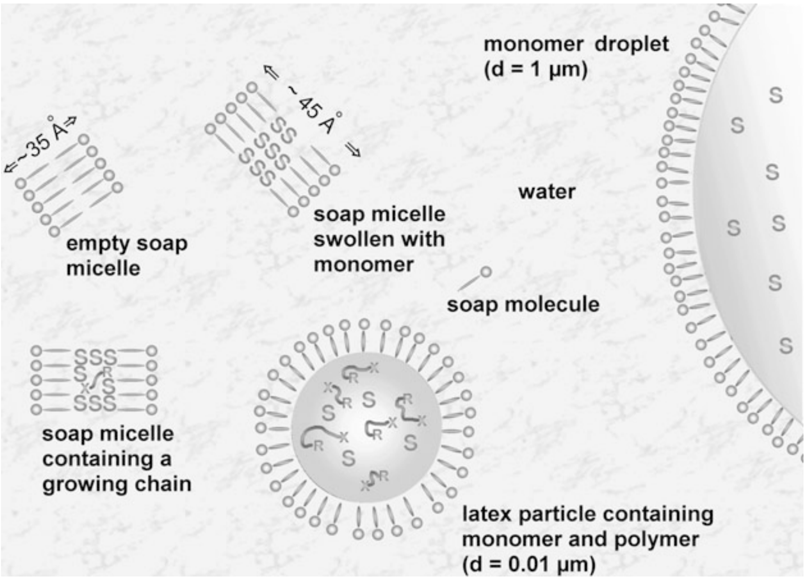


Fig. 2.1 Schematic presentation of species present in an emulsion polymerization (S = styrene monomer, R-X = growing polymer chain)

consumed in the micelles is replaced by diffusion from the monomer droplets through the aqueous phase. According to the theories of Harkins and of Smith and Ewart, the kinetic course of an emulsion polymerization is divided into three intervals: At first some of the micelles increase rapidly in size as the polymerization advances and are transformed into so-called latex particles, containing both monomer and polymer. These are still very much smaller than the monomer droplets and have an initial diameter of about 20–40 μm, corresponding to about 10^{14} particles per ml of liquor. The monomer used up is continuously replaced from the monomer droplets via diffusion through the aqueous phase. More and more emulsifier molecules are adsorbed from the aqueous phase onto the surface of the growing latex particles, assisting their stabilization; the micelles that still contain no polymer thereby slowly disappear. The concentration of free emulsifier finally falls below the critical micelle concentration; at this point, the surface tension increases significantly. From then on, practically no new latex particles can be formed. The first phase of the emulsion polymerization, the so-called particle-formation period, is completed after about 10–20% conversion.

From this point onwards, the polymerization occurs only in the latex particles, whose number, however, remains constant. The monomer droplets still have the function of a reservoir that delivers the monomer to the latex particles, so that the concentration of monomer in the latex particles and therefore the rate of

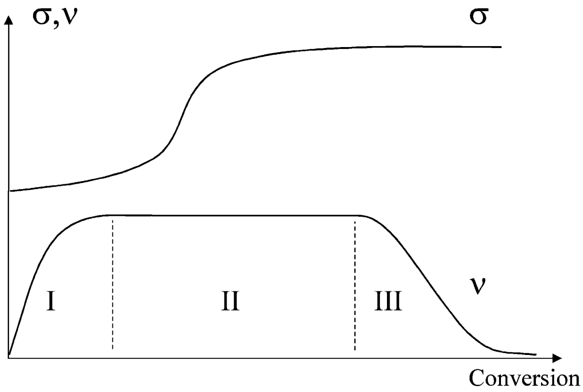


Fig. 2.2 Overall rate of reaction ν, and surface tension σ as function of conversion in emulsion polymerization

polymerization remains constant. During this second period, the reaction is thus of zero order with respect to the monomer.

When the polymerization has proceeded to such an extent that all of the monomer droplets have vanished, which occurs after 60–80% conversion, all of the residual monomer is located in the latex particles. The monomer concentration in the particles now declines as polymerization proceeds further, i.e., in this final period the reaction is first order. At the end of the polymerization, the emulsion consists of polymer particles with a size distribution between 50 and 150 μm, which is larger than the original micelles, but smaller than the original monomer droplets (Fig. 2.1). The changes of surface tension and overall rate of polymerization with conversion are schematically shown in Fig. 2.2.

A special procedure is reverse emulsion polymerization. In this case, a hydrophilic monomer (e.g., acrylamide) is dissolved in water and the resulting solution is emulsified using special water-in-oil emulsifiers in a water-immiscible organic liquid (petroleum ether). Then the polymerization is initiated with a water- or an oil-soluble radical generator. The resulting latex consists of very small water-swollen polymer particles, which are suspended in the oil phase. As in aqueous systems, the advantage of these latex systems lies in their low total viscosity, which is influenced by the nature of the oil phase. This is also the case when the water droplets contain extremely high-molecular-weight polymer products. The swollen polymer particles can be coagulated and isolated from the oil phase by adding special reverse emulsifiers, which abolish the effect of the water-in-oil emulsifiers.

With emulsion polymerization it is possible to prepare very high-molecular-weight polymers at high rates of polymerization. The required reaction temperatures are low and can even be below 20°C when redox systems are used for initiation (see Example 3.11). Polymer emulsions with solid contents of 50% and higher can be very stable. In many cases, e.g., poly(vinyl acetate), they are directly used as paints (paint latices), coatings, or adhesives (see Sect. 2.5.4).

2.2.5 General Laboratory Techniques for the Preparation of Polymers

2.2.5.1 Safety in the Laboratory

All persons being exposed to chemicals have to be instructed about the effects of dangerous substances (toxicity, point of ignition, etc.) as well as about preventive measures. Especially the following points are relevant:

- Wearing of suitable protective clothing (protective goggles, gloves, gas mask, laboratory coat, etc.).
- Knowledge about the safety devices (e.g., laboratory hood, fire extinguisher, emergency shower, first aid boxes, etc.).
- Avoidance or ban of unsafe techniques in the laboratory, e.g., oral suction of chemicals in pipettes, sucking of halogenated compounds with a water-jet pump because of effluent contamination.
- Controlled disposal of toxic substances in compliance with legal regulations.
- Strict ban on smoking and eating in the laboratory.

2.2.5.2 Working with Exclusion of Oxygen and Moisture

Molecular oxygen has an influence on the course of most polymerizations. In radical polymerizations this may occur through an effect on the initiation or termination reactions; in ionic polymerizations the initiator may be either activated or deactivated by oxygen. Oxygen may also cause oxidative degradation of macromolecules that have already been formed (especially in polycondensations at high temperatures). These effects are often already detectable at very low oxygen concentrations and it is therefore advisable to work under a nitrogen or argon atmosphere.

Charging of reaction vessels with nitrogen should always be done by repeated evacuation and admission of nitrogen rather than by simply passing nitrogen through the vessel, since one can never be sure when all the air has been displaced. The removal of oxygen in the vessels is easier if argon is used because the density of argon is higher than the density of air. Connections should be made with PVC tubing or glass tubing rather than long rubber tubing.

When conducting a reaction or distillation under a continuous flow of nitrogen or argon rather than in a closed system, a suitable outlet valve must be used in order to prevent back-diffusion of oxygen into the apparatus from the surrounding air. In the simplest cases, it is sufficient to use a Bunsen valve (a rubber tube with two lengthwise slits, closed at one end with a glass rod), or a paraffin oil valve.

If small volume experiments are carried out under exclusion of oxygen, an approved method is to use a balloon filled with inert gas attached to an otherwise closed apparatus. Likewise, using a balloon can easily compensate for changes in pressure. It is also recommended to use glove boxes when smaller amounts are to be handled under an inert gas.

When working with spontaneously inflammable substances (e.g., organometallic compounds) or with reactions on a larger scale, where there are rapid changes of pressure, it is advantageous to employ a backstop valve.

It is especially important to exclude oxygen and water in ionic polymerizations; the drying procedures normally used for preparative work are then generally inadequate. Glassware can be freed from water by drying in an oven at 150°C, but better by baking with a hot air ventilator under high vacuum. Gases can be dried by freezing out the moisture or by passage through columns filled with suitable solid reagents. Likewise, liquids can be dried by treatment with suitable drying agents at room temperature or by boiling under reflux or by azeotropic or extractive distillation.

Agents for the drying of liquids must, of course, be chemically inert, as otherwise undesired side reactions could occur (e.g., styrene polymerizes explosively on contact with concentrated sulfuric acid at room temperature).

Suitable drying agents are, for example, calcium chloride, silica gel, molecular sieves, calcium hydride, or phosphorus pentoxide; however, their use must be adapted to the requirements and conditions of each polymerization.

2.2.5.3 Purification and Storage of Monomers

In all polymerizations, the purity of the starting materials is of prime importance. Impurities present at concentrations of 10^{-2}–10^{-4} wt.% often have a considerable influence on the course of the reaction. With unsaturated monomers the impurities mentioned below may be encountered:

By-products formed during their preparation (e.g., ethylbenzene and divinylbenzenes in styrene; acetaldehyde in vinyl acetate); added stabilizers (inhibitors); autoxidation and decomposition products of the monomers (e.g., peroxides in dienes, benzaldehyde in styrene, hydrogen cyanide in acrylonitrile); impurities that derive from the method of storage of the monomer (e.g., traces of metal or alkali from the vessels, tap grease etc.); dimers, trimers, and polymers that are generally soluble in the monomer, but sometimes precipitate, for example, polyacrylonitrile from acrylonitrile. Likewise, in polycondensation reactions it is important to remove reactive impurities because they can cause considerable interference during the polyreaction.

The purification procedures to be applied depend on the monomer, the expected impurities, and especially on the purpose for which the monomer is to be employed, e.g., whether it is to be used for radical polymerization in aqueous emulsion or for ionic polymerization initiated with sodium naphthalene. It is not possible to devise a general purification scheme; instead the most suitable method must be chosen in each case from those given below. A prerequisite for successful purification is extreme cleanliness of all apparatus (if necessary, treating with hot nitrating acid and repeatedly thorough washing with distilled water).

The usual procedures of fractional, azeotropic, or extractive distillation under inert gases, crystallization, sublimation, and column chromatography, must be carried out very carefully. For liquid, water-insoluble monomers (e.g., styrene, Example 3.1), it is recommended that phenols or amines which may be present as stabilizers, should first be removed by shaking with dilute alkali or acid, respectively; the relatively high volatility of many of these kinds of stabilizers often makes it difficult to achieve their complete removal by distillation. Gaseous monomers (e.g., lower olefins, butadiene, ethylene oxide) can be purified and stored over molecular sieves in order to remove, for example, water or CO_2.

So-called prepolymerization is frequently used to achieve a very high purification: a monomer that has already been purified by the normal methods is polymerized to about 10–20% conversion by heating or irradiation, or if necessary by addition of initiator. It is then separated from the polymer by fractional distillation under nitrogen. Impurities that affect the initiation (e.g., by reaction with the initiator or its fragments) or react with the growing macromolecules (causing chain termination or chain transfer) are thereby removed.

Measurements of the common physical constants such as boiling point or refractive index are not sufficiently sensitive to determine the trace amounts of impurities in question. Besides the common spectroscopic methods, techniques like gas chromatography (GC), high-pressure liquid chromatography (HPLC), or thin-layer chromatography (TLC) are useful. The surest criterion for the absence of interfering foreign compounds lies in the polymerization itself: the purification is repeated until test polymerizations on the course of the reaction under standard conditions are reproducible (conversion-time curve, viscosity number of the polymers).

Storage of monomers and solvents also requires special precautions. The vessels must be specially constructed and be closed with a self-sealing cap through which the distilled contents can be transferred with a pipette or hypodermic syringe under inert gas. The contents should also not come in contact with tap grease.

Most monomers can be stored unchanged under nitrogen only for short times (hours or days), even in the dark at low temperature. For long-term storage, a suitable stabilizer is therefore indispensable. Effective stabilizers (inhibitors) of radical polymerization are quinones, phenols, amines, nitro compounds, and some metals or metal compounds. The addition of 0.1–1 wt.% of hydroquinone or 4-*tert*-butylpyrocatechol results in sufficient stabilization of many monomers.

Water, alcohols, ethers, or amines can cause inhibition of ionic polymerization. However, these substances can act in different ways according to their concentration. For example, in polymerizations initiated by Lewis acids (BF_3 with isobutylene) or organometallic compounds (aluminum alkyls), water in small concentrations behaves as a cocatalyst, but in larger concentrations as an inhibitor (reaction with the initiator or with the ionic propagating species).

2.2.5.4 Reaction Vessels for Polymerization Reactions

Numerous special experimental arrangements that are suitable for particular monomers and types of polymerization are described in the literature, but they may all be regarded as modifications of the equipment described below.

Radical polymerizations as well as polycondensation and polyaddition reactions of solid or liquid monomers are frequently conducted under inert gas in simple glass ampoules or vessels. Larger amounts are prepared in three or more necked flasks (flat-flanged flasks) equipped with adequate reflux condensers, tap funnels, stirrers and, if needed, a dip-in cooling coil and thermometer or temperature sensor for automatic temperature control. The flasks should be made from thick-walled glass in order to withstand any internal pressure built up during the reaction and should be sealed off as strain-free as possible. If strong exothermic reactions are expected, safety precautions must be taken against possible explosion (wrapping round with adhesive tape, protective shield, etc.). For safety reasons, ampoules with small volume should be used and should never be filled more than half full. In the filling process, it is necessary to ensure that none of the content remains adhering to the upper part of the vessel. Using a funnel can easily prevent this.

For many trial experiments it is sufficient to carry out the reaction on a gram scale in round-bottomed or Erlenmeyer flasks of 5–10 ml size. The reaction mixture should be layered with an inert gas using a pipette and should be stirred by using a magnetic bar. For closure of the reaction flask, a balloon filled with inert gas can be used. Flasks containing higher boiling reaction mixtures can be closed with a convenient taper-ground stopper, which should be protected with a metal clamp. If needed, a dropping funnel allows, for example, the addition of monomers under inert gas during polymerization.

For reactions in which only a slight pressure rise is expected (e.g., emulsion polymerization of gaseous monomers), thick-walled pressure bottles which are carefully placed behind a protective shield, can be used. For higher pressures or large-scale experiments, autoclaves are always to be preferred.

For polymerizations initiated by catalyst suspensions (e.g., alkali metals), a suitable high-speed stirrer is used. It should also be mentioned that high-speed mixers can be used as reaction vessels for polyreactions (interfacial polycondensations). Flasks with self-sealing septums made of silicon rubber, used in combination with hypodermic syringes, are very suitable as reaction vessels, especially for ionic polymerizations. They have the advantage that catalyst can be injected, or samples removed, with practically complete exclusion of air and moisture. It is recommended to puncture a second hypodermic needle through the septum for pressure compensation while injecting. Likewise, during sample taking, a second hypodermic needle is needed for volume compensation of the inert gas. If the polymerization is to be initiated by radiation, one generally uses ampoules or cells with well-defined dimensions. A proper geometrical relationship between the vessel and the radiation source is important.

In (living) anionic polymerizations (e.g., Example 3.19) in the laboratory, a vacuum line is often employed; all operations are then conducted under the same, rather high vacuum. Thus, optimum polymer yield and uniformity are secured.

For kinetic investigations of homogeneous polymerizations, a variety of methods and apparatus has been developed. The dilatometric method is especially worthy of mention on account of its simplicity and general applicability (Fig. 2.3).

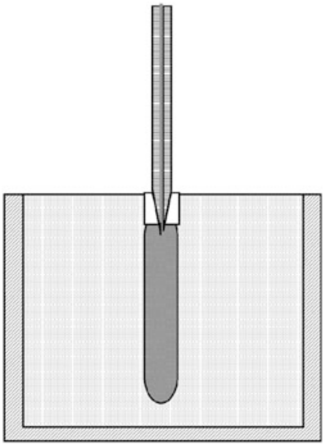


Fig. 2.3 Dilatometer in a thermostat. Conversion-time curves are obtained through volume contraction in the capillary

This procedure is based on the measurement of the contraction of volume that results from the different densities of the monomer and polymer. The conversion of the volume contraction to the yield of polymer can be made by means of a gravimetrically determined calibration curve or by calculation from the specific volumes (see Example 3.6).

With appropriate precautions, condensation and addition polymerization reactions can be carried out in the same apparatus as customarily used for organic preparative work (see Sects. 4.1 and 4.2). In order to obtain high molecular weights by polycondensation in solution, a special circulation apparatus can advantageously be used (Fig. 2.4).

Exact temperature control is very important for polymerization reactions, since, among other things, the rate and degree of polymerization are strongly dependent on temperature. For accurate work, for example, for kinetic analysis with a dilatometer, a thermostat filled with water or paraffin oil may be used instead of thermostatting in the normal way with the aid of a contact thermometer and an immersion heater.

2.2.5.5 Control and Termination of Polymerization Reactions

In chain growth polymerization reactions the average molecular weight, the molecular weight distribution and in some cases the type of terminal group of the polymer can be varied within certain limits by proper choice of reaction conditions and/or the addition of low-molecular-weight compounds (regulators, chain stoppers). It depends on the synthetic method which step is most suitable.

Thus, in a *radical polymerization* an increase of reaction temperature or amount of initiator causes an increase in the number of growing radicals. Since the rate of the propagation reaction is first order with respect to the concentration of growing radicals, while that of the termination reaction is second order, the average molecular weight is reduced (with simultaneous increase in rate of polymerization).

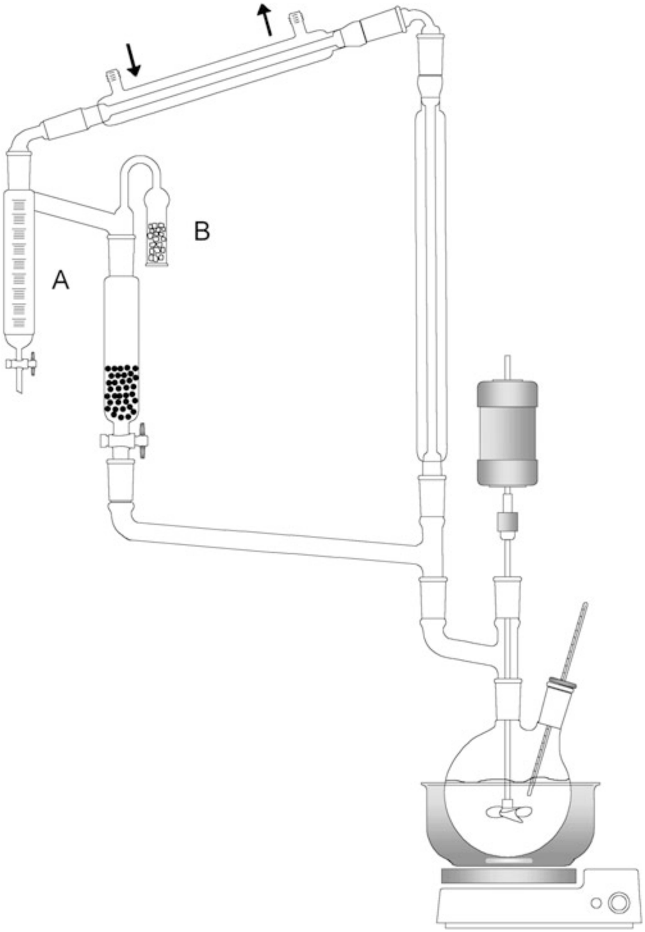


Fig. 2.4 Circulation apparatus for preparation of polyesters. A: water separator, B: drying tube

A decrease of monomer concentration also leads to lower molecular weights, but the rate of polymerization then decreases as well. Since side reactions may intervene at high temperatures or high initiator concentrations, the molecular weight is often better controlled by the addition of regulators, i.e., substances with high transfer constants (see Sect. 3.1 and Example 3.8b). Even at low concentrations, such compounds decrease the average molecular weight markedly by terminating the growth of polymeric chains; at the same time, a new chain is started so that, as a rule, the rate of polymerization is unaffected. The fragments of the regulator are built into the macromolecule as end groups. Especially suitable as regulators are thiols (1-butanethiol, 1-dodecanethiol) and other organic sulfur compounds, (e.g., diisopropylxanthogen disulfide).

In *ionic polymerizations,* the molecular weight can be regulated by temperature, type of catalyst and nature of solvent. In some cases also regulators can be used which, as in the case of cationic polymerization of trioxane, lead to the incorporation of special endgroups.

In polymerizations with *Ziegler-Natta* catalysts, molecular hydrogen is the preferred regulation agent for controlling the molecular weight.

In many cases (e.g., in kinetic investigations, in determination of the reactivity ratios, or in the preparation of unbranched polymers) it is not appropriate to allow polymerization to proceed to complete conversion of the monomer. Polymerization reactions can be stopped in different ways. Sometimes the reaction can be brought to a halt simply by cooling. In most cases pouring the reaction mixture, or a sample of it, into a sufficient quantity of precipitant can end the polymerization, whereby the polymer formed is precipitated and the residual monomer and initiator are highly diluted. Polymerizations are most effectively stopped by addition of an inhibitor or some compound that destroys the initiator; the details of this method depend on the type of polymerization. For radical polymerizations one uses, for example, hydroquinone or hydroquinone monoethers. Most ionic polymerizations can be stopped by addition of water, acids, or bases. When an ionic polymerization is carried out at low temperature, it is essential to terminate it by destruction of the initiator since otherwise warming to room temperature is likely to make the reaction go very quickly. Organometallic initiators (also Ziegler-Natta catalysts) can be destroyed with water or alcohols, and Lewis acids (BF_3) with amines.

Control of molecular weight is much simpler for those polymerizations where the macromolecules are built up stepwise (*condensation* and *stepwise addition*). In such cases, the reaction can be stopped at any time, for example by cooling, so that every step of molecular weight can be obtained. In principle, the molecular weight of the polymer formed in these reactions can also be controlled or the reaction can be interrupted by changing the molar ratio of the two bifunctional reactants or by adding an appropriate amount of monofunctional compound.

2.2.5.6 Isolation of Polymers

Isolation is simplest when the polymer is insoluble in the reaction mixture and precipitates during its formation. In these cases, the product can be separated by filtration or centrifugation. Aqueous solutions can be filtered through paper filters; solutions in organic solvents are better filtered through cloth or sintered glass discs. If the polymer remains dissolved in the reaction mixture, there are two possible ways of proceeding: either the excess monomer, solvent, and other volatiles can be distilled off under vacuum or the polymer can be precipitated by addition of a precipitant. The first procedure is only applied in exceptional cases, since it generally leads to a resinous polymer contaminated with initiator residues and especially with trapped monomer and solvent. The most usual procedure is, therefore, precipitation by means of a precipitant that should satisfy the following requirements: it must be miscible with the monomer and solvent, and dissolve all additives (e.g., initiator) as well as by-products (e.g., oligomers). Furthermore, the polymer should be nonswellable and should separate in flocculent form (not oily or

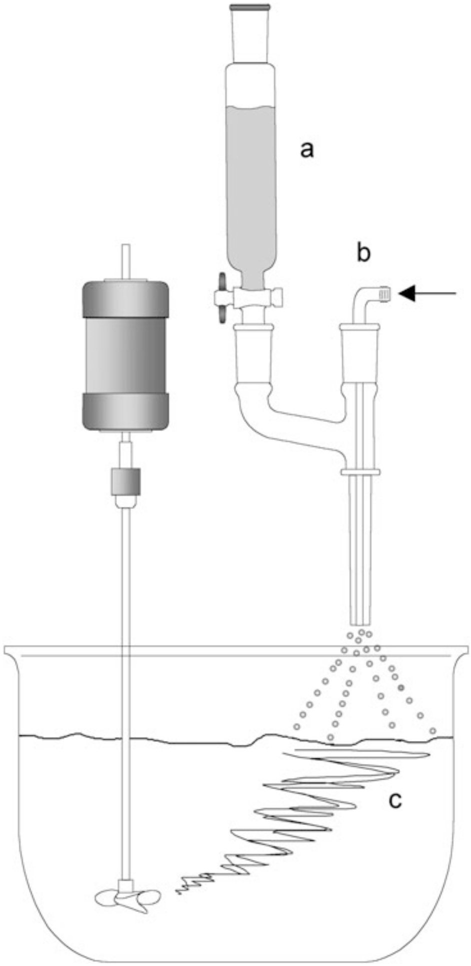


Fig. 2.5 Spray-type separator (**a** polymer solution; **b** compressed air; **c** precipitating agent)

resinous). Finally, the precipitant should be readily volatile and be absorbed or occluded by the polymer as little as possible.

The general procedure is to drop the reaction mixture or polymer solution into a 4- to 10-fold amount of precipitant under vigorous stirring. The concentration of the polymer solution (generally not above 10%) and the amount of precipitant are chosen so that the polymer precipitates in a flocculent, readily filterable form. It often happens that the precipitated polymer remains in colloidal suspension; in this case, it may help either to lower the temperature (external cooling or addition of dry ice) or to add electrolytes (solutions of sodium chloride or aluminum sulfate, dilute hydrochloric acid, acetic acid, or ammonia). Sometimes coagulation of the polymer can also be achieved by prolonged vigorous stirring or shaking (rheopexy). Polymers that tenaciously retain solvent and tend to resinify can be precipitated advantageously by the spray method (see Fig. 2.5). For this purpose, the polymer solution is sprayed in the form of a mist into the precipitant, thereby producing a fine floccular precipitate, the large surface area of which favors the outward diffusion of unpolymerized monomer and other compounds present.

Regarding industrial methods for isolation of polymers, the reader is referred to the relevant literature.

2.2.5.7 Purification and Drying of Polymers

Careful purification and drying of polymers is important not only for analytical characterization, but also because the mechanical, electrical, and optical properties are strongly influenced by impurities. Not the least important aspect of purification is the fact that even traces of impurities may cause or accelerate degradation or crosslinking reactions.

The conventional techniques for the purification of low-molecular-weight compounds, such as distillation, sublimation, and crystallization, are not applicable to polymers. In some cases, it is possible to remove the impurities by cold or hot extraction of the finely powdered polymer with suitable solvents or by steam distillation. Separation of low-molecular-weight components from water-soluble polymers (e.g., poly(acrylic acid), poly(vinyl alcohol), poly(acryl amide)) can be accomplished by dialysis or electrodialysis. However, the most widely used method of purification is by reprecipitation in which the solution of polymer (concentration less than 5–10 wt.%) is dropped into a 4- to 10-fold excess of precipitant, with stirring. If necessary, this operation is repeated with other solvent/precipitant pairs until the impurities are no longer detectable.

The drying of polymers often presents great difficulty, since many polymers tenaciously retain or trap solvent or precipitant; this phenomenon is termed “occlusion”. The magnitude of this effect can be judged by the following examples. Cyclohexane is occluded so strongly by cellulose that, after drying for 2 days at 100°C and 0.1 mbar, one cyclohexane molecule is still retained for every six cellulose CRUs. A 0.2-mm-thick polystyrene film, prepared from a solution in THF by drying to constant weight in a stream of nitrogen at 75°C, still retains 13% THF.

There is no general rule for the prevention or avoidance of occlusion. In some cases, a change of solvent/precipitant system may help to achieve this goal. Raising the drying temperature is also beneficial.

An important prerequisite for successful drying is to subdivide the polymer as finely as possible (see Sect. 2.5.1).

2.3 Characterization of Macromolecules

For the unequivocal characterization of a low-molecular-weight compound, it is sufficient to specify a few physical or chemical properties, for example, boiling point, melting point, angle of optical rotation, refractive index, elemental analysis, IR and NMR spectra. If two low-molecular-weight samples have the same characteristic properties, they may be considered as identical.

The characterization of macromolecular substances is considerably more difficult. Owing to the high intermolecular forces, macromolecules are not volatile without decomposition and so, no boiling point can be determined. The melting points of partially crystalline polymers are generally not sharp. Amorphous polymers frequently show only sintering or softening, often accompanied by decomposition. In addition to elemental analysis, other data must be determined, for example, solubility, viscosity of the solution, mean molecular weight, molecular weight distribution, and degree of crystallinity.

The fundamental difficulty is that polymeric substances cannot be obtained in a structurally and molecularly uniform state, unlike low-molecular-weight compounds. Thus, macromolecular materials of the same analytical composition may differ not only in their structure and configuration (see Sect. 1.2) but also in molecular size and molecular weight distribution; they are polydisperse, i.e., they consist of mixtures of molecules of different size. Hence, it is understandable that the expression "identical" is not, in practice, applicable to macromolecules. Up to the present time, there is no possibility of preparing macromolecules of absolutely uniform structure and size. It follows, therefore, that physical measurements on polymers can only yield average values. The aforementioned peculiarities of macromolecular substances mean that the methods of characterization suitable for low-molecular-weight compounds are frequently not applicable or only applicable in a substantially modified form; often completely new methods of investigation must be employed.

Since the properties of a polymer can be noticeably influenced by small variations in the molecular structure, and these in turn depend on the preparation conditions, it is necessary when reporting data to indicate not only the type of measurement (e.g., molecular weight by end group analysis; crystallinity by infrared measurement or by X-ray diffraction; etc.), but also the type of preparation (e.g., radical polymerization in bulk at 80°C; polymerization with a particular organometallic catalyst at 20°C).

The following Table 2.6 lists the most important characteristics of polymers together with appropriate analytical methods that can be applied for their determination.

2.3.1 Determination of Solubility

When studying a polymer, one should first determine its solubility. This is very characteristic for macromolecules and can serve as an early means of characterization. Important examples are the recognition of crosslinking, the separation and distinguishing between tactic and atactic macromolecules and the identification of copolymers. Moreover, solubility is a prerequisite for most physical measurements.

Table 2.6 Important polymer characteristics and analytical methods for their determination

Characteristics	Analytical methods
1. Composition and constitution	
(a) Chemical composition	Elemental analysis, UV, IR, NMR, pyrolysis-GC-mass spectrometry
(b) Endgroups	Elemental analysis, spectroscopy, titration
(c) Head/tail linkages	Spectroscopy
(d) Branching	Solution viscosity, melt viscosity, light scattering, NMR
(e) Crosslinking	Solution viscosity, melt viscosity, modulus of elasticity
(f) *cis*/*trans* Isomerism	Spectroscopy
(g) Stereoregularity (tacticity)	Spectroscopy
(h) Optical isomerism, optical activity	Polarimetry
(i) Refractive index	Refractometry
(j) Liquid crystalline domains	Polarization microscopy, X-ray scattering
(k) Composition of copolymers	Elemental analysis, spectroscopy, pyrolysis-GC-mass spectrometry
2. Molecular weight	*Absolute methods:* end group analysis, membrane osmometry, vapor pressure osmometry, static light scattering, mass spectrometry, sedimentation measurements
	Relative Methods: solution viscosity, melt viscosity, size-exclusion chromatography
3. Coil dimensions	Light scattering, sedimentation measurements, small angle X-ray, solution viscosity
4. Molecular weight distribution	Fractionation, size-exclusion chromatography
5. Bulk properties	
(a) Density	Pyknometer technique: flotation method
(b) Crystallinity	Birefringence, density, differential scanning calorimetry, X-ray diffraction
(c) Glass transition temperature	DTA, DSC, dynamic mechanical measurements
(d) Softening point	Vicat-method, Martens-method, heat distortion temperature
(e) Crystallite melting point	Polarization microscopy, DTA, DSC, dynamic mechanical measurements
(f) Melt viscosity	Capillary viscometry, rotational viscometry
(g) Tensile strength and elongation	Stress–strain measurements
(h) Modulus of elasticity	Dynamic-mechanical measurements
(i) Impact strength	Charpy-method, Izod-method
(k) Hardness	Ball hardness test
6. Morphology	
(a) Crystallites	Electron microscopy
(b) Spherulites	Polarization microscopy
(c) meso- and nano-Morphologies in copolymers and polymer blends	Electron microscopy
7. Surface properties	Scanning electron microscopy, scanning probe microscopy, ATR-IR spectroscopy, contact angle measurements

Table 2.7 Solubility of various polymers

Polymer	Solvents	Non-solvents
Polyethylene, poly-(1-butylene), isotactic polypropylene	*p*-Xylene[a], trichlorobenzene[a], decane[a], decalin[a]	Acetone, diethyl ether, lower alcohols
Atactic polypropylene	Hydrocarbons, isopentyl acetate	Ethyl acetate, propanol
Polyisobutylene	Hexane, toluene, carbon tetrachloride, THF	Acetone, methanol, methyl acetate
Polybutadiene, polyisoprene	Aliphatic and aromatic hydrocarbons	Acetone, diethyl ether, lower alcohols
Polystyrene	Toluene, methylene chloride, cyclohexanone, butyl acetate	Lower alcohols, diethyl ether, acetone
Poly(vinyl chloride)	THF, cyclohexanone, methyl ethyl ketone, DMF	Methanol, acetone, heptane
Poly(vinyl fluoride)	Cyclohexanone, DMF	Aliphatic hydrocarbons, methanol
Poly(tetrafluoroethylene)	Insoluble	
Poly(vinyl acetate)	Toluene, methylene chloride, methanol, acetone, butyl acetate	Diethyl ether, petroleum ether, butanol
Poly(isobutyl vinyl ether)	2-Propanol, methyl ethyl ketone, methylene chloride, aromatic hydrocarbons	Methanol, acetone
Poly(methyl vinyl ketone)	Acetone, methylene chloride	Water, aliphatic hydrocarbons
Polyacrylates and poly-methacrylates	Methylene chloride, acetone, ethyl acetate, THF, toluene	Methanol, diethyl ether, petroleum ether
Polyacrylonitrile	DMF, dimethyl sulfoxide, conc. sulfuric acid	Ethanol, diethyl ether, water, hydrocarbons
Polyacrylamide	Water	Methanol, acetone
Poly(acrylic acid)	Water, dil. alkali, methanol, DMF	Hydrocarbons, methyl acetate, acetone
Poly(vinylsulfonic acid)	Water, methanol, dimethyl sulfoxide	Hydrocarbons, acetone
Poly(vinyl alcohol)	Water, dimethylformamide[a], dimethyl sulfoxide[a]	Hydrocarbons, methanol, acetone, diethyl ether
Starch	Water, chloral hydrate, copper ethylenediamine	Acetone, methanol
Cellulose	*N*,*N*-Dimethyl acetamide (100 ml)/lithium chloride (5 g), aqueous tetraaminecopper(II) hydroxide, aqueous zinc chloride, aqueous calcium thiocyanate	Acetone, methanol, water
Cellulose triacetate	Acetone, chloroform, 1,4-dioxane	Methanol, diethyl ether
Cellulose trimethyl ether	Chloroform, toluene	Ethanol, diethyl ether, petroleum ether

(continued)

Table 2.7 (continued)

Polymer	Solvents	Non-solvents
Carboxymethyl cellulose	Water	Methanol
Aliphatic polyesters	Methylene chloride, formic acid, toluene	Methanol, diethyl ether, aliphatic hydrocarbons
Poly(ethylene terephthalate)	*m*-Cresol, 2-chlorophenol, nitrobenzene, trichloroacetic acid	Methanol, acetone, aliphatic hydrocarbons
Polyamides	Formic acid, *m*-cresol, γ-butyrolactone, DMF/calcium chloride, *N*-methylpyrrolidone/lithium fluoride	Methanol, acetone, aliphatic hydrocarbons
Polyurethanes (not cross-linked)	Formic acid, γ-butyrolactone, DMF, *m*-cresol	Methanol, diethyl ether, hydrocarbons
Polyoxymethylene	γ-Butyrolactone[a], DMF[a], benzyl alcohol[a]	Methanol, diethyl ether, aliphatic hydrocarbons
Poly(ethylene oxide)	Water, toluene, DMF	Methanol, diethyl ether, aliphatic hydrocarbons
Poly(tetrahydrofuran)	Toluene, methylene chloride, THF	Aliphatic hydrocarbons, diethyl ether
Poly(dimethylsiloxane)	Methylene chloride, heptane, toluene, diethyl ether	Methanol, ethanol
Poly(aryl ether sulfone)	Dimethyl sulfoxide, DMF	Alcohol, ether
Poly(aryl ether ketone)	Conc. sulfuric acid, trifluoromethanesulfonic acid, diphenyl sulfone[a], sulfolane[a]	Alcohol, ether, methylene chloride
Poly(phenylene sulfide)	Above 200°C: dichlorobiphenyl, 1-chloronaphthalene, *N*-ethylpyrrolidone, ε-caprolactam, diphenyl ether, diphenyl sulfone[a]	
Poly(phenylene oxide)	Chloroform, chlorobenzene, toluene	Methanol, ethanol

[a]Only soluble on heating

When determining the solubility it has to be remembered that macromolecules show extremes of behavior, like swelling and incompatibility (for details see Sect. 1.4.1.2). Although there are many thermodynamic theories for the description of polymer solutions, there is still no full understanding of these systems and quite often, one needs application of empirical rules and conclusions by analogy. As a guide, some solvents and non-solvents are listed in Table 2.7 for various polymers. However, not all combinations of solvent and non-solvent allow sufficient purification of a polymer via dissolution and reprecipitation, and trial experiments are often needed.

For the investigation of the solubility of a polymer one may proceed as follows:

- 30–50 mg samples of finely divided polymer are placed in small test tubes with 1 ml solvent and allowed to stand for several hours. The solution process is significantly influenced by the state of subdivision of the polymer.

- From time to time, the contents are stirred or shaken, and examined for the appearance of streaks. If no solution occurs after several hours at room temperature one can slowly raise the temperature, if necessary to the boiling point of the solvent. Any coloration or gas formation is indicative of decomposition of the polymer.
- If the polymer dissolves at higher temperature, which may require a long time, the solution should be allowed to cool slowly to check whether the polymer comes out of solution again and if so at what temperature (important for subsequent measurements).
- If the polymer simply swells without going into solution, the procedure is repeated with other solvents or solvent mixtures. If it swells in all solvents, without dissolving, one may assume that it is crosslinked.

2.3.2 Methods for Determination of Polymer Constitution

When a polymer synthesis is carried out, it is important to check whether this process was successful or not. This question has many facets. First of all, we may ask, for example,

– Whether the obtained chain molecules have the expected constitution
– How the monomer units are connected,
– What the structure of the repeating units is,
– What the composition of copolymers is,
– How complete a macromolecular substitution process was,
– What the configuration / tacticity of the repeating units is,
– Whether or not branches were formed,
– Which end groups the obtained macromolecules have.

To answer all these questions, spectroscopic and spectrometric techniques are required. Some of the most important techniques will be mentioned in the following.

2.3.2.1 High-Resolution NMR Spectroscopy

Chemical constitution, steric configuration and, in some cases, details about chain conformation, aggregation, association, and supramolecular self-organization behavior of macromolecular substances can be determined using high-resolution nuclear magnetic resonance (NMR) spectroscopy. This spectroscopic technique is sensitive towards nuclei with a nuclear spin different from zero. Identical nuclei (protons for example) incorporated at different places of a molecule – or bond to different molecules – have different shielding constants s and thus – at constant external field H_0 – different resonance frequencies n_1. This effect is called "chemical shift" d and is usually given relative to that of a standard compound like tetramethylsilane (TMS). Because of the smallness of this shielding constant the value of the chemical shift of a nucleus i is given in ppm (parts per million). For protons, the chemical shifts d are between 0 and approx. 12 ppm, for ^{13}C between 0 and approx. 220 ppm. Just by analyzing the chemical shifts of the signals found in an NMR spectrum a first rough analysis of the polymer constitution is possible. Moreover, the intensity of the absorptions of each nuclei is independent of the chemical environment but proportional to their relative concentration. This feature – together with the characteristic chemical shifts – is of special importance for qualitative as well as quantitative structural elucidation via NMR spectroscopy: position (δ/ppm) and intensity of an absorption give clear and direct information about constitutional, configurational, and other features of the material to be analyzed. And there is one more dominant effect which consolidates and deepens the structural information obtained from NMR investigations. This is the indirect spin-spin coupling of neighboring, nonequivalent nuclei of a molecule via the bond electrons. It leads to a fine-structure (muliplet structure) of the absorption signals which is caused by the generation of additional small magnetic fields at the locus of the observed nucleus. This is due to the relative orientation of the spins in the neighboring nuclei of the same molecule. In general, the number of absorptions of a multiplet, i.e., the "multiplicity" M, is given by

$$M = 2n\,I + 1 \tag{2.13}$$

where n is the number of equivalent neighboring atoms and I (= 0, $^1/_2$, 1, 1 $^1/_2$, 2, . . .) is their nuclear spin quantum number. Magnetically equivalent nuclei do not lead to any splitting due to indirect spin-spin coupling but give a common resonance line. The strength of the coupling is given by the spin-spin coupling constant J. The NMR spectra of dissolved polymers can be interpreted in the same way as those of low-molecular-weight compounds. Hence, it is a powerful tool for constitutional analyses: The chemical constitution of repeating units and end groups, the content of comonomers, or the steric configuration (tacticity; see below) of macromolecules can be determined in dilute solution using high-resolution NMR spectroscopy. Also, NMR spectra of linear polymers of low molar mass often show unique absorptions due to their end-groups. By referencing these absorptions to those of the nuclei in the repeating units it is possible to obtain the ratio of the number of end-groups to the number of repeating units. Thereby it is possible to evaluate the M_n of such a polymer. For branched polymers, NMR absorptions due to the branch point can be identified and reveal the chemical structure of those branch points, thus leading to a better understanding of the mechanism by which the branches form, and to information about the relative number of branch points within a macromolecule.

Using NMR spectroscopy, it is also possible to determine the polymer's tacticity. The constitutional repeating unit of polymethylmethacrylate (PMMA), for example, possesses three different types of (magnetically nonequivalent) protons with different chemical shifts d, i.e., the CH_2 protons (d ≈ 2 ppm), the α-CH_3 protons (d ≈ 1 ppm), and the OCH_3 protons (d ≈ 3.5 ppm).

Let us consider the –CH_2– group first. Depending on the tacticity, it can be the part of either a *racemic* or a *meso* diade (see Fig. 2.6).

It is evident that in the racemic diade both –CH_2– protons are imbedded into an identical microenvironment. Consequently, they are magnetically equivalent, absorb

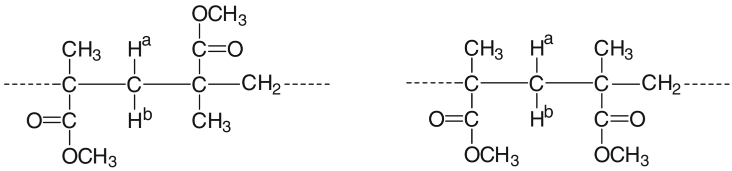


Fig. 2.6 Racemic (r; syndiotactic, *left*) and meso (m; isotactic, *right*) diade in PMMA

at the same resonance frequency ν (have the same value of δ), and do not couple with each other. Therefore, the proton in a racemic diade appears as a singlet in the NMR spectrum. For the meso diade, on the other hand, it is obvious that the two $–CH_2–$ protons have a clearly different microenvironment: while H^a has two methyl groups as neighbors, there are the ester groups for proton H^b. Consequently, the two $–CH_2–$ protons of the meso diade are magnetically nonequivalent, absorb at different resonance frequencies ν_a and ν_b, respectively, and couple with each other. Therefore, these protons in a meso diade appear as a set of two doublets in the NMR spectrum.

The absorptions of the α-CH_3 group reflect the respective triade substructure (see Fig. 2.7):

One observes different values of δ for the isotactic, syndiotactic, and heterotactic triade, respectively, but all signals are singlets due to the lack of a proton at the carbon atom next to the CH_3 group (see Fig. 2.8). Via quantitative evaluation of the intensity of the respective absorptions information is available about the homogeneity of the chain configuration.

High magnetic fields and in particular ^{13}C-NMR spectroscopy allow the analysis of even longer configurational sequences (tetrads up to nonads). This proved to be important in particular for the analysis of polyolefins like polypropylene or cycloolefin copolymers (COC). These polymers are available via transition-metal mediated (Ziegler-Natta, metallocene) insertion polymerizations, and the configurational analysis provides deep insight into the respective polymerization mechanisms as well as into the structure–property relationships.

When high-resolution NMR spectra have to be recorded of a polymeric sample, one has to recognize that polymer solutions are in general highly viscous. To prevent excessive signal broadening caused by this restricted mobility of the solution, polymer solutions for NMR studies have to be highly diluted (approx. 1–2 mg · ml^{-1}). Accordingly, rather long acquisition times are required for readily resolved spectra, in particular for ^{13}C. Nevertheless, despite of high dilution, some polymer absorptions may remain broadened, especially those of atoms incorporated directly into the polymer backbone, while absorptions of lateral substituents tend to be well-resolved. This broadening even at high dilution is mainly due to the restricted mobility of the polymer backbone, preventing complete averaging of the dipolar environment within the time-window of the NMR experiment. Increase of temperature might sharpen some of these signals to a certain extent.

The limit of accuracy of ^{1}H-NMR experiments carried out in dilute solution is around 1–5%, depending on the resolution of the spectrum, and of approx. 10% for

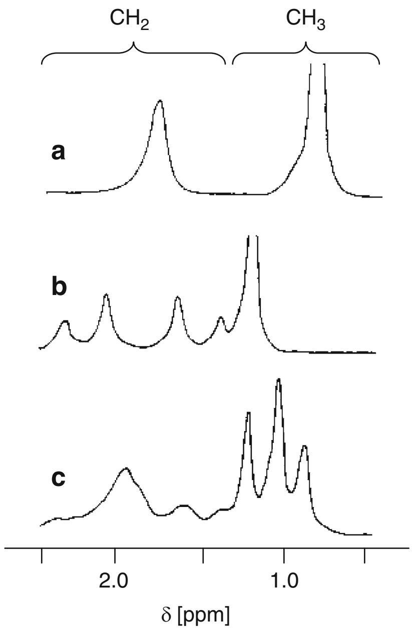


Fig. 2.7 Aliphatic regions of ^{1}H-NMR spectra of (**a**) syndiotactic, (**b**) isotactic, and (**c**) atactic PMMA

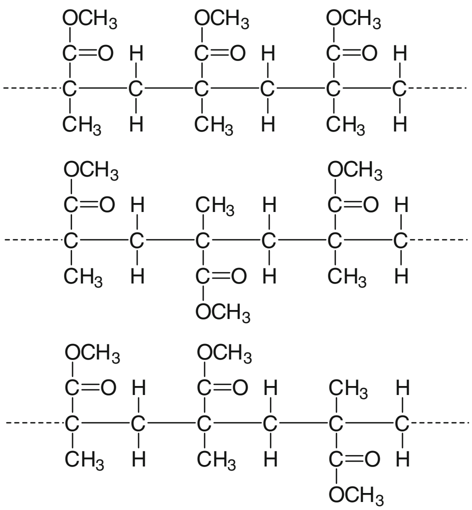


Fig. 2.8 Isotactic (*i, top*), syndiotactic (*s, middle*) and heterotactic (*h, bottom*) triades of PMMA

^{13}C NMR. If the polymer to be investigated proved to be insoluble, solid-state NMR techniques are available for further investigation. Solid-state NMR methods are also very useful for determining bulk properties of polymers such as relaxation behavior of local motions as well as mutual arrangements of chains and chain segments.

2.3.2.2 IR Spectroscopy

Electromagnetic radiation having wavelengths from approx. $\lambda = 760$ nm (n $\approx$ 13,000 cm^{-1}; near visible light) down to $\lambda \approx 1$ mm (n $\approx$ 10 cm^{-1}), where the microwaves begin, is usually called infrared (IR) light. Thus, IR photons have energies between 1.6 and 0.001 eV. These energies are insufficient to induce electronic transitions but are able to excite vibration motions of molecules and parts thereof in condensed matter. The intensity of interaction between IR radiation and a molecule depends on the molecule's structure, on the symmetry of the molecule's skeleton, and on its electron distribution. This is because a vibration transition of a molecule is IR active only if the dipole moment changes during the excited vibration motion. Also, the frequency of the absorbed IR radiation as well as the efficiency of IR light absorption strongly depend on the environment of the observed molecule's fragment. Therefore, IR spectroscopy is an important technique in polymer characterization. It allows the analysis of soluble polymers but also of insoluble (crosslinked) materials. It is sensitive towards structural features like functional groups (carbonyl, aromatics, . . .), chain constitution (1,2- vs. 1,4- and *cis-trans* isomerism in polymeric dienes, head-to-tail vs. head-head-tail-tail placements in vinyl polymers or branches in polymers like polyethylene, for example), end groups (M_n determination), and copolymer composition (in PE/PP copolymers, for example). Moreover, it is very useful in determining the components and compositions of blended, filled, or modified polymer compounds and composites and, in some special cases, to determine the crystallinity of a solid polymer sample.

IR spectroscopy is experimentally much simpler as compared to other methods of vibrational spectroscopy. In order to record an IR spectrum, in most cases the polymer is brought onto discs of NaCl or KBr either as a thin solid film (made from polymer solution in a volatile solvent or – for low-T_g polymers – from the melt; film thicknesses are typically 30–300 μm) or as a fine and homogeneous suspension in, for example, paraffin oil. Alternatively, solid polymers can be milled together with a large excess of KBr, and the resulting powder can be compressed to a (homogeneous, transparent) disc. Then, IR radiation is transmitted through the sample, and the absorbance (extinction) is measured as a function of the wavelength λ or of the wave number ν using a detector placed at the opposite site of the sample. In some other cases the ATR (attenuated total reflection) method is used. Here, the sample is placed as a thin film on the top of an ATR crystal, and the IR spectrum is recorded in reflection geometry. The IR spectra thus obtained provide information on what efficiency IR light is absorbed by the polymer sample at which wavelength λ or at which wave number ν. Characteristic IR spectra of PMMA and PE are shown in Fig. 2.9.

Despite the fact that a full assignment of all the observed absorptions to the respective macromolecule's natural frequencies is not possible in all cases – in particular for complex co- and terpolymers, stereoregular polymers, crosslinked

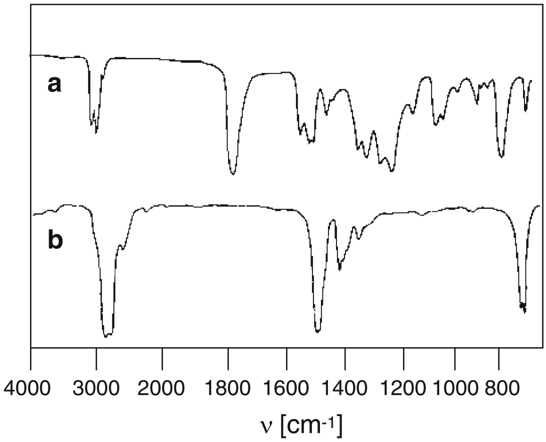


Fig. 2.9 IR spectra of (**a**) PMMA and (**b**) PE

systems, composites, compounds or blends this is very difficult – there are many bands caused by local group vibrations of a few atoms which can be interpreted very nicely. As an example, the C = O band (stretching vibration) is usually observed as an intense absorption between n ≈ 1850–1650 cm^{-1}. Because of the coupling with other vibrations of the molecule its frequency is characteristic for the constitution and the neighborhood of the observed atom group.

Hence, in principle, the identification of local atom groups of polymers proceeds in the same way as for low-molecular-weight materials, and the position of the respective bands is nearly unchanged. Also, IR spectra of oligomers are hardly different from those of high polymers if a minimum degree of polymerization is exceeded ($P_n > 5$–10). Moreover, characteristic absorption for chain end-groups might be observed in the spectra – in particular for strongly IR-active end-groups. Then, IR spectroscopy can be used to roughly estimate the degree of polymerization provided that the molecular weight is not too high ($M < 10^4$): While qualitative IR analysis is a rather simple technique, quantitative evaluation of the IR spectra is a more complicate matter. The samples have to be prepared very carefully (only measurements in transition are possible, using very homogeneous samples), and some further requirements have to be fulfilled in addition to this. The evaluation of the signal intensities is based on the Lambert-Beer law:

$$E = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot d \tag{2.14}$$

E being the optical density or absorbance, I_0 and I the intensities at a fixed wavelength λ (wave number ν) of the exciting beam and the beam after passing through the sample, ε is the decade molar extinction coefficient, c the polymer concentration, and d the layer thickness. E is determined directly by the

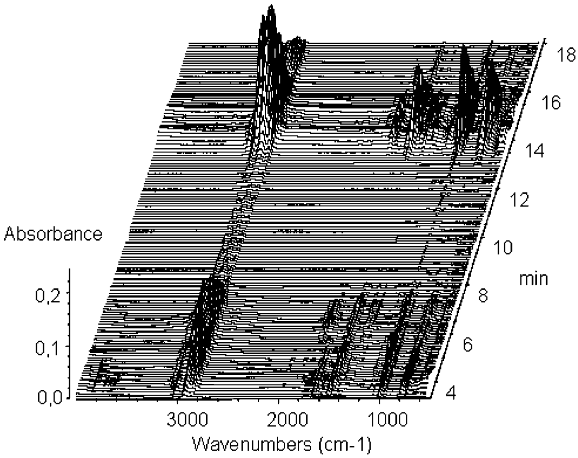


Fig. 2.10 Sequence of IR spectra recorded from the individual fractions of an SEC run taken at regular intervals

spectrometer but evaluation requires further considerations: in general, many bands in an IR spectrum at least partially overlap and are placed on a continuous background. A band shape analysis has to be carried out, and signal intensities caused by neighboring absorptions and the background have to be subtracted from the absorption of interest. Then, either the absorbance at maximum absorption, E_{max}, or the full signal intensity (obtained via integration over the whole signal) can be used for quantitative information.

Also, there might be absorptions in the IR spectra which are characteristic for syn- or isotacticity (such as in PMMA) or for branching points of nonlinear polymer chains (such as in polyethylene). Using data pools and programs which simulate IR spectra it is possible nowadays to characterize nearly all kinds of polymers very quickly using IR spectroscopy with respect to their constitution and their composition. Also, IR spectroscopy can be coupled with polymer chromatography (SEC, HPLC). Then it provides detailed chemical information on each individual chromatographic fraction (Fig. 2.10).

In the *near-IR range* (NIR, $\lambda = 0.76$–2.5 μm; $\nu = 13{,}200$–$4{,}000$ cm^{-1}) overtones and combinational vibrations are found. Because of the huge number of possible combinations of vibrations, this range usually shows a tremendous number of (rather weak) absorptions which overlap or even cover each other. The absorptions found in this range are very characteristic for the investigated material – and are thus of increasing importance – but computers are needed to evaluate these spectra. The *intermediate IR range* (MIR, $\lambda = 2.5$–50 μm; $\nu = 4{,}000$–200 cm^{-1}) is the most important range for structural elucidation using IR spectroscopy. Here, one can find the characteristic fingerprint bands which allow a fast and reliable first structural assignment for an unknown polymeric material, and many spectra are available as references in data pools. Finally, the range of the far-IR ($\lambda = 50$ µm–1 mm; $\nu = 200$–10 cm^{-1}) is of only limited use for polymer analysis.

IR spectroscopy is not only useful for determining the chemical constitution of polymers. It additionally provides profound information on chain orientation and on the orientation of attached lateral substituents of polymers. In this case, polarized IR radiation is applied which is only absorbed by an IR-active bond if the plane in which the electrical field vector E of the IR beam oscillates is parallel to the transition dipole moment μ of the vibration to be excited. If, on the other hand, the transition dipole moment μ is perpendicular to the electrical field vector E of the IR beam no absorption is observed. Using this effect, the degree of orientation of a polymer sample (film, fiber) can be estimated by comparing the intensity at maximum $I(\|)$ and at minimum $I(\perp)$ absorption, i.e., the dichroic ratio.

2.3.2.3 UV–vis Spectroscopy

Alike IR spectroscopy, ultraviolet and visible light (UV–vis) spectroscopy are important optical methods for polymer characterization. For standard spectroscopic investigations in the UV–vis range, unpolarized light having wavelengths from 185 nm to 760 nm is used. The absorption spectra are usually recorded using double-beam spectrometers, and the transmissibility $T = I/I_0$ or the extinction, $\log I_0/I$, is recorded as a function of the wavelength. The UV–vis measurements are carried out on highly diluted solutions, but studies on (ultra)thin films are possible as well. This is because of the very high extinction coefficients of most chromophors and the fact that the extinction must not exceed a certain value in order to maintain the validity of the Lambert Beer law (see above). If this is the case, quantitative interpretation of the UV–vis spectra is possible. As indicated, however, UV–vis spectroscopy is limited to polymers that contain specific chromophores such as aromatic groups, conjugated double- or triple bonds, carbonyls or azo-subunits: When molecules absorb light in the UV–vis range, electronic transitions are induced in the molecules between electronic levels (usually $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the most important range of wave length, i.e., between 200 nm and 600 nm). These transitions can be used for the quantitative determination of residual monomers in a polymer or of copolymer composition (e.g., copolymers of styrene). However, application of the Lambert-Beer's law might be affected here in some cases since the observed chromophors have a different next neighbors environment in these macromolecules. For example, in copolymers containing repeating units A and B with a chromophoric subunit in A, the extinction coefficient of the chromophor at maximum absorption (λ_{max}) might depend on whether it is the center of triades AAA, AAB, or BAB. Thus the possibility of quantitative evaluation has to be checked first by means of reference experiments in these cases. Also, configurational and constitutional features of macromolecules can be determined. In the case of conjugated p systems, for example, the $\pi \rightarrow \pi^*$ absorptions shift towards longer wavelengths at increasing conjugation length.

Last but not least, ageing and destruction processes can be monitored in polymers under application, and structural and quantitative analysis of unknown additives (stabilizers etc.) is possible in commercial polymers using UV–vis spectroscopy. Advantage can be taken here of the fact that the position of an electronic absorption in unsaturated systems depends only weakly on the surrounding medium. Even though UV–vis spectroscopy is not very specific in the absorption band, it is highly sensitive and therefore much better than NMR or IR spectroscopy to detect small amounts of chromophors.

2.3.2.4 Fluorescence Spectroscopy

Fluorescence spectroscopy is commonly used to characterize fluorescence effects in the UV and visual range of the electromagnetic spectrum. Such fluorescence is caused by the fact that the absorption of UV or visible light of specific wavelengths causes excitation of electrons within a molecule. If radiating relaxation occurs directly from the singlet S_1 state, the process is called fluorescence.

Readily measurable fluorescence intensities are found for molecules having aromatic and heteroaromatic rings, in particular when annulated rings are present, and in the case of conjugated π-electron systems. If the polymer molecules contain such fluorescence-active subunits they can be characterized by this technique, either directly via their fluorescence spectrum or via fluorescence quenching experiments (for polymers with appropriate quencher groups). It is also possible to introduce a very small amount of fluorescent-active groups (as comonomer units; "fluorescence marker") into a polymer. Inspection through a fluorescence microscope allows, for example, the monitoring of the molecule's movements (Brownian motions in solution, segment motions in the bulk above glass transition), or the determination of chain orientation in stretched samples. In polymer materials and composites, fluorescence spectroscopy can be used for the qualitative and quantitative determination of additives (stabilizers, for example) even when present at very high dilution only. This is possible due to the tremendous sensitivity of fluorescence spectroscopy.

2.3.2.5 Refractometry

The refractive index is an important quantity for characterizing the structure of polymers. This is because it depends sensitively on the chemical composition, on the tacticity, and – for oligomeric samples – also on the molecular weight of a macromolecular substance. The refractive indices n_D (determined using the sodium D line) of many polymers are collected in the literature. In order to characterize a molecule's constitution one requires knowledge of the mole refraction, R_g. For isotropic samples, it can be calculated in good approximation by the Lorentz-Lorenz equation:

$$R_g = \frac{n^2 - 1}{n^2 + 2} \cdot V_{g,mol} \tag{2.15}$$

where R_g is the mole refraction per monomer unit and $V_{g,mol}$ is the base mole volume. R_g can be calculated from well-known atom- and bond refraction increments. In the case of ideal mixtures the mole refractions behave additively like the specific volume of the components. For transparent samples, refractometry is therefore a well-appropriate technique for the determination of the polymerization kinetics – similar to dilatometry – and the characterization of mixtures (polymer solutions, compatibility etc.).

2.3.2.6 Elemental Analysis

Qualitative and quantitative elemental analysis of polymers can be carried out by the conventional methods used for low-molecular-weight compounds. So a detailed description is not needed here. Elemental analysis or determination of functional groups is especially valuable for copolymers or chemically modified polymers. For homopolymers where the elemental analysis should agree with that of the monomer, deviations from the theoretical values are an indication of side reactions during polymerization. However, they can also sometimes be caused by inclusion or adsorption of solvent or precipitant, or, in commercial polymers, to the presence of added stabilizers. The preparation of the sample for analysis must, therefore, be very carefully carried out (several reprecipitations, if necessary using various solvent/precipitant combinations; thorough drying).

2.3.2.7 Composition of Copolymers

In the characterization of copolymers one distinguishes between *qualitative* analysis, designed to test whether the material is a genuine copolymer or only a physical mixture of homopolymers, and *quantitative* analysis of the weight fraction of the incorporated comonomers.

The *qualitative* analysis is quite simple if the homopolymers differ in their solubility, for example, when one homopolymer is soluble in a solvent where the other is not. In this case a sample of the material is extracted with that solvent. The reprecipitated extracts and residues are examined for composition. The extraction must, however, be very carefully carried out and repeated several times since polymer mixtures are frequently quite difficult to separate by extraction. If no pure homopolymer is isolated in this way one can be sure that the sample is a genuine copolymer. If the solubility properties of the original homopolymers are insufficiently different it is sometimes possible to induce such differences through chemical transformation, for example, by oxidation and/or hydrolysis.

The qualitative investigation of copolymers is considerably more difficult when the homopolymers cannot be distinguished by their solubility. In this case other physical data of the supposed copolymer can be compared with the corresponding data for various physical mixtures of homopolymers, for example, softening point and melting range, density, and crystallinity. Copolymers can frequently be distinguished from physical mixtures of homopolymers by the qualitative and quantitative composition of their pyrolysis products.

Quantitative analysis of copolymers is relatively simple if one of the comonomers contains a readily determinable element or functional group. However, C,H elemental analyses are only of value when the difference between the carbon or hydrogen content of the two comonomers is sufficiently large. If the composition cannot be determined by elemental analysis or chemical means, the problem can be solved usually either by spectroscopic methods, for example, by UV measurements (e.g., styrene copolymers), by IR measurements (e.g., olefin copolymers), and by NMR measurements, or by gas chromatographic methods combined with mass spectroscopy after thermal or chemical decomposition of the samples.

In principle the composition of a copolymer may also be determined by analyzing the composition of the residual monomer by a suitable method after polymerization. It will usually be necessary first to separate the copolymer by precipitation, followed by careful recovery of the filtrate containing the residual monomer, but the direct method of analysis of the copolymer will generally be preferred. *Block* and *graft* copolymers can be characterized in the same manner. However, consideration must be taken of the fact that they usually contain large amounts of the homopolymers which must first be removed. The more refined characterization of a statistic copolymer involves the determination of the reactivity ratios r_1 and r_2 (copolymerization parameters), as well as the calculation of Q- and e-values (see Chap. 3.4, Example 3.36).

2.3.3 Determination of Molecular Weight and Molecular-Weight Distribution

The degree of polymerization, P, and the molecular weight, M, are some of the most important characteristics of a macromolecular substance. They indicate how many monomer units are linked to form the polymer chain and what their molecular weight is. In the case of homopolymers, the molecular weight of a macromolecule is given by:

$$M = P \times M_{\mathrm{ru}}$$

with M_{ru} being the molecular weight of the constitutional repeating unit. However, while low-molecular-weight substances consist, by definition, of molecules of identical structure and size, this is generally not the case for polymers. Synthetic macromolecular substances are nearly always composed of macromolecules of similar structure but different molecular weight. These materials are therefore called *polydisperse*. As a consequence, chemical formulas of polymers are generally given in a way where the constitutional repeating unit is drawn in square brackets, bearing an index n indicating the average number of repeating units tied together to give the polymer chain. Full characterization of a macromolecular substance is not an easy task, therefore, and quite often statistical methods are required: because of polydispersity, the values of P and M are mean values only, and the macromolecular chain molecules of a synthetic polymer are characterized by a (more or less) well-defined chain-length distribution (or molecular-weight distribution). The respective molecular-weight distribution is the direct consequence of chain formation statistics and, moreover, in many cases very

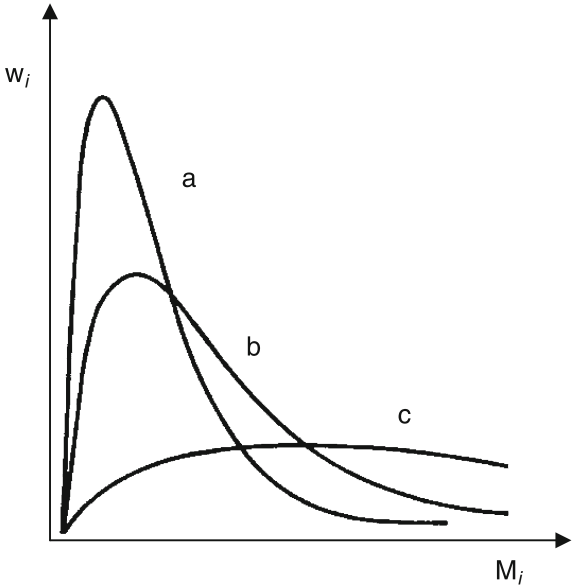


Fig. 2.11 Schematic presentation of the weight fractions of i-mers as a function of their molecular weight, M_i, for polycondensates of **a** low, **b** medium, and **c** high molecular weights

characteristic for the respective chain growth process. Let us ignore potentially different end groups which may also depend on the way of preparation of the respective polymer. Then macromolecules having the identical overall chemical constitution but different molecular weights represent so-called polymer-homologous series.

Depending on the selected polymerization reaction, the polymerization conditions, and potential side reactions one may obtain different molar mass distributions – even if only one single type of monomer is polymerized. As an example, Fig. 2.11 shows the plot of the overall masses w_i (w = weight) of all macromolecules i in the sample vs. their respective molecular weights M_i:

In order to normalize the molecular-weight distribution, mass fractions W_i are often used instead of the total masses w_i ($= n_i \cdot M_i$).

$$W_i = \frac{w_i}{\sum\limits_{i=1}^{i=\infty} w_i} \tag{2.16}$$

Most molecular-weight distributions are sufficiently represented by a set of specific distribution parameters represented by different averages of the molecular weight. The most important averages of the molecular weight will be discussed in the following. The number-average molecular weight M_n (n = average number) is defined as:

$$M_n = \frac{\sum_{i=1}^{i=\infty} n_i M_i}{\sum_{i=1}^{i=\infty} n_i} \tag{2.17}$$

n_i is the *number* of molecules in the sample having the molecular weight M_i. Thus M_i is the arithmetic average of the molecule's number distribution. Consequently, it can be determined using methods which are sensitive towards the number of the molecules present in a sample.

Many experimentally accessible and technically important properties of macromolecules do not depend directly on the number n_i of macromolecules in a sample but rather on their respective masses, w_i. Thus a weight-average molecular weight M_w (w = average weight) is defined as:

$$M_w = \frac{\sum_{i=1}^{i=\infty} w_i M_i}{\sum_{i=1}^{i=\infty} w_i} = \frac{\sum_{i=1}^{i=\infty} n_i M_i^2}{\sum_{i=1}^{i=\infty} n_i M_i} \tag{2.18}$$

M_w corresponds to the first moment of the mass distribution of the molecular weight. Moments of the molecular weight distributions with other arguments do not have any descriptive meaning. For example:

$$M_z = \frac{\sum_{i=1}^{i=\infty} z_i M_i}{\sum_{i=1}^{i=\infty} z_i} = \frac{\sum_{i=1}^{i=\infty} w_i M_i^2}{\sum_{i=1}^{i=\infty} w_i M_i} \tag{2.19}$$

is the z-average (centrifuge average) of the molecular weight, M_z. It can be determined by the measurement of sedimentation equilibria in an ultracentrifuge. A further important average of molecular weight is the viscosity-average molecular weight, M_h:

$$M_\eta = \left(\frac{\sum_{i=1}^{i=\infty} w_i M_i^a}{\sum_{i=1}^{i=\infty} w_i} \right) \tag{2.20}$$

The exponent a can be determined experimentally from the relation between the intrinsic viscosity, [η], and the molecular weight, M (Mark-Houwink-Kuhn relation):

$$[\eta] = K \cdots M^a \tag{2.21}$$

In most cases a is between 0.5 (ϑ solvent) and 0.9. In general, it is:

$$M_n \leq M_\eta \leq M_W \leq M_Z \tag{2.22}$$

Identity is only given for monodisperse samples, i.e., polymers whose macromolecules have all the same molar mass. Moreover, M_η might be equal to M_w if the exponent a in the $[\eta]$ to M relation is equal to 1.

As a simple measure of the width of a molecular-weight distribution the quotient of two averages is sufficient in many cases. The ratio of M_w and M_n is in particular important:

$$PDI = \frac{M_w}{M_n} \tag{2.23}$$

It is called polydispersity index (PDI). The value of PDI can range between approx. 1.01 (for anionically prepared polymers) up to more than 30 (high-pressure polyethylene). In general, it is between 2 and 5.

Averages of the degree of polymerization, P, are defined analogously to those of the molecular masses, M. As an example, it is for the weight-average degree of polymerization, P_w:

$$P_w = \frac{\sum_{i=1}^{i=\infty} w_i P_i}{\sum_{i=1}^{i=\infty} w_i} \tag{2.24}$$

where w_i is the mass of all molecules i having a degree of polymerization of P_i.

The number-average molecular weight, M_n, can be obtained by osmotic measurements or by determination of end-groups. The weight-average molecular weight, M_w, is measured by methods like light or X-ray scattering and – with limitations – viscosity measurements. Depending on the method of evaluation, ultracentrifuge analysis allows determination of M_n, M_w, and M_z. The latter one is characterized by a superproportional consideration of the larger macromolecules.

When the molecular-weight distribution needs to be described, the ratio of two different averages such as M_w/M_n is insufficient in some cases. This is because samples of identical values of M_n, M_w, and M_z might have completely different molecular-weight distribution curves. For the full description of a polymer sample with respect to the molecular weight it is, therefore, necessary to give the full molecular-weight distribution curve. Different ways are available to give this more profound information in a graphical diagram: quite often the molecular-weight distribution is represented as the integral (cumulative) mass distribution, $J_w(M)$, of the molecular weights. It represents the overall mass of the molecules having a molecular weight equal or smaller than $M = M_i$:

$$J_w(M) = \sum_{M=M_0}^{M=M_i} w_i \cdot \Delta M \tag{2.25}$$

Because of the high numerical value of the argument M it is allowed to replace the summation (step function) by an integration (smooth curve), despite the discrete nature of the values of ΔM which are equal to the integer multiple of the molecular weight of the repeating unit, M_0, in the case of homopolymers:

$$J_w(M) = \int_{M_0}^{M_i} w(M)dM \tag{2.26}$$

where $w(M)$ is the mass of all macromolecules having the molecular weight M, and $w(M)dM$ is the mass of macromolecules having a molecular weight ranging between M and $M + dM$. Since $w(0) = 0$, it is possible to set the lower integration limit equal to zero. For normalization reasons, moreover, the overall mass of the polymer, W, is set equal to 1:

$$W = \int_0^{\infty} w(M)dM = 1 \tag{2.27}$$

It follows that $J_w(M) = 1$ as well for $M = 0 \rightarrow M = \infty$. Using the thus normalized integral mass distribution curves of the molecular weights – as can be determined by fractionated precipitation of a polymer – it is possible to calculate the averages of the molecular weights according to the above equations.

The thus obtained integral mass distribution curves of the molecular weight can be transformed into the differential mass distributions $w(M)$ of the molecular weight by differentiation with respect to M:

$$w(M) = \frac{dJ_w(M)}{dM} \tag{2.28}$$

It shows us which mass fraction of the sample lies between M and $M + dM$.

2.3.3.1 Classification of the Methods for Molecular-Weight Determination

Knowledge of the molecular weight and of the molecular-weight distribution of a polymeric material is indispensable for scientific studies as well as for many technical applications of polymers. They effect the solution and melt viscosity, the processability, and the resulting mechanical properties tremendously. Therefore, we will give a short introduction into methods that allow us to determine the required information. Roughly, the methods developed for the determination of molecular weights are subdivided into absolute and relative methods:

Absolute methods provide the molecular weight and the degree of polymer-ization without any calibration. Their calculation from the experimental data requires only universal constants such as the gas constant and Avogadro's number, apart from readily determinable physical properties such as density, refractive index, etc. The most important methods in use today are mass spectrometry, osmometry, light scattering, and – to some extent – sedimentation and diffusion measurements. Also, some chemical and spectroscopic methods (determination of end-groups) are important because of their relative simplicity.

Relative methods measure properties that depend clearly on molecular weight, for example, the hydrodynamic volume of the polymer coils (GPC, viscosimetry) or their solubility as a function of chain length. However, these measurements can only be evaluated with respect to the molecular weight of the macromolecules if experimental calibration curves are available which were generated by comparison with an absolute method of molecular-weight determination.

A necessary prerequisite for application of the above methods is that the polymer is soluble in a suitable solvent. Moreover, one must ensure that the dissolved macromolecules exist as isolated species and do not form associates or aggregates. Proof of this can be obtained by carrying out reactions on functional groups of the polymer that do not lead to cleavage of the polymer chains. If the degree of polymerization of the original polymer agrees with that of the modified polymer, association can be excluded. Values of molecular weight determined in different solvents should also be in agreement if association is absent.

2.3.3.2 Absolute Methods

End-Group Analysis

If the macromolecules in a polymeric sample contain end groups which can be readily detected, analytically identified and quantified, and if the macromolecule's molecular weight is not too high ($<5 \times 10^4$), their number-average molecular weight, M_n, can be determined by chemical as well as by physical methods. Specific and very exact analytical methods must be applied here since the end groups to be estimated constitute only a small fraction of the macromolecule (less than 0.5%, depending on the molecular weight). Chemical methods are based mainly on titrations of the end groups. The most common procedure is potentiometric pH titration. Elemental analysis or trace analysis might be appropriate as well (halogen analysis, for example, when *p*-dibromobenzoyl peroxide has been used as the initiator in a radical polymerization). Physical methods are based on spectroscopic techniques such as IR, UV–vis (when azo compounds with characteristic absorption bands are used as initiator, for example), and NMR spectroscopy (especially for polymers made by step-growth polymerization). In the early days of polymer research, radiochemical analysis was used. This highly sensitive technique is based on the introduction of radioactive nuclei (^{3}H, ^{14}C) into the polymer chain ends using, for example, appropriately labeled per- or azo compounds as initiators.

The most important aspect for a reliable end-group analysis is that it must be absolutely clear what kind of end groups are present in a polymeric material and – if more than one kind of end group is present – how they are distributed over the material (one per chain, two per chain, more than two per macromolecule for branched systems etc.). In order to assure well-defined end groups, the macromolecules formed by radical polymerization can be labeled by choosing a suitable initiator (or chain transfer agent) whose radical fragments become incorporated into the polymer. In this case it is also important to know the type of chain termination since this determines the number of labeled end groups per macromolecule (two for termination by combination, one for termination by disproportionation). Errors can occur if, for example, there is uncontrolled chain transfer to the monomer which reduces the number of labeled end groups per molecule. As a consequence, end-group analysis will lead to a too high apparent molecular weight. The molecular weights of macromolecules made by step-growth polymerization involving two compounds can also be obtained by end-group determination. In particular, the amino, hydroxyl, and carboxyl end-groups in polyesters and polyamides can be estimated very precisely both by potentiometric pH titration and by colorimetry. Hydroxy end groups (e.g., in polyoxymethylenes) can also be determined by acetylation or methylation.

The number-average molecular weight is calculated from the analytically determined end-group content according to the following relationship:

$$M_n = \frac{100 \cdot z \cdot E}{e}$$

where E denotes the molecular weight of the end groups, z is their number per macromolecule, and e is the experimentally determined content of end-groups in grams per 100 g, i.e., wt%.

Membrane Osmometry

An important group of absolute methods allowing the determination of the molecular weight of macromolecules is based on the measurement of colligative properties. Here, the activity of the solvent is measured in a polymer solution via determination of the osmotic pressure Π_{os}. The value of Π_{os} required to determine the number-average molecular weight can be obtained using a membrane osmometer. Here, in a measuring cell having two chambers separated by a semipermeable membrane, one chamber contains the pure solvent and the second one the polymer solution in the same solvent (a membrane is called semipermeable if only the solvent can pass through but not the polymer molecules). Due to the lower activity (lower chemical potential) of the solvent in the polymer solution as compared to the pure solvent, solvent molecules migrate through the membrane from the solvent chamber into that of the polymer solution and dilute it. Therefore, the volume of the polymer solution increases until an equilibration is reached between the osmotic pressure Π_{os} and the hydrostatic pressure generated by the diluted polymer solution

$$\Pi_{os} = \varrho \, g \, \Delta h \tag{2.29}$$

where ϱ is the density of the solvent and g is the acceleration of gravity. Following van't Hoff, it is

$$\Pi_{os} V = n RT \tag{2.30}$$

for diluted solutions, with V being the volume of the polymer solution and n the number of moles of the dissolved polymer. Since $n = m/M_n$ (m is the mass (in g) of dissolved polymer) and $c = m/V$ it follows that:

$$\Pi_{os} = \frac{m}{V} \frac{RT}{M_n} = \frac{cRT}{M_n} \tag{2.31}$$

Since van't Hoff's law is valid only for infinitely diluted solutions, one develops Π_{os}/c in power law series (break after the linear term in c)

$$\frac{\Pi_{os}}{c} = \frac{RT}{M_n} + A_2 \cdot c \tag{2.32}$$

Thus, the osmotic pressure is first measured at different polymer concentrations, Π_{os}/c is then plotted vs. c, the values are linearly extrapolated to $c \to 0$, and the value of M_n is determined from the y axis intercept. A_2 is the second virial coefficient of the osmotic pressure. Solvents where $A_2 = 0$ are called "ideal" or ϑ solvents.

For membrane osmometry (as well as for all other techniques of molecular-weight determination via colligative properties) it is very important that the samples to be analyzed are very pure. In particular low-molecular-weight impurities have to be removed reliably. Otherwise, they will migrate through the semipermeable membrane and lower the chemical potential of the solvent in the reference chamber. An overestimation of the molecular weight will follow. The same effect applies when there are very small oligomers in the test sample. Therefore, the lower limit of M for application of membrane osmometry is approx. 10.000 – depending on the available membrane pore size. On the other hand, M should be below approx. 50.000 because of the limited sensitivity of this method. Moreover, complete dissolution and absence of aggregates is required for reliable measurements.

Vapor Pressure Osmometry

Not only is the osmotic pressure an appropriate quantity for the determination of the number-average of the molecular weight, M_n, of a polymer but also – at least in principle – all other colligative properties such as the lowering of the freezing point, the increase of the boiling point, or the lowering of the vapor pressure. While ebullioscopy and cryoscopy are less common for M_n determination, vapor pressure osmometry is a well-established technique for this purpose. It is based on Raoult's law according to which – for the dilute solution of a compound 2 in a solvent 1 – the vapor pressure of the solvent, p_1, decreases proportionally with the mole fraction x_1 of the solvent:

$$\frac{p_1}{p_{1,0}} = x_1 = 1 - x_2 \tag{2.33}$$

The relative decrease of the vapor pressure is:

$$\frac{\Delta p_1}{p_{1,0}} = 1 - \frac{p_1}{p_{1,0}} = x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \tag{2.34}$$

with $p_{1,0}$ the vapor pressure of the pure solvent and $\Delta p_1 = p_{1,0} - p_1$. So the measurement of the vapor pressure of a dilute polymer solution might lead to P_n and M_n. However, precise determination of the vapor pressure is not so easy as it should be for a standard method of polymer analysis. Therefore, the effect of vapor pressure lowering is measured indirectly by determining the increase of the solution temperature (due to the heat of condensation) when the solution is in contact with a saturated atmosphere of solvent vapor. Here, two adjusted thermistors are placed in a tempered cell containing a saturated solvent atmosphere. One of the thermistors bears a drop of the pure solvent, the other one a drop of the polymer solution (in the same solvent). The drop of the pure solvent assumes precisely the temperature of the measuring cell because condensation and evaporation of solvent molecules is balanced in the saturated atmosphere. In the polymer solution, however, the activity of the solvent molecules is decreased due to the presence of the polymer and thus their vapor pressure is lowered. Consequently, some more solvent condensates onto the solution drop and due to the condensation heat its temperature rises. Finally, its temperature is higher than the surrounding temperature by ΔT^*. This temperature difference is just enough to compensate the lowered vapor pressure of the solution, and the chemical potentials of the solvent are now identical in the solution and in the pure solvent. (In practice, however, this temperature difference ΔT^* is never reached completely because the experiment cannot be carried out adiabatically. Continuously, the solution drop loses some heat to the surrounding vapor phase. Therefore, a slightly lower temperature difference ΔT is measured instead of ΔT^*, and vapor pressure osmometry needs calibration despite the fact that it is – at least in principle – an absolute method). Introduction of the Clausius Claperon relation leads to:

$$\frac{\Delta T}{c} = K \cdot \frac{1}{M_n} \tag{2.35}$$

with

$$K = \frac{const. \ \cdot \ RT^2}{L_1 \rho_s} \tag{2.36}$$

K being a constant which is usually determined experimentally during cell calibration. L_1 is the heat of evaporation of the solvent, ρ_s the density of the solution, and c the polymer concentration. Finally, because the given deviation is valid only for ideal solutions but only real solutions can be studied in practice, the above equation is developed in a power law series with respect to c:

$$\frac{\Delta T}{Kc} = \frac{1}{M_n} + A_2 c + A_2 c^2 + \ldots \tag{2.37}$$

Experimentally, ΔT is determined for approx. five different polymer concentrations. After several minutes, a constant temperature difference ΔT of the two drops is reached which is proportional to their initial difference in vapor pressure and thus proportional to the number of dissolved macromolecules in the solution drop. ΔT can then be determined by measuring the difference in electric resistance of the two thermistors. Then, $\Delta T/Kc$ is plotted vs. c (thus the power law series is broken after the linear term in c) and the plotted values are extrapolated to $c \to 0$. M_n is finally calculated from the y axis intercept.

Vapor pressure osmometry is slightly less sensitive than membrane osmometry ($M_n < 2 \times 10^4$) but is not affected by very short chains in the polymer sample which migrate through the semipermeable membrane in the case of membrane osmometry. Therefore, it is in particular valuable for the analysis of oligomeric materials.

Static Light Scattering

Electromagnetic radiation excites electrons bound to atoms or molecules. If the energy of the radiation is insufficient – i.e., the wavelength is too long – to cause a transition from the electronic ground state into an electronically excited one, the excited electrons fall back immediately after excitation while they emit the absorbed radiation again in all directions in space. This light is observed as scattered light. In a different way of describing this process it is said that the electrons are excited by the light to vibrations which have the same frequency as the exciting light. These vibration of which positive (the nuclei) and negative charges (the electrons) are permanently shifted with respect to each other induce a dipole moment μ which is proportional to the absolute value E of the electric field vector of the light wave. The polarizability α is the constant of proportionality here. The oscillating dipoles again emit electromagnetic waves, i.e., light, with the same vibration frequency as the vibrating dipoles and thus as the incident light. This so-called ideal Rayleigh scattering is coherent and elastic.

The theory developed by Rayleigh and Debye for coherent light scattering shows that only sub-volume elements in a sample (whose size is determined by the wave length of the incident radiation) contribute to the scattering which are different in polarizability and thus refractive indices with respect to their surrounding: the scattering intensity is proportional to the square of the refractive index difference. In a pure solvent scattering is caused only by thermal density fluctuations and thus very weak for visible light. For solutions there is an additional contribution due to the dissolved material which causes concentration fluctuations. Here, the intensity of the scattered light is proportional to the square of the refractive index increment, d*n*/d*c*, of the dissolved substance in the solution. For much diluted solutions ($c \rightarrow 0$), the scattering intensity caused by the dissolved molecules, R_ϑ, is given by:

$$R_\vartheta = R_{\vartheta,solution} - R_{\vartheta,solvent} = \frac{I_\vartheta r^2}{I_0} = \frac{4\pi^2 n_0^2 f \cdot p}{\lambda^4 N_L}\left(\frac{dn}{dc}\right)^2 \cdot c \cdot M$$
$$= K \cdot c \cdot M \qquad (2.38)$$

Here, I_0 is the intensity of the incident light, I_ϑ the scattered light intensity at a scattering angle ϑ, r is the distance between sample and detector, n_0 is the refractive index of the solvent, f a depolarization factor (≈ 1), p a polarization factor (≈ 1), and λ is the wavelength of the light. K can be calculated for known values of d*n*/d*c*, n and λ. Hence, the molecular weight M of the dissolved material can be determined by measuring R_ϑ at concentration c.

The above considerations are valid only for monodisperse samples of rather low molecular weight. When characterizing polydisperse samples, all components i having different molecular weights M_i and concentrations c_i, scatter independently from each other. Thus one obtains the following equation:

$$R_\vartheta = K \sum c_i M_i = K_c M_w \qquad (2.39)$$

or

$$\frac{Kc}{R_\vartheta} = \frac{1}{M_w} \qquad (2.40)$$

Thus light scattering delivers the weight-average molecular weight of a polydisperse sample. The usually high molecular weight of polymers enforces a further aspect: since the diameter of the polymer coil is usually larger than approx. $\lambda/20$, intramolecular interference effects become relevant in the scattered light. This interference is zero at $\vartheta = 0°$ and has a maximum at $\vartheta = 180°$.

This internal interference is described by the particle form factor, P_ϑ. It allows the direct calculation of the radius of gyration, $<s^2>^{1/2}$, of the macromolecules and thus provides information about their chain conformation:

$$P(\vartheta)^{-1} = 1 + \frac{16\pi^2 n_0^2 <s^2>}{3\lambda^2} \sin^2\frac{\vartheta}{2} \qquad (2.41)$$

Because all the above deductions are valid for infinite low polymer concentrations but practical measurements have to be carried out at finite values of c, it is necessary to include the second virial coefficient A_2. Thus the equation according to which evaluation of light-scattering experiments can be done is:

$$\frac{Kc}{R_\vartheta}\frac{1}{M_w} = \left(1 + \frac{16\pi^2 n_0^2 <s^2>}{3\lambda^2}\sin^2\frac{\vartheta}{2}\right) + 2A_2c \qquad (2.42)$$

Light-scattering investigations are carried out in a way that the scattering intensity of several polymer solutions having different polymer concentrations c are measured at different scattering angles. Then, Kc/R_ϑ is plotted versus $\sin^2(\vartheta/2) + kc$ (with k an arbitrary constant) and then simultaneously extrapolated to $c \rightarrow 0$ and $\vartheta \rightarrow 0$ (Zimm plot). While M_w is obtained from the y axis intercept, the slope of the two extrapolated straight lines delivers $<s^2>$ and A_2.

The sensitivity of a light-scattering experiment is basically determined by the refractive index increment, dn/dc. Its value determines the lowest limit of M which is still accessible by light scattering. In general, the molecular weights of the polymers to be analyzed should be above approx. 30,000–50,000. Because light scattering is the more sensitive the larger the molecular weight of the scattering species is, special care has to be taken to remove all dust or other scattering particles from the solution. Therefore, special procedures are needed for the purification of the cuvettes, and the solvents and solutions have to be filtered carefully (preferentially using syringe filters). Here, however, one has to ensure that no polymer is filtered off during this process. This may happen in particular when the polymer tends to aggregate or not sufficient time was given for polymer dissolution. Last but not least, one has to assure that the polymer does not absorb the light used for the scattering studies.

Mass Spectrometry

Polymers are not easily converted to gas-phase ions but this is a requirement for compounds analyzed by mass spectrometry. Despite this difficulty, mass spectrometry has been utilized to study various aspects of polymers: polymers can be characterized – among others – with respect to their chemical composition, to their end groups, and to their molecular weight. Moreover, mass spectrometry can be used to study polymer surfaces.

Field desorption (FD) and fast atom bombardment (FAB) mass spectrometry provides mass spectral information about compounds that are not very volatile but these two techniques are not used often in polymer science since they have several disadvantages. Electrospray ionization (ESI) mass spectrometry can also be used to obtain the above information about polymers, but ESI spectra are generally complicated due to differences in charge state distributions. Static secondary ion mass spectrometry (static SIMS) is a surface-sensitive MS technique, which is suitable for studying the interfaces of polymers with respect to chemical structure and molecular weight as well as end groups and surface contaminants. Laser desorption mass spectrometry (LDMS) has been used for detection of polymer additives, characterization of polymer end groups, repeat units, and average molecular weights. Depth profiling experiments and film characterization have also been carried out using LDMS. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), however, is the most widely used MS technique for bulk polymer analysis. MALDI can be used to determine the average molecular weight for both high and low mass polymers, the mass of the end groups, and monitor polymerization reactions by characterizing the chemical structure of the products and the rate of polymerization. Also, MALDI can be used to examine the surface and bulk composition of biomaterials, whereas SIMS is used for examining monolayer and submonolayer coverage of polymers on surfaces. As a whole, the development of soft ionization methods has led to an increased use of mass spectrometry in characterizing polymers. MALDI appears to exhibit the best performance for reliable molecular weight determination at higher masses.

In MALDI, a polymer is dissolved in a solvent, and a special ingredient is added which has to absorb ultraviolet light very efficiently. Usually about 10^4 times more of the UV absorber are added to the solution than polymer. Then, the solution is placed in an airtight chamber, on the tip of the sample probe. The chamber is evacuated, and the solvent evaporates. Finally, a thin layer remains of the UV-absorbing compound together with a small amount of the polymer in it, i.e., the polymer is now dispersed in a matrix of the UV-absorbing compound. Then the sample is irradiated by a laser shoot (usually by an ultraviolet laser working in the 330–360-nm range). The UV-active matrix material absorbs the laser energy and reacts with the polymer in such a way that the macromolecules become charged ions. It is still unknown how this happens. Depending on what kind of polymer and what kind of matrix material is used, the polymers may be cations or anions. When the polymer forms cations, the positive cathode is placed right behind the sample, and the negative anode in front of it. Most of the time, there is only one single positive charge on each polymer molecule (ionized via alkali metal ion attachment). Moreover, the absorbed laser energy heats up the sample, causing evaporation of the matrix together with some of the polymer molecules at these high temperatures and low pressures. Now, the ionic polymers floating around in gaseous state between the electrodes are accelerated in the applied electric field (the positively charged polymers are travelling in the direction of the anode, attracted to its negative charge). The same electrical force is applied on each polymer molecule while it is being accelerated in the electric field between the two electrodes. But the more mass, the slower the acceleration. This means that the polymer will take longer to reach the detector at the end of the chamber. So the polymers will hit the detector, the small ones first, then the big ones. When a macromolecule reaches the detector, it registers a peak. The size of the peak is proportional to the number of molecules that hit at one time. So a series of peaks is obtained. Because the time a molecule needs to reach the detector is proportional to its mass, a plot of molecular weight on the x-axis and the number of molecules having given molecular weight on the y-axis is obtained, i.e., the molecular weight distribution. The Fig. 2.12 shows the MALDI spectrum of a poly(*p*-phenylene) derivate. It shows clearly the different chain lengths as well as the patterns of the end groups.

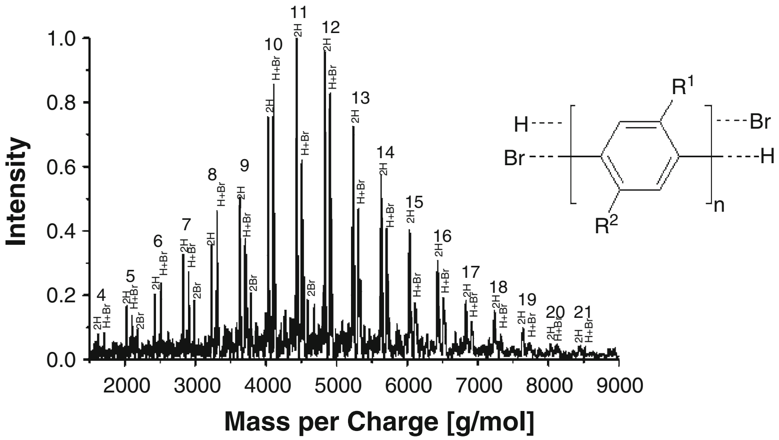


Fig. 2.12 MALDI mass spectrum of a side-chain substituted poly(*p*-phenylene). The splitting of the mass peaks of the respective *n*-mers is caused by the different combinations of end groups, i.e., H,H, H,Br, or Br,Br

MALDI measures the mass very accurately, and it gives an absolute measurement of mass. Still, sample and solution conditions must be optimized for the best performance of the matrix and therefore, it cannot yet be used as a routine method. Also, characterization of synthetic polymers by MALDI is sometimes limited by their solubility and mass discriminating desorption behavior, and the mass spectrum might be affected by the properties of the solvents used for polymer dissolution or by the matrix material.

There are also some further mass spectrometric applications in polymer science. Gas chromatography/mass spectrometry (GC/MS), for example, can be used to identify and characterize small volatile polymers and contaminants. GC/MS can also be used to characterize the degradation products of polymers. Pyrolysis-GC/MS can be used to determine the chemical structure of polymers and to examine their thermal degradation pathways. It is used to determine the chemical structure of analyte molecules by analyzing analyte fragmentation. This technique can also be used to monitor polymerization by identifying characteristic pyrolates. Usually, relatively low-mass fragments of the polymer can be analyzed; however, by controlling the temperature, pyrolysis-GC/MS can be used to analyze higher-mass pyrolates. Glow discharge mass spectrometry (GDMS) is another technique that is able to fingerprint polymer materials.

Ultracentrifuge Measurements

In a centrifugal field, dissolved molecules or suspended particles either sediment (if their density exceeds that of the pure solvent), or flotate for the opposite case (negative or inverse sedimentation). Under otherwise identical experimental conditions, the velocity of the molecules or particles depends on the viscosity of the solution or suspension and – very importantly – on the mass and shape of the dissolved species. Sedimentation and flotation are antagonized by the diffusion. Depending on the rotor speed and the molar mass of the dissolved/dispersed polymers/particles there are different ways for the evaluation of thus obtained experimental data.

(a) Svedberg method

Here the speed of the rotor is selected in a way that the sedimentation velocity of the molecules is very high in comparison to their diffusion velocity. Thus, diffusion can be disregarded and in the cell a zone is formed where a clear concentration gradient is obvious. Assumed the density of the dissolved molecules or particles is larger than the density of the pure solvent, this concentration gradient migrates from the meniscus to the bottom of the cell during the experiment. This sedimentation process can be described as follows: In a distance x from the center of rotation, the centrifugal force K_Z acts on a particle of mass m being in the centrifugal field. The centrifugal force K_z is antagonized by a friction force K_r which is proportional to the sedimentation velocity:

$$K_r = F\frac{dx}{dt} \tag{2.43}$$

The proportionality factor F is called friction factor and is identical for diffusion and sedimentation. Using the Einstein Sutherland equation

$$D = \frac{RT}{F \cdot N_L} \tag{2.44}$$

the Svedberg equation of sedimentation is obtained:

$$M_{s,D} = \frac{s \cdot RT}{D \cdot (1 - \bar{v}\rho_{solvent})} \tag{2.45}$$

If (1) the diffusion coefficient D of the polymer in the used solvent, (2) the specific volume $\bar{v}$ of the dissolved polymer, and (3) the density of the solvent ρ_{solvent} are known, one can determine the molecular weight of the dissolved polymer according to the above equation by measuring the sedimentation coefficient (by measuring the maximum of the concentration gradient at regular time intervals).

The thus determined molecular weight is an apparent one since s and D depend on the polymer concentration. Therefore, extrapolation to concentration zero is required. The sedimentation coefficient obtained by extrapolating $c \rightarrow 0$ is called sedimentation constant s_0:

$$\frac{1}{s} = \frac{1}{s_0}(1 + k_s c) \tag{2.46}$$

Here k_s is a constant which depends on solvent and temperature. Thus the sedimentation constant can be calculated from the y-axis intercept when the reciprocal of the sedimentation coefficient s determined at different polymer concentrations c is plotted vs. the polymer concentration, c, and then c is extrapolated to zero. Using the thus determined sedimentation constant s_0 – which increases with growing molecular weight – and the known diffusion coefficient $D_{0(c\rightarrow 0)}$ ("diffusion constant") the Svedberg equation gives the molecular weight $M(s_0, D_0)$ of the polymer. This molecular weight is – in the case of polydisperse samples – in most cases somewhere between the viscosity average, M_η, and the number average, M_n, of the molecular weight.

When dispersions are analyzed where nonsolvated, sphere-like particles sediment, the sedimentation coefficients s are independent of concentration at low solid contents and, therefore, it is possible to determine the particle size distribution in dispersion from the distribution of the sedimentation coefficients.

(b) Sedimentation equilibrium

At low rotor revolution numbers an equilibrium state can be reached between sedimentation and diffusion. Now, a time-independent concentration gradient is established, i.e., $(dc/dt)_x = 0$. Under these conditions, the Svedberg equation becomes:

$$M = \frac{dc/dx}{\omega^2 xc} \frac{RT}{(1 - \bar{v}\rho_{solvent})} \tag{2.47}$$

If c and dc/dx are known as a function of x and the measurement is carried out in a theta solvent, the molecular weight M of monodisperse polymers can now be calculated precisely. If the solvent is not a theta solvent, the obtained value of M is an apparent molecular weight from which the true value can be calculated upon plotting $1/M$ vs. c and extrapolation to $c \rightarrow 0$. For polydisperse samples, one has to insert the average of dc/dx in the above equation, and the thus calculated molecular weight represents a weight-average, M_w.

An alternative approach for determining the molecular weight of a polymer in theta solvents includes the determination of the polymer's concentration at the meniscus (c_m) and at the bottom (c_b) (or alternatively at two other positions x_1 and x_2) in the cell. These two outstanding positions have a distance of $x_m(x_1)$ and $x_b(x_2)$, respectively, from the center of rotation. Then, one obtains the weight-average molecular weight of a polydisperse polymer sample via the equation:

$$M_w = \frac{c_b - c_m}{\omega^2 \left(x_b^2 - x_m^2\right) \cdot c_0} \frac{2RT}{(1 - \bar{v}\rho_{solvent})} \tag{2.48}$$

Here, c_0 is the polymer concentration of the original solution.

(c) Sedimentation in a gradient of density

When mixtures of solvents of different density are used for polymer dissolution, an equilibrium is established during ultracentrifugation where the concentration of the solvent of higher specific gravity is increased at the bottom of the cell while the specifically lighter solvent is enriched near the meniscus. Hence, the dissolved macromolecules encounter a density gradient in the cell, and they move to the place in the cell where the density of the solvent mixture is identical to their own density (one should take care that there is no preferential solvation in either one of the constituents of the solvent mixture!). However, due to Brownian motion monodisperse macromolecules do not collect at a single place x within the cell but rather in a certain zone. This zone has – for identical polymer molecules – the shape of a Gauss curve. The width of this curve decreases with increasing molecular weight:

$$\frac{c}{c_{x_0}} = \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right) \tag{2.49}$$

with

$$\sigma^2 = \frac{RT}{M\bar{v}\left(\frac{d\rho}{dx}\right)_{x_0}\omega^2 x_0} \tag{2.50}$$

where x_0 is the distance between the center of the Gauss curve and the rotor axis, and $(\mathrm{d}\rho/dx)_{x0}$ is the gradient of density at x_0. Chemically different molecules often have different densities and thus are enriched at different locations within the cell. For example, the chemical composition of (graft, block, statistic) copolymers and the tacticity of homopolymers can be characterized in the gradient of density. In the case of dispersions information is available about the density and the density distribution of the dispersed particles, and thus conclusions concerning their chemical composition are possible.

2.3.3.3 Relative Methods

Solution Viscosity

When a polymer is dissolved in a solvent, it makes the solution viscous. The caused thickening effect can be used to estimate a macromolecule's molecular weight because the higher the molecular weight, the more viscous the polymer solution will be. This is reasonable because the higher the molecular weight, the bigger the hydrodynamic volume is, and being bigger, the polymer molecule can block more motion of the solvent molecules. Also, the bigger a polymer is, the stronger its secondary forces are. So the higher the molecular weight, the more strongly solvent molecules will be bound to the polymer. This reduces even more the mobility of the solvent molecules.

For most polymers there is a definite relationship between molecular weight and solution viscosity. The viscosity method of molecular-weight determination was introduced by Staudinger. However, it is applicable only to linear and slightly branched molecules; it fails mostly for sphere-like or strongly branched molecules (globular proteins, glycogens). For the determination of the molecular weight of a polymer via solution viscosity measurements it is not necessary to determine absolute values of the solution viscosity. In principle, it is enough to measure the time t which a given volume of the polymer solution needs to flow through the capillary and to compare this with the time t_0 which is needed by the pure solvent. Then, to have a first measure of the viscosity-increasing effect of the polymer to be analyzed, the elution or flow time, t of the polymer solution at a given concentration c, is divided by t_0. This quotient is called the relative viscosity η_{rel}:

$$\frac{t}{t_0} = \eta_{rel} \tag{2.51}$$

However, the required information is the difference in the elution times of the solution and the pure solvent relative to the elution time of the pure solvent. Therefore, the elution time of the pure solvent t_0, is subtracted from the elution time of the solution t. The thus obtained result is divided by t_0. The resulting quantity is called the specific viscosity, η_{sp}, which is a dimensionless quantity:

$$\frac{t - t_0}{t_0} = \eta_{sp} \tag{2.52}$$

If the measurement is made in a capillary viscometer of specified dimensions and at low polymer concentration (so that the density of the solution is approximately the same as that of the solvent), the viscosities η and η_0 are represented in a good approximation by the elution times t and t_0. It follows that:

$$\frac{t - t_0}{t_0} = \eta_{sp} \approx \frac{\eta - \eta_0}{\eta_0} \tag{2.53}$$

If this value is divided by the concentration c of the polymer in solution, one obtains the reduced specific viscosity, η_{red}.

$$\frac{\eta_{sp}}{c} = \eta_{red} \tag{2.54}$$

Polymer solutions are never ideal since dissolved macromolecules influence each other even at very low concentration. On the other hand, a reliable correlation of solution viscosity and molecular weight is only possible if the dissolved macromolecules are not affected by mutual interactions: they must be actually independent of each other. Therefore, the viscosity of polymer solutions should be determined at infinite dilution. However, such measurements are impossible in practice. So one works at an as low as possible polymer concentration and extrapolates the obtained values to zero concentration. To do so, the elution time measurements are not only carried out for one single polymer concentration but for varying polymer concentrations (e.g., 10, 5, 2.5, 1.25 g/l). For each solution, the value of the reduced specific viscosity is figured out (the data will make evident that this quantity is clearly concentration-dependent even at the lowest possible polymer

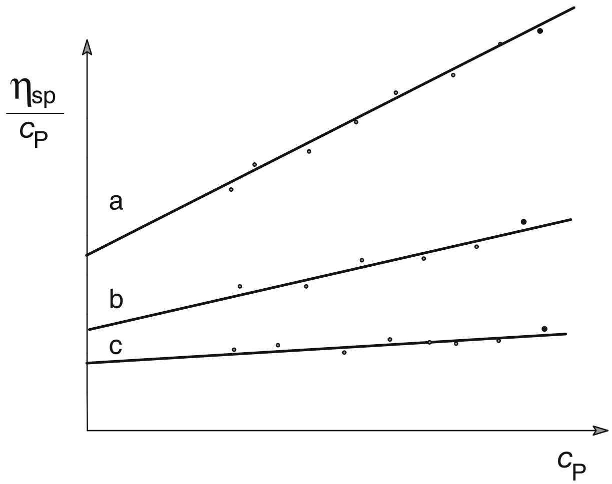


Fig. 2.13 Graphical evaluation of the limiting viscosity number (intrinsic viscosity) from viscosity measurements at different concentrations for (**a**) a high-molecular-weight, (**b**) a medium-molecular-weight, and (**c**) a low-molecular-weight polymer sample

concentrations). Then, the limiting value (intrinsic viscosity, Staudinger index or limiting viscosity number) [η] is determined as a reliable measure of the viscosity behavior of the isolated thread-like molecule at infinite dilution. It is defined by the following expression:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \tag{2.55}$$

Practically, the η_{sp}/c values are plotted against the concentration c, and linear extrapolation is done. [η] is obtained as the y-axis intersect (Fig. 2.13).

Since η_{sp} is dimensionless, [η] has units of reciprocal concentration (e.g., l/g or dl/g). Hence in viscosity measurements the concentration units must always be stated.

Since the intrinsic viscosity depends not only on the size of the macromolecule but also on its shape, on the solvent, and on the temperature, there is no simple relationship for the direct calculation of molecular weights from viscosity measurements. However, the Mark-Houwink-Kuhn equation gives a general description of how the molecular weight can be calculated from the intrinsic viscosity:

$$[\eta] = K \cdot M^a \tag{2.56}$$

M is the viscosity average molecular weight, and K and a are the Mark-Houwink constants. There is a specific set of Mark-Houwink constants for every polymer-solvent combination. So one has to know these values for the applied

Table 2.8 K_m- and a-values for the calculation of molecular weights from viscosity measurements according to Eq. 2.56, $[\eta]$ in ml/g

Polymer	Solvent	Temperature (°C)	K_m (10^3 ml/g)	a
Polystyrene (atactic)	Toluene	25	7.5	0.75
	Cyclohexane	28	108.0	0.479
Poly(α-methylstyrene)	Toluene	25	7.06	0.744
	Cyclohexane	34.5	73.0	0.5
Polyisobutylene	Cyclohexane	25	40.0	0.72
Polybutadiene (98% *cis*)	Toluene	30	30.5	0.725
Polyisoprene	Toluene	25	50.2	0.667
	Cyclohexane	27	30.0	0.7
Poly(vinyl acetate)	Acetone	25	21.4	0.68
Poly(vinyl alcohol)	Water	25	20.0	0.76
Poly(methyl methacrylate)	Acetone	25	5.5	0.73
Polyacrylonitrile	DMF	20	17.7	0.78
Polyacrylamide	Water	30	6.31	0.8
Poly(ethylene glycol terephthalate)	*o*-chlorophenol	25	17.0	0.83
	Tetrachloroethane	50	13.8	0.87
Polycarbonate from bisphenol A	Chloroform	25	12.0	0.82
Nylon 6,6	*o*-chlorophenol	25	168.0	0.62
Poly(phenylene ether)	Toluene	25	28.5	0.68
Polysiloxane	Toluene	25	18.7	0.66
Cellulose triacetate	Dichloromethane	20	24.7	0.704

polymer-solvent combination in order to obtain an accurate measure of molecular weight. Therefore, for a new polymer for which no Mark-Houwink constants are available no good measure can be achieved. Under these conditions, one obtains only a qualitative idea of whether molecular weight is high or low. One is, therefore, always obliged to establish for each polymer a calibration curve or calibration function by comparison with an absolute method. This, however, is only valid for a given solvent and temperature (Table 2.8).

Mathematical evaluation of M is somewhat inconvenient. Graphical methods are preferable. The above equation can be expressed in logarithmic form:

$$\log[\eta] = \log K + a \cdot \log M \tag{2.57}$$

so that a double logarithmic plot of $[\eta]$ versus M gives a straight line whose slope corresponds to the exponent a (see Fig. 2.14).

The exponent a depends on the shape of the macromolecules in solution. For rigid spheres $a = 0$; however, most macromolecules are present in solution as more or less expanded coils. Accordingly for most polymers a-values lie between 0.5 and 1.0, with 0.5 being the extreme value for nonexpanded ideal statistic coils (ϑ system) and 1.0 for fully expanded coils. Cases are also known where a is

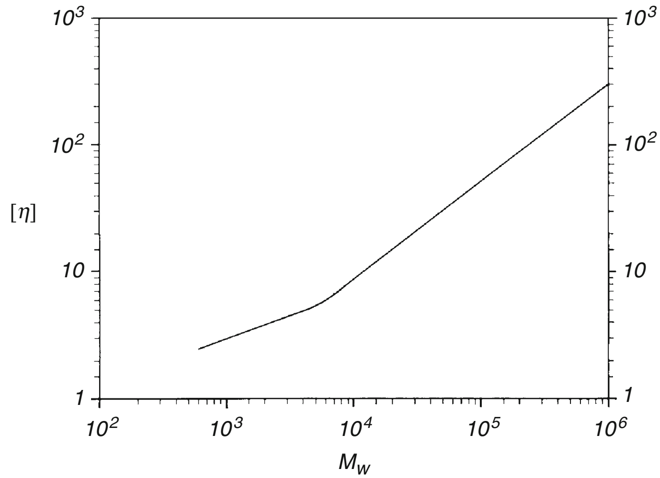


Fig. 2.14 Relation between viscosity and molecular weight for polystyrene in benzene at 20°C

greater than 1. This occurs with particularly stiff and elongated macromolecules, which approximate to the model of a rigid rod in solution, for which $a = 2$.

Since the degree of expansion of the polymer coils is directly dependent on the solvating power of the solvent, under otherwise comparable conditions, both a and $[\eta]$ provide a measure of the "goodness" of a solvent: high values of a and $[\eta]$ (at constant molecular weight and temperature) indicate remarkable coil expansion and therefore a good solvent. Low values of a and $[\eta]$ indicate a bad solvent. For example, the values a for poly(vinyl acetate) in methanol and acetone are 0.60 and 0.72, respectively.

The interactions between solvent and polymer depend not only on the nature of the polymer and type of solvent but also on the temperature. Increasing temperature usually favors solvation of the macromolecule by the solvent (the coil expands further and a becomes larger), while with decreasing temperature the association of like species, i.e., between segments of the polymer chains and between solvent molecules, is preferred. In principle, for a given polymer there is a temperature for every solvent at which the two sets of forces (solvation and association) are equally strong; this is designated the theta temperature. At this temperature the dissolved polymer exists in solution in the form of a nonexpanded coil, i.e., the exponent a has the value 0.5. This situation is found for numerous polymers; e.g., the theta temperature is 34°C for polystyrene in cyclohexane, and 14°C for polyisobutylene in benzene.

The following apparatus is needed to carry out viscosity measurements: a capillary viscometer with suitable mounting, a thermostatted bath, a stopwatch (0.1 s), several graduated 10-ml flasks, and graduated 5-ml and 3-ml pipettes. For the reasons already given the measurements are performed only on dilute solutions. The most commonly used capillary viscometer is the Ostwald viscometer

(Fig. 2.15a). The diameter of the capillary (in general between 0.3 and 0.4 mm) is chosen so that the flow time for the solvent is about 60–150 s. Special versions of the Ostwald viscometer have been developed for measurement of solution viscosity at higher temperatures. Since the viscosity of a solution depends strongly on the temperature, good thermostatting is necessary (accuracy within 0.05–0.1°C).

The viscosity measurements are conducted as follows: 100 mg of well-dried polymer are weighted into a 10-ml graduated flask and dissolved in somewhat less than 10 ml solvent. After the solution has been brought to the temperature of measurement, the solution is made up to the mark (polymer concentration 10 g/l). The polymer solution is now filtered through a glass frit in order to remove dust particles which would seriously disturb the measurement. It is filtered directly into bulb 4 of the viscometer.

The viscometer is suspended vertically in a thermostatted bath (Fig. 2.15.b). After temperature equilibration (about 5 min at 20°C), the surface of the polymer solution can be transferred from arm 2 to mark M_1 in arm 1 only by applying a slight pressure on the opening of arm 2 with a rubber bulb. The time required for the solution to flow from mark M_1 to mark M_2 is measured and the average of five measurements is taken as the flow time t. Depending on the total flow time, they should not deviate from one another by more than 0.2–0.4 s. The flow time of the solvent t_0 is likewise determined with a filtered 3-ml sample; this determination should be carried out each time before beginning the measurements on the solutions since it provides a simple and accurate check of the entire set-up (temperature control, cleanliness of the viscometer, etc.) The viscometer is now removed and the polymer solution is poured out through arm 2. After attaching the headpieces *a* and *b*, the viscometer is rinsed several times with pure solvent (application of slight vacuum at headpiece *a*) and then with purified acetone. It is finally dried by drawing air through the viscometer (the sintered glass filter should be covered with a piece of filter paper). The viscometer is then ready for the next measurement.

The viscosity behavior described so far is valid only for uncharged polymers. If polyelectrolytes are analyzed, a quite different viscosity behavior may be found in polar solvents (e.g., polymeric acids in water). The η_{sp}/c values at first fall off with decreasing concentration as for uncharged polymers but then climb steeply and may drop down later again (see Fig. 2.16). Addition of salt to the solution of polyelectrolytes (e.g., 1% and 5% sodium chloride in aqueous solution) restores, step by step, the normal behavior (see Fig. 2.16, curves *b* and *c*).

This is connected with the fact that in polyelectrolytes the shape and density of the macromolecular coils is affected by the degree of ionization and that the long-range intermolecular coulomb forces depend on the ionic strength of the solution. In the ionized state, the like charges distributed along the length of a macromolecule repel each other, leading to a marked coil expansion and hence a considerable increase in viscosity. Also, upon diluting the polymer solution the range of the intermolecular repulsion becomes larger, and mutual electrostatic interaction of the dissolved macromolecules becomes stronger despite of the increasing distance of the charged coils. Every factor that causes an increase in the degree of dissociation or a decrease in ionic strength, therefore, leads to a rise in the solution viscosity, and

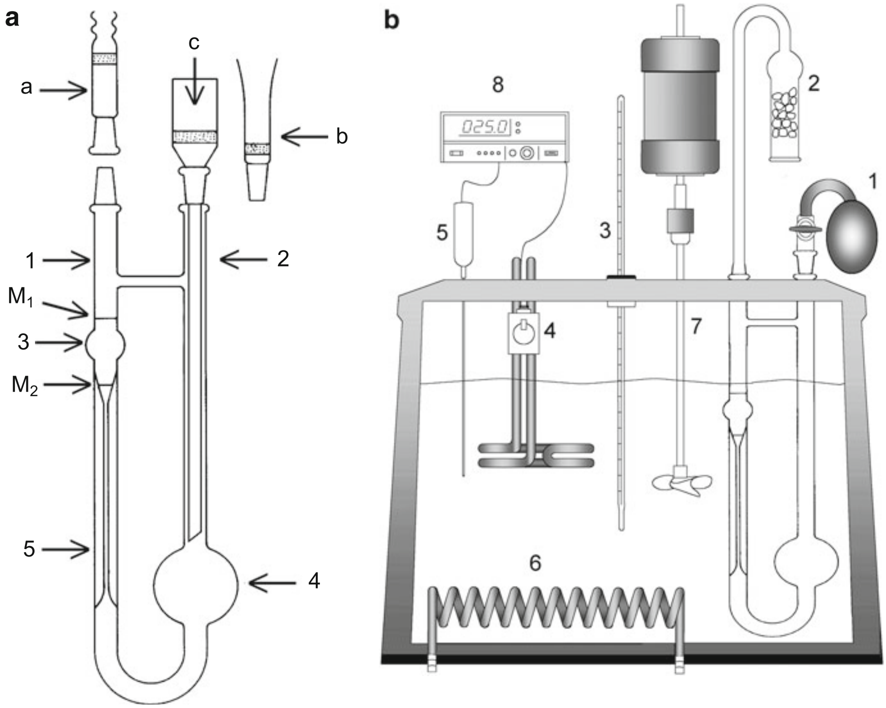


Fig. 2.15 (**a**) Ostwald viscometer: Total length: 25 cm; capillary length: 10 cm; bulb 3: diameter 1.3 cm, bulb 4: diameter 2.2 cm, filling level: 2 or 3 ml, flow volume: 0.5 ml; *a, b*: head pieces; *c*: sintered glass filter for filtration of solvent and polymer solution (**b**) Thermostatted bath and mounting for Ostwald viscometer: 1: rubber bulb; 2: drying tube; 3: thermometer; 4: heating coil; 5: thermo indicator; 6: cooling coil; 7: stirrer; 8: power and controlling unit

vice versa. The viscosity behavior of aqueous solutions of polymeric acids [e.g., poly(methacrylic acid)] of various concentrations can then be explained as follows: On dilution of the aqueous solution the normal effect is first observed, i.e., the viscosity decreases. With further dilution the increasing degree of dissociation of the carboxylic groups becomes noticeable and the ionic strength is as much lowered that intermolecular repulsion of the coils becomes relevant. This leads to an increase of the viscosity. The effect caused by the higher degree of dissociation and the high Debye length exceeds first that resulting from dilution; hence η_{sp}/c rises. Finally, the predominance is inverted, and the reduced viscosity drops down again. On addition of sodium chloride, the degree of ionization is essentially held steady, and therefore also the coil expansion; the rise in viscosity with decreasing concentration of polymer is thus suppressed.

Size-Exclusion (Gel Permeation) Chromatography

Synthetic polymers do not contain macromolecules of only one single molecular weight but are composed of macromolecules having a distribution of molecular

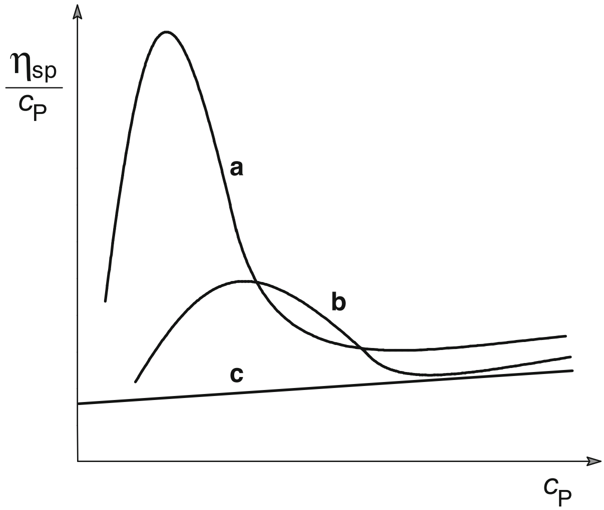


Fig. 2.16 Behavior of a polyelectrolyte in dilution viscosimetry in water: (**a**) without, (**b**) with a low quantity and (**c**) with a higher quantity of a low-molecular-weight electrolyte (salt) which screens the electrostatic interactions

weights. All the analytical techniques described so far (except MALDI-MS) represent the distribution curve by means of different averages of the molecular weight, i.e., M_n, M_w, M_η. Gel permeation chromatography (GPC, also called size-exclusion chromatography, SEC) does deliver such averages as well. However, it is moreover able to give the entire distribution curves. Thus GPC is a very powerful method of polymer fractionation and has become a standard method for determination of molecular-weight distribution and relative molar mass.

In a GPC experiment, the polymer is separated in a column which is filled with a swollen, uniformly packed resin ("gel", called stationary phase, while the solvent which passes through the column is called mobile phase). The gel beads are usually made of crosslinked polymers (in particular polystyrene but also various inorganic porous materials) with little holes and pores of different size where the pore diameter is of the dimension of the size of the solvated polymer coils, i.e., the pore-size distribution is approx. 10–10^5 nm.

A solution of the polydisperse polymer in the same solvent as was used to swell the resin is placed on the top of the column and eluted in the same manner as for standard column chromatography or high-pressure liquid chromatography (HPLC). In GPC, however, it is not the interaction of the dissolved analyte molecules with the stationary phase relevant for separation but the different (hydrodynamic) volumes of the polymers associated with their different molecular weights. Only solvent molecules and those macromolecules whose size is less than the prevailing pore size can diffuse into the pores of the swollen gel: their separation succeeds because the polymer molecules get caught up in the holes in the beads, then come out, pass on down the tube a little way, then get caught in another pore, and so on.

Big polymer molecules with higher molecular weights do not fit in some of the smaller holes. Because there are fewer pores that the big ones can get caught in, these molecules pass through the column fairly quickly. But smaller polymer molecules with lower molecular weights can fit into the small pores and therefore will penetrate into a larger number of pores. So it takes them longer to pass the column. Accordingly, the elution time increases with decreasing molecular size.

Molecules which are small enough that not only the external volume V_0 but also the total internal volume V_i is available to them, leave the column with an elution volume, V_e:

$$V_e = V_0 + V_i \tag{2.58}$$

For intermediate-sized macromolecules only a fraction K_d of the internal volume is accessible ($0 < K_d < 1$) and the value of V_e is then given by:

$$V_e = V_0 + K_d \cdot V_i \tag{2.59}$$

The constant K_d is the apparent distribution coefficient for the distribution of a substance between the swelling medium inside and outside the gel particles. K_d depends mainly on the molecular size and to a lesser extent on the shape of the molecule in solution.

Very large macromolecules cannot penetrate into the pores of the gel. Hence, such large molecules cannot be separated from one another. The so-called exclusion limit gives an approximate indication of the limiting molecular weight up to which the macromolecules of the polymer to be fractionated can penetrate the network and therefore be separated. Network structure and exclusion limit are closely related: the tighter the network, the smaller the exclusion limit.

The efficiency of fractionation by gel chromatography not only depends on the type of gel but also on the dimensions of the column. The internal volume V_i of the gel pores is determined by the amount of dry resin used and by its swellability, which in turn depends upon the eluting agent. The total volume of the gel bed V_t is thus made up of the volume of the gel framework, the internal volume V_i of the gel, and the external volume V_0 between the gel particles. The external volume V_0 is identical with the elution volume V_e of a substance with a molecular weight above the exclusion limit. Macromolecules of this size cannot penetrate the network but pass through the column unimpeded. V_0 can thus be readily determined.

In order to detect the macromolecules that elute from the column, detectors are needed that can count how many polymer molecules are coming out of the end of the column at a given time interval. The polymer concentration in the eluate can be determined discontinuously by precipitation and weighing of the dry polymer. The commercially available GPC equipment measures continuously the refractive index or the difference in refractive index between the solution and the pure solvent. The polymer concentration can also be determined spectroscopically (e.g., by UV–vis) providing the macromolecules possess relevant absorption bands. Using the thus collected data, a plot of time can be made on the x-axis and the number of polymer molecules coming out at a given time on the *y*-axis. As GPC is not an absolute method, calibration is required. For this, one usually takes samples of very narrow and well-known molecular-weight distribution. Calibration of the GPC column(s) in use delivers a calibration curve which correlates the elution time (or volume) with the logarithm of the polymer's molecular weight, log *M*. Using this calibration curve, the molecular weight can be calculated from elution time. This results in a plot of molecular weight on the *x*-axis and the number of molecules with a particular weight on the *y*-axis. On this plot, molecular weight *decreases* from left to right.

When a size-exclusion chromatograph is calibrated correctly, one can know the molecular weight of a polymer just based on the time it takes to pass, or *elute* through the column. From Fox and Flory's theory of solution viscosity one can learn that the size of a solvated macromolecular coil is directly correlated with its solution viscosity. The correlation is:

$$[\eta]M = \Phi\left(<r^2>_0\right)^{3/2} \cdot \mathrm{a}^3 \tag{2.60}$$

A universal calibration is therefore possible for SEC by plotting log ($[\eta] \cdot M$) vs. V_e when a viscosity detector is used. Absolute molar masses can be obtained using a light-scattering detector.

SEC became the most widely used method for molar mass and molar mass distribution determination due to its broad applicability, easy sample preparation, and the large amount of information resulting from the full distribution curve. The commercially available SEC systems work automatically with small sample amounts and even at elevated temperatures. In addition, chromatographic systems coupled with spectroscopic methods giving chemical information on the separated fractions gain more and more importance for analysis of complex polymer systems and mixtures.

2.3.3.4 Determination of Molecular-Weight Distribution by Fractionation

Polymer syntheses nearly always result in polydisperse products, i.e., are composed of macromolecules of different molecular weights. Since many physical properties depend not only on the average molecular weight but also on the broadness and the shape of the molecular-weight distribution (MWD) curve, it is an important technique to determine (and perhaps to modify) the MWD by fractionation. While there is no separation procedure which provides truly monodisperse samples from the polydisperse starting material, nevertheless, one can obtain fractions whose MWD is really small. These fractionation methods are based on the (slightly) decreasing solubility of polymers with increasing molecular weight: simplisticly, phase separation into a polymer-rich gel phase and a solvent-rich sol phase occurs in an originally homogeneous polymer solution when the Flory-Huggins interaction parameter χ exceeds a critical value χ_c. The critical value of χ_c decreases with increasing molecular weight of the polymer:

$$\chi_c = \frac{1}{2}\left(1 + m^{-\frac{1}{2}}\right)^2 \approx \frac{1}{2} + m^{-\frac{1}{2}} \tag{2.61}$$

with $m = V_p/V_{solvent}$ and V_p and $V_{solvent}$ being the mole volume of the polymer and the solvent, respectively. In dilute solutions the second virial coefficient of the osmotic pressure, A_2, depends on c as follows:

$$A_2 = \left(\frac{1}{2} - \chi\right)RT \cdot \rho_p^{-2} \cdot V_{solvent}^{-1} \tag{2.62}$$

with ρ_p being the density of the dissolved polymer. Phase separation starts as soon as the value of A_2 drops below a critical value $A_{2,c}$:

$$A_{2,c} \approx -m^{-\frac{1}{2}}RT \cdot \rho_p^{-2} \cdot V_{solvent}^{-1} \tag{2.63}$$

For $m \to \infty$, the critical value is identical with that in a ϑ solvent, i.e., $A_2 = 0$ and $\chi = 0.5$. Since the solubility of macromolecules decreases with increasing molecular weight, it is possible to separate these materials with respect to their molecular weights by changing the composition of the solvent and/or the temperature. In general, one roughly distinguishes between two methods, namely fractional precipitation and fractional extraction.

To fractionate a polymer by precipitation, a precipitant is slowly added to the polymer solution (concentration of polymer 0.1–1 wt.%) at constant temperature until a persistent cloudiness appears. After some time the droplets separate as a second liquid (or swollen gel) phase. This fraction contains the highest molecular weight components and is separated by decantation or centrifugation. Further precipitant is then added to the majority layer until further phase separation is observed. Then the above procedure is repeated several times until all polymer is separated off. A disadvantage of fractional precipitation is that the residual solutions become more and more dilute so that separation of the late fractions might be difficult. Furthermore, the method is rather time consuming since the formation of the gel phase occurs very slowly.

These disadvantages can be circumvented to some extent by means of the Meyerhoff's triangular fractionation technique. Here, precipitant is added to the dilute polymer solution until about approximately half the polymer material is separated off in the gel phase. After separating the gel it is redissolved. Now, one has two solutions with which one proceeds as for the original solution, i.e., enough precipitant is added to bring about separation of approximately half the polymer in each case, and so on. In this way large volumes of solution can be avoided and there is a considerable saving in time, since several fractions can be worked up simultaneously.

In some cases the molecular-weight distribution can be determined by turbidimetric titration, a technique which is based on the fractional precipitation. A precipitant is added to a very dilute solution of the polymer, and the resulting turbidity is measured as a function of the amount of added precipitant; the preparative separation of the fractions is thereby avoided. If the polymer is chemically homogeneous, the mass distribution function can then be calculated. Turbidimetric titration is also suitable as a means for establishing the best fractionation conditions (e.g., choice of solvent/precipitant combination, size of fractions, etc.), before carrying out a full-scale fractionation by precipitation.

Fractional extraction is free from the disadvantages encountered in fractional precipitation. Here, the technique consists in extracting the polymer with a series of solvent/precipitant mixtures, the proportion of solvent being increased stepwise. Since one begins with the poorest solvent mixture – in contrast to fractional precipitation – the first fraction contains the low-molecular-weight components and the final fraction the high-molecular-weight components. The isolation of large fractions is possible by fractional extraction using a modified technique. The physical state of the polymer is very important for the efficiency of fractional extraction.

Once the amounts and molecular weights of the fractions have been determined, the molecular-weight distribution of a polydisperse material can be expressed graphically in the form of a distribution curve. The mass distribution function is written as:

$$m_P = H(P) \tag{2.64}$$

where m_p is the mass fraction (in gram or in%) of macromolecules with a degree of polymerization of P. At first sight it seems reasonable to present the fractionation results in the form of a histogram in which the amount in percentage is plotted directly vs. the degree of polymerization P. However, this representation only gives a realistic picture if each individual fraction deviates from its molecular weight average by the same amount, i.e., if the width of the steps are all equal. Unfortunately this condition is rarely fulfilled in practice. Therefore, the amount of the fraction should not be represented by a line (height of step), but by an area, i.e., so that the mass distribution function should be applied in integral form:

$$I(P) = \int_1^P H(P) \cdot dP \tag{2.65}$$

The integral distribution function is obtained from the experimental data as follows: The mass distribution within a given fraction is approximately symmetrical. Assumed the degree of polymerization of the m$^{\text{th}}$ fraction is P_m one can expect that half the fraction has a smaller degree of polymerization and the other half a larger one. Moreover, since fractions 1 to (m–1) all have a degree of polymerization smaller than P_m one obtains – by summing the amounts of all fractions from 1 to (m–1) and adding half the amount of the m$^{\text{th}}$ fraction – the mass fraction of all

Table 2.9 Fractionation of polystyrene of average degree of polymerization P = 800

Fraction No.	Amount [%]	I (P) [%]	$m_p \cdot 10^2$ [%]	P
8	3.4	1.7	1.10	170
7	3.7	5.25	3.45	360
6	7.3	10.75	4.35	430
5	16.8	22.8	6.95	680
4	24.9	43.7	7.55	900
3	9.9	61.6	5.30	1,300
2	26.5	79.25	4.25	1,470
1	7.5	96.25	1.40	2,240

degrees of polymerization from zero to P_m and hence a pair of values of the above integral equation.

For example, to obtain the value of I(P) for fraction 5 in Table 2.9 one adds the percentage amounts of fractions 8, 7, and 6 (3.4 + 3.7 + 7.3 = 14.4) and adds half the amount of fraction 5 (14.4 + 8.4 = 22.8). The integral distribution curve (see Fig. 2.17) is obtained by plotting *I(P)* values obtained in this way, versus the corresponding degree of polymerization.

A polymer is the more uniform with respect to the molecular weight the steeper the integral distribution curve is. The differential mass distribution function

$$dm_P = H(P) \cdot dP \tag{2.66}$$

in which dm_p is the mass fraction (in gram or %) with degrees of polymerization between P and $P + dP$, can be most simply obtained by graphical differentiation of the integral curve. This gives the values of dm_p/dP. An inflection point in the integral curve corresponds to a maximum in the differential curve. This procedure gives information about the distribution that is more detailed, the sharper the fractions and the greater their number. This kind of differential distribution curve tells us how many macromolecules there are with a given degree of polymerization P in the polymer sample. It normally has a single maximum and resembles a Gaussian bell-shaped curve. Distribution curves with two or more maxima are an indication of side reactions during the preparation, or degradation reactions during fractionation.

Proper fractionation according to molecular weight can only be expected if the macromolecules are chemically uniform. For polymers that are nonuniformly branched, or in which partial chemical conversions were carried out, or which are statistic, graft, or block copolymers, the solubility also depends on factors other than the molecular weight. Fractionation can then lead to separation according to the chemical composition of the polymer. These results will, therefore, only lead to a reliable molecular-weight distribution if there is convincing evidence for the chemical uniformity of the single fractions. This can be achieved by elemental analysis, spectroscopy, or pyrolysis gas chromatography. By changing the solvent,

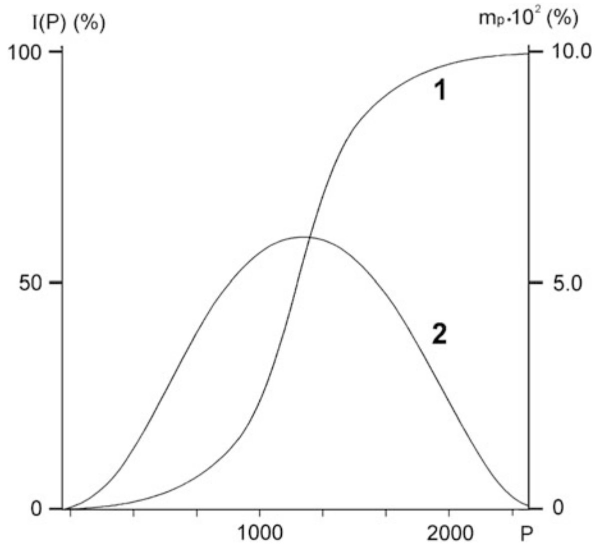


Fig. 2.17 Integral (1) and differential (2) mass distribution function of a polystyrene sample

precipitant, or eluent, it is sometimes possible to choose between fractionation according to molecular size and fractionation according to chemical composition.

2.3.4 Determination of size distribution of Polymers Dynamic Light Scattering (DLS)

Dynamic Light Scattering (DLS) is a fast method for the determination of size distributions of polymers in solution. A clear distinction must be drawn between DLS and static light scattering, discussed in Sect. 2.3.3.2.4, which is an absolute method for the determination of $\overline{M}_w$. Instead of angle dependent light scattering intensity (R_ϑ), *fluctuation* of light scattering intensity (I) of a polymer in solution is observed over a certain period of time by the DLS-method.

Brownian motion causes dispersed macromolecules to diffuse in and out of a certain volume of the solution. Hence, the number of scattering centres and therefore the light scattering intensity changes permanently, which can be observed in a short time scale. In case of small molecules, intensity fluctuations of scattered light are fast but low in their amplitude and for large molecules vice versa. Figure 2.18 shows the observable measurement signal for two different sizes.

If the obtained intensity curve is correlated with itself by a small time shift (τ), curves for larger molecules resemble themselves over a longer period as small molecules. Plotting the similarity versus applied time shift results in an exponential decaying curve. This curve is called the correlogram (chart 1) and can be fitted by the autocorrelation function (1). This equation depends on the translational

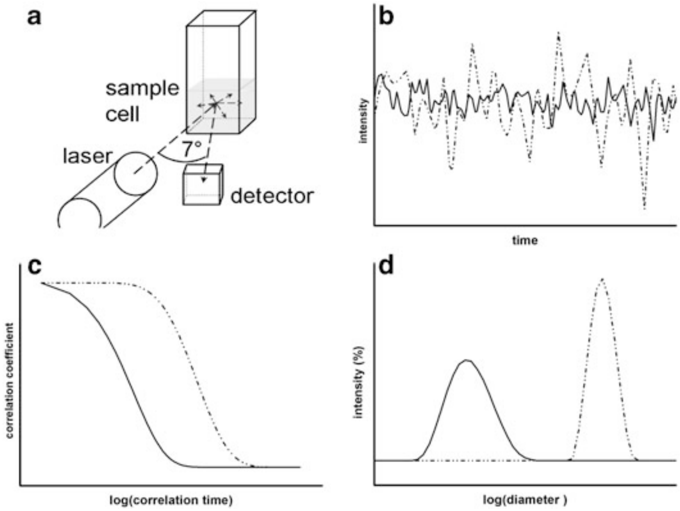


Fig. 2.18 Schematic drawing for the progress of a DLS measurement: (**a**) Setup of a DLS-apparatus in backscattering mode. (**b**) Typical intensity fluctuation for a large (▪▪▬▪▪) and a small (—) molecule. (**c**) Correlogram for a large (▪▪▬▪▪) and a small (—) molecule. As can be seen, correlograms for small molecules decay more rapidly. (**d**) Obtained size distributions by intensity for a large (▪▪▬▪▪) and a small (—) molecule

diffusion coefficient (D), which is easy to understand regarding the explanation given above. Other parameters, which affect the autocorrelation function are: the wavelength of the laser λ_0, the scattering angle θ and the refractive index of the dispersant $\tilde{n}$:

$$G(t) = \int_0^\infty I(t)I(t+\tau)dt = B + Ae^{-2\frac{4\pi\tilde{n}}{\lambda_0}\sin\left(\frac{\theta}{2}\right)D\tau} \tag{2.67}$$

By knowledge of the measurement temperature (T) and the system viscosity (η), the averaged size of observed molecules can be calculated via the Stokes-Einstein equation (Eq. 2.68):

$$d_h = \frac{kT}{3\pi\eta D} \tag{2.68}$$

It should be noted that it is the *hydrodynamic* diameter (d_h), which is determined by DLS. d_h represents a sphere consisting of the dispersed macromolecule as well as surrounding molecules, which have the same value of D as the macromolecule. Particularly the solvent shell and polar interactions with ions should be considered. Moreover, aggregation of macromolecules may occur, which lead to bigger spheres.

A further parameter, which is of relevance beside d_h, is the width of size distribution. This parameter, referenced as polydispersity index (PDI), is calculated from the deviation between the autocorrelation function and values actually measured. For narrowly dispersed samples PDI is below 0.1. PDI values above 0.3 point at widely size dispersed samples, which should be fitted by a more complex model. Several algorithms have been developed, which all base on a sum of autocorrelation functions. As each autocorrelation function results in one Gaussian distribution, the obtained size distribution turns out to be a sum of optionally superimposed curves. Thus, these complex algorithms reproduce reality better but are also more affected by measurement errors.

Special attention should be given to the measurement parameter I. So, the resulting distribution received from DLS measurement is an intensity distribution. In fact, number distributions are more interestingly. Though, for small molecules ($d_h \leq \lambda/10$), Rayleigh scattering theory is applicable involving $R_\vartheta \propto {d_h}^6$! Hence, DLS is much more sensitive to larger molecules or aggregates entailing the calculation of number distributions is strongly affected by small measurement errors in the region of small values of D. Thus, DLS results should always be created from a couple of measurements regarding carefully their standard deviation. In addition samples have to be prepared accurately as it is described for static light scattering in Sect. 2.3.3.2.4.

2.3.5 Polymer Characterization in Bulk

2.3.5.1 Determination of Density

The densities of polymers can be determined by the pyknometer technique or by the flotation method. In the pyknometer technique the liquid volume displaced by the polymer sample is determined by weighing. Most polymers have a density larger than that of water, which can, therefore, be used as the liquid. Polymers in the form of powders or pressed discs tend to adsorb or occlude air bubbles, which can lead to serious errors. This can be largely prevented by careful degassing of the pyknometer and polymer sample under vacuum before filling with liquid, and/or by addition of a small amount (0.1%) of commercial detergent to lower the surface tension of the water.

The flotation method is especially suitable for powdered polymers. A liquid of higher density is added to a liquid of lower density until the test particles neither sink nor rise to the surface. The densities of the solid and liquid mixture are then equal and it remains only to determine the density of the latter. The experiment is conducted as follows: The powdered polymer is placed in a small beaker with a certain amount of less dense liquid. The heavier liquid is then run in from a burette with gentle stirring until the state of suspension is attained.

The density of the liquid mixture can be determined using a pyknometer or it can be derived from a previously determined calibration curve. For the determination of densities less than unity (e.g., polyethylene), ethanol/water mixtures are suitable; for densities larger than unity one may use mixtures of water with aqueous salt solutions (40% $CaCl_2$ solution: $d_4^{20} = 1.40$ g/ml; 72% $ZnCl_2$ solution: $d_4^{20} = 1.95$ g/ml). The density gradient method, which is an elegant variation of the flotation method, should also be mentioned.

2.3.5.2 Determination of Crystallinity

The simplest way of establishing qualitatively the crystallinity of a polymer is by the observation of birefringence under a suitable microscope, taking care to exclude the possibility of orientation birefringence. Also thermotropic liquid crystalline polymers can show birefringence combined with relatively low viscosity. X-ray diffraction allows a quantitative determination of the degree of crystallinity as well as the usual crystallographic data.

In some cases crystalline polymers show additional absorption bands in the infrared spectrum, as in polyethylene ("crystalline" band at 730 cm^{-1}, "amorphous" band at 1300 cm^{-1}) and polystyrene (bands at 982, 1318, and 1368 cm^{-1}). By determining the intensity of these bands it is possible to follow in a simple way the changes of degree of crystallinity caused, for example, by heating or by changes in the conditions of preparation.

The degree of crystallinity is also reflected in the density of the polymer so that the determination of density provides at least a relative measure for crystallinity. Differential scanning calorimetry (DSC) is frequently applied to determine the crystallinity from the heat of crystallization or melting (see Sect. 2.3.5.8).

2.3.5.3 Glass Transition Temperature

Below a certain temperature any amorphous polymer behaves as a hard glass. When heated above this temperature individual segments of the macromolecules achieve larger mobility (micro-Brownian motion); as a result the polymer becomes soft and elastomeric. The temperature at which this change sets in is called the glass transition temperature T_g. This temperature is very important in technological applications and depends, amongst other things, on the chemical nature of the polymer, on the configuration, on the degree of crystallinity, on the length of the side chains, and on the degree of branching. The glass transition temperature is generally determined with specialized equipment and depends to some extent on the method used. One measures the temperature dependence of a particular physical quantity such as refractive index, elastic modulus (or torsional modulus), dielectric constant, heat capacity, expansion coefficient, or specific volume; all these change abruptly at the glass transition temperature. In amorphous polymers the glass transition temperature T_g frequently coincides with the softening point. In crystalline polymers, on the other hand, the crystallite melting point lies considerably above T_g. For crystalline polymers the glass transition temperature can be estimated rather well by rule of thumb (Boyer-Beaman rule): it is about two-thirds of the crystallite melting point, expressed in Kelvin.

The measurements of Young's modulus in dependence of the temperature (dynamic-mechanical measurements, see Sect. 2.3.6.2) and the differential thermal analysis (DTA or DSC) are the most frequently used methods for determination of

Table 2.10 T_g- and T_m-values of some polymers (Source: Polymer Handbook 3rd edition, 1989, Wiley & Sons, Inc., pp VI/393)

Polymer	T_g [°C]	T_m [°C]
cis-1,4-Polyisoprene	−73	–
Poly(*n*-butyl acrylate)	−55	–
Poly(ethyl acrylate)	−24	–
Poly(isobutyl acrylate)	−24	–
Poly(methyl acrylate)	6	–
Poly(*n*-butyl methacrylate)	20	–
Poly(vinyl acetate)	31	–
Poly(ethyl methacrylate)	65	–
Polystyrene	100	–
Poly(methyl methacrylate)	105	–
Polycarbonate	145	–
Poly(α-methylstyrene)	168	–
cis-1,4-Polybutadiene	−102	11[a]
trans-1,4-Polybutadiene	−93	83[a]
Polyoxymethylene	−83	183
Polyisobutylene	−73	44[a]
Poly(tertrafluoroethylene)	−33	332
Polyethylene	−21	142
Polypropylene	−13	188
Polyamide-6 (Nylon-6)	40	260
Polyamide-6,6 (Nylon-6,6)	50	280
Poly(ethylene terephthalate)	69	280
Poly(vinyl chloride)	81	273[a]
Polyacrylonitrile	105	320[a]

[a]A few percent crystallinity can be reached after special post-treatment, e.g., stretching or by influencing the chain structure

the glass transition temperature. In Table 2.10 are listed T_g and T_m values for several amorphous and crystalline polymers.

2.3.5.4 Softening Point

The softening point is generally determined by slowly heating a test piece under constant load until it experiences a certain deformation. The temperature at which this occurs is known as the softening point. Since the methods used involve empirical and arbitrarily chosen test parameters, the softening point is physically less well-defined than the glass transition temperature. In practice, the softening point is generally determined by one of three relatively simple methods.

The most widely used method is that of Vicat in which a blunt steel needle (area of point 1 mm^2) is applied vertically to the surface of a test piece (about 1 cm^2 and 3–4 mm thick) under a load of 49 N. The oven temperature is then raised at 50°C/h and the temperature determined at which the needle has sunk 1 mm into the test piece; this is taken as the softening point (Vicat temperature).

In the method of Martens a test rod is mounted upright in a support and the upper free end is put under a bending stress via a small weighted lever. The rod is slowly heated in an oven until a specified deflection is attained. The softening point determined in this way is called the Martens temperature.

Finally, in the English-speaking countries, there is another extensively used method in which a rod is supported at its two ends and a load is placed on the center; this is slowly heated in a liquid bath until a certain distortion is attained; the temperature at which this occurs is called the heat distortion temperature (HDT). These methods are applicable both to thermoplastics and to crosslinked polymers. Interconversion of the softening temperatures determined by the different techniques is not possible.

2.3.5.5 Crystallite Melting Point

The melting point of a low-molecular-weight compound is an important quantity, which, through determination of the mixed melting point with a reference sample, can serve for its identification. On the other hand, macromolecular substances seldom have a precise melting point, but melt instead over a certain temperature range that is influenced by various factors. The melting point or the melting range of a polymer can thus assist its characterization, but not its identification in the sense used for low-molecular-weight compounds.

Recognition of the melting range is relatively simple if the polymer is partly crystalline because the change of birefringence can then be observed using a hot-stage polarizing microscope. First, the approximate melting temperature of the polymer is determined on a Kofler hot-block. A small amount of polymeric substance is then melted on a microscope slide using the hot-block at a temperature somewhat above the melting range. A normal coverslip, heated to about the same temperature, is finally pressed onto the molten polymer with a cork, so that a thin homogeneous film is produced. The slide is now placed on the hot stage of a melting-point microscope at a temperature about 20°C below the melting point. The sample is observed under polarized light and slowly heated. The temperature range from the first noticeable change to the final disappearance of birefringence is noted. The mean value of the first and last readings may be taken as the crystallite melting point. Many polymers recrystallize on cooling so that duplicate measurements are possible. The temperature at which crystallization commences on cooling from the melt is called the *crystallization temperature*. It is not identical with the melting point of the crystallites but lies somewhat below it, on account of the hindered motion of the macromolecules in the molten state.

The determination of the melting range according to the method described can be upset by the fact that a noncrystalline polymer can also show birefringence if its macromolecules have been oriented by the action of external forces. For example, orientation can occur when the coverslip is pressed onto the molten polymer, or, if a film is used, during the preparation or cutting of the test piece. The disappearance of birefringence due to orientation does not then occur at the melting point of the sample. Such errors can be avoided by duplicate determinations on the same sample, since once the polymer has been melted it is unlikely to undergo any reorientation in the absence of external forces. Today's usual standard procedure to characterize the melting process of polymers is differential scanning calorimetry (DSC; see Sect. 2.3.5.8). From the thus obtained thermogram (see Fig. 2.19, for example), the melting temperature T_m corresponds to the temperature at the peak maximum. In addition, the heat of melting can be obtained through integration of the curve in reference to an imaginary baseline. Conducting the measurement by cooling the molten probe, one can observe and record the crystallization process.

For amorphous polymers the melting range depends, amongst other things, on the molecular weight distribution and the degree of branching. An effect of molecular weight is only observed in the oligomeric region, e.g., for poly(oxymethylene dimethyl ethers) or for oligoamides and oligoesters. This is similar to the usual increase in melting point with molecular size observed in a homologous series of low-molecular-weight compounds. The glass transition temperatures (T_g) and the melting points (T_m) of some selected polymers are listed in Table 2.10. Crosslinked polymers do not melt, but possess a softening range that generally lies in the vicinity of the decomposition temperature. There are also some uncrosslinked polymers that likewise have no melting point or range (e.g., polyacrylonitrile). They begin to decompose above a certain temperature.

2.3.5.6 Melt Viscosity (Melt Flow Index)

Polymer melts are in most cases viscoelastic, meaning the viscosity is dependent on measurement conditions, like frequency or shear rate. Most polymer melts show a viscosity plateau at low shear rates, called Newtonian plateau and the viscosity drops with increasing shear rate.

Two main types of rheometers are suitable for the determination of the viscosity of polymer melts: Rotational rheometers (working in rotation or oscillation mode, geometries used are Couette-geometry, cone and plate, or plate and plate) and capillary rheometers where a stamp is pressed with a certain velocity trough a capillary filled with the melt. Whereas rotational rheometers have a limited shear rate range and are suitable for rheological investigations characterizing structural changes, capillary rheometers and especially high pressure capillary rheometers give information about the processability of the polymer at high shear rates, as they apply in extrusion or injection molding.

Simplified versions of capillary rheometers are melt flow testers, which are especially suitable for laboratory use since they are relatively easy to handle and represent a fast measure. However, they only give information about the fluidity at a certain shear rate which however for chemists in most cases is enough to judge the material's fluidity. Using a melt flow tester the measure of fluidity is not expressed in terms of the melt viscosity but as the amount of material extruded in a given time (10 min). The amount of extrudate per unit of time is called the melt index or melt flow index i (MFI). It is also necessary to specify the temperature and the shearing stress or load. Thus $MFI/2$ (190 C) = 9.2 g/10 min means that at 190 C and 2 kg load, 9.2 g of polymer melt are extruded through a standard nozzle in 10 min. Today the expression melt flow index is often replaced by the melt flow rate (MFR)

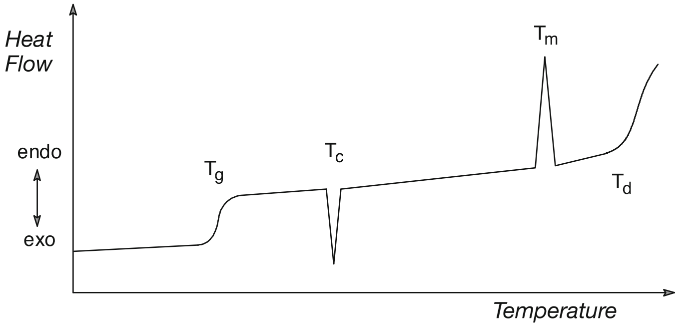


Fig. 2.19 Schematic DSC thermogram of a semicrystalline polymer: T_g = glass transition temperature; T_c = crystallization temperature; T_m = melting temperature; T_d = decomposition temperature

indicating the volume extruded under the above mentioned conditions (unit cm^3/10 min).

The melt flow tester consists of a heatable cylinder fitted with a standard nozzle at the lower end, the upper opening being closed by a piston that can be loaded with different weights. The cylinder is heated to the required temperature and then filled with powdered or granulated polymer; the piston is loaded with the desired weight. After a specified initial melting period (about 5 min) the piston catch is released so that the polymer melt is forced through the nozzle. At intervals of 1 min (longer for highly viscous melts) the extruded polymer is cut off at the nozzle and weighed. The time is measured with a stopwatch. The melt index is calculated from the mean of at least five measurements.

The frequency dependent viscosity of a polymer melt reflects even small changes in molecular weight or molecular weight distribution as well as branching and crosslinking or chemical variation, especially when using rotational rheometers in oscillation mode and regarding low frequencies/shear rates. Therefore, measuring of melt viscosity curve delivers not only valuable data for the selection of methods and conditions for the processing of thermoplastic polymers; moreover, it is an easy analytical tool for characterizing macromolecular substances. In this respect it is superior to the measurement of solution viscosity.

2.3.5.7 Thermogravimetry

Prior to any other bulk characterization of a polymer it is necessary to know more about its thermal stability under inert conditions (spontaneous chain degradation, carbonization, dehydration, etc.) as well as in the presence of oxygen (oxidation). Also, it might be of interest whether there is still monomer, solvent, or other volatile material present in the sample. The activity of stabilizers (against depolymerization or oxidation, for example) and the content of inorganic fillers and reinforcing fibers is, moreover, often required information. All these aspects can be studied by thermogravimetric analysis (TG or TGA). This technique monitors the weight loss of a sample in a chosen atmosphere as a function of temperature. The temperature program is in general a linear increase, but isothermal studies can be carried out as well.

The equipment required for TGA is a thermobalance. It is composed of a recording balance, a furnace, a temperature programer, a sample holder, an enclosure for establishing the required atmosphere, and a means of recording and displaying the data. Balance sensitivity is usually approx. one microgram, with a total capacity of a few hundred milligrams. A typical operating range for the furnace is ambient to 1000°C, heating rates are up to 100 $K \cdot min^{-1}$. The sample temperature is measured by a thermocouple close to the sample. Sample holder materials commonly available include aluminum, platinum, silica, and alumina. Many factors affect the TGA curve. The primary factors are heating rate and sample size. The particle size of the sample material, its morphology, and the gas flow rate can affect the progress of the thermal reaction.

Gas chromatography (GC) and mass spectrometry (MS) can be coupled to the TGA instrument for online identification of the evolved gases during heating: pyrolysis-GC/MS is a popular technique for the evaluation of the mechanism and the kinetics of thermal decomposition of polymers and rubbers. Moreover, it allows a reliable detection and (semi)quantitative analysis of volatile additives present in an unknown polymer sample.

2.3.5.8 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyzes thermal transitions occurring in polymer samples when they are cooled down or heated up under inert atmosphere. Melting and glass transition temperatures can be determined as well as the various transitions in liquid crystalline mesophases. In a typical DSC experiment, two pans are placed on a pair of identically positioned platforms connected to a furnace by a common heat flow path. One pan contains the polymer, the other one is empty (reference pan). Then the two pans are heated up at a specific rate (approx. 10 $K \cdot min^{-1}$). The computer guarantees that the two pans heat at exactly the same rate – despite the fact that one pan contains polymer and the other one is empty. Since the polymer sample is extra material, it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. A plot is created where the difference in heat flow between the sample and reference is plotted as a function of temperature. When there is no phase transition in the polymer, the plot parallels the x-axis, and the heat flow is given in units of heat, q, supplied per unit time, t:

$$\frac{q}{t} = heat\,flow \tag{2.69}$$

With the heating rate defined as rise of temperature, ΔT, per unit time, t

$$\frac{\Delta T}{t} = heating\ rate \tag{2.70}$$

the heat capacity, C_p, follows as:

$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = heat\ capacity \tag{2.71}$$

When the glass transition temperature of the polymer sample is reached in the DSC experiment, the plot will show an incline. It is obvious that the heat capacity increases at T_g, and therefore DSC can monitor the T_g of a polymer. Usually the middle of the incline is taken to be the T_g. Above T_g, the polymer chains are much more mobile and thus might move into a more ordered arrangement: they may assume crystalline or liquid-crystalline order. When polymers self-organize in that way, they give off heat which can be seen as an exothermal peak in the DSC plot. The temperature at the highest point is usually taken as the crystallization temperature, T_c. The area of the peak corresponds to the latent energy of crystallization. When the thus obtained (semi)crystalline polymer is heated further in the DSC pan, its melting temperature, T_m, can be reached. Here, either thermotropic liquid-crystalline phase might be formed or the material changes into its amorphous melt. The sample absorbs heat during melting, and thus an endothermal peak appears in the DSC plot. The heat of melting is obtained by measuring the peak area, and the temperature at the apex of the peak is taken to be the melting point. When all transitions are compiled in one single plot, an idealized DSC plot of a semicrystalline polymer is obtained (see Fig. 2.19).

Amorphous polymers will not show crystallization or melting peaks but a glass transition; liquid-crystalline polymers show some additional endotherms between T_m and isotropization. Semicrystalline polymers show also a defined exothermic recrystallization peak in a cooling cycle after reaching full isotropization (T_m). Because glass transition is associated with a change in heat capacity but no latent heat is involved with this process, the glass transition is called a second-order transition. Transitions like melting and crystallization, which do have latent heats, are called first-order transitions.

The observation and the exact position of T_g, and especially of T_c and T_m are strongly dependent on the thermal history of the sample. Therefore, often several DSC temperature cycles are carried out (maximum temperature must be clearly below decomposition temperature) with analyzing the thermal transitions usually in the second and not in the first run after a defined cooling cycle.

DSC measurements can be used, moreover, to determine how much of a polymer sample is crystalline. For that purpose, the area of the melting peak has to be measured: the DSC plot gives the heat flow per gram of material as a function of temperature. Heat flow is heat given off per second. So the area of the peak is given as:

$$peak\ area = \frac{heat\ \times\ temperature}{time\ \times\ mass} \left[\frac{J\ \cdot\ K}{s\ \cdot\ g}\right] \tag{2.72}$$

When the peak area is divided by the heating rate

$$\frac{peak\ area}{heating\ rate} \equiv \frac{\frac{J \cdot K}{s \cdot g}}{\frac{K}{s}} = \frac{J}{g} \tag{2.73}$$

and multiplied with the mass of the sample

$$\frac{J}{g} \cdot g = J \tag{2.74}$$

the total heat is obtained that is given off when the polymer melts. The same calculation can be done for the peak of crystallization, leading to the total heat evolved during the crystallization. With $H_{m,total}$ the total heat given off during melting and $H_{c,total}$ the heat of crystallization it follows that:

$$H_{m,total} - H_{c,total} = H' \tag{2.75}$$

H' is the heat given off by that part of the polymer sample which was already in the crystalline state before the polymer was heated above T_c. With this number H' it is possible to figure out the percent crystallinity: it is divided by the specific heat of melting, H_c*, which is the amount of heat given off by a certain amount of the polymer. So the mass of crystalline material, m_c, follows as:

$$\frac{H'}{H_C^*} = m_c \tag{2.76}$$

This is the total amount of grams of polymer that were crystalline below T_c. Now, if this number is divided by the weight of the sample, m_{total}, the fraction of the sample is obtained that was crystalline:

$$\frac{m_c}{m_{total}} = crystalline\ fraction \tag{2.77}$$

and

$$crystalline\ fraction \times 100 = \%crystallinity \tag{2.78}$$

Last but not least, DSC is a powerful technique for many other polymer-relevant aspects such as monitoring of curing reactions, detection of degradation, determination of heat capacity of chemical conversions, monitoring of initiator decomposition, etc.

2.3.5.9 Small- and Wide-Angle X-Ray Scattering (SAXS and WAXS)

Scattering of electromagnetic radiation can be used to obtain information about structures within materials having dimensions of the same order as the radiation wavelength. In X-ray scattering experiments, a sample is irradiated with X-rays, and the resulting scattering pattern is recorded, i.e., the intensity of the scattered radiation as a function of the scattering angle, θ. Then, the structure that caused the observed pattern is calculated. Scattering of X-rays is caused by differences in electron density.

Small-angle X-ray scattering (SAXS) is typically done at angles in the vicinity of the primary beam (extending to less than 2° for standard wavelengths). The scattering features at these angles correspond to structures ranging from tens to thousands of Ångstroms and are used to explore microstructure on the colloidal length scale as found, e.g., in phase-separated block copolymers. On the other hand – since the larger the diffraction angle, the smaller the length scale probed – wide-angle X-ray scattering (WAXS) is used to determine crystal structure on the atomic length scale. A typical WAXS pattern produced by a crystalline polymer looks as follows: The sharp peaks are caused by reflections from the various crystalline planes in the sample. They are observed at different angles according to Bragg's law:

$$2d\,\sin\theta = n\lambda \tag{2.79}$$

where θ is the spacing between crystalline planes, θ is the angle that those planes make with the incoming X-ray beam, l is the wavelength of the X-ray beam, and n is an integer. Since the crystalline parts of polymers are randomly oriented with respect to each other, the scattering is the same in all directions. So only a one-dimensional slice of the scattering pattern is needed to be sampled. However, only part of the polymer is crystalline, and the thickness of the crystalline lamellae is typically about 10–50 nm. For $d = 250$ Å, for example, the angle at which we observe the scattering caused by these lamellae is 0.17° for a fixed wavelength of 1.5 Å. This is an order of magnitude smaller than the angles at which the crystalline peaks are observed in the WAXS. Hence the structure of the lamellae has to be determined by SAXS, while the crystalline part is studied by WAXS: regular WAXS tends to focus on the location, width, shifts, etc. of Bragg peaks which arise from crystalline lattice structures. It is also a characteristic feature of WAXS patterns of semicrystalline polymers that the reflexes sit on the top of an amorphous halo. Upon graphic separation of the scattering intensities contributing to the sharp reflexes, A_c, and to the amorphous halo, A_a, respectively, it is possible to estimate the weight fraction of the crystalline phase, w_c:

$$w_c = \frac{A_c}{A_c + A_a} \tag{2.80}$$

For SAXS investigations, the primary experimental requirement is a well-collimated X-ray beam with a small cross-section. Synchrotron radiation sources with their intense brightness and natural collimation are ideal because most polymers are very poor scatterers. In most typical experiments, SAXS is performed in transmission mode. In this mode, polymer samples are typically 1–3 mm thick, offering about 63% absorption of the incident X-ray beam. In situations where transmission mode operation is not a feasible option, such as when the sample of interest is a thin film on an opaque substrate or when only the surface microstructure is of interest, one must use a combination of Grazing Incidence Diffraction geometry and SAXS, known as GISAXS. An extended sample-detector distance is usually required for SAXS to give the barely scattered photons room to spread out from the main beam, and also to reduce the detected X-ray background. A position-sensitive detector is required to measure the scattered intensity.

Interpreting SAXS data can be a very difficult task. At very small angles, the shape of the scattering in the so-called Guinier region can be used to give an idea of the radius of gyration of any distinct structures that are on this lengthscale. At higher angles, if a diluted system of relatively identical particles is considered, one might be able to see broad peaks that would also give information on the shape of the particles. In a system of strongly interacting particles, on the other hand, Bragg peaks may be observed which will obscure single-particle information but give structural information. At still higher angles, in the Porod region, the shape of the curve is useful in obtaining information on the surface-to-volume ratio of the scattering objects and on the dimensions of the scattering particles. This regime is also important for the analysis of regular structures shown by, for example, block copolymers.

2.3.5.10 Phase Contrast Microscopy

Phase contrast microscopy is a contrast-enhancing optical technique. It can be used to produce high-contrast images of transparent specimens such as lithographic patterns, fibers, multiphasic polymer samples, polymer morphologies, and latex dispersions. It is moreover useful for examination of surfaces, including integrated circuits, crystal dislocations, defects, and lithography.

In effect, the phase contrast technique employs an optical mechanism to translate minute variations in phase into corresponding changes in amplitude, which can be visualized as differences in image contrast. Light waves that are diffracted and shifted in phase by the specimen (termed a phase object) are transformed into amplitude differences that are observable in the eyepieces.

In a phase contrast microscope, an incident wavefront present in an illuminating beam of light becomes divided into two components upon passing through a phase specimen. The primary component is an undeviated (or undiffracted) planar wavefront, commonly referred to as the surround (S) wave. It passes through and around the specimen but does not interact with it. In addition, a deviated or diffracted spherical wavefront (D-wave) is also produced. It becomes scattered in many directions. After leaving the specimen plane, surround and diffracted light waves enter the objective front lens element and are focused at the intermediate image plane where they combine through interference to produce a resultant particle wave (often referred to as a P-wave). The mathematical relationship between the various light waves generated in phase contrast microscopy can be described simply as:

$$P = S + D \tag{2.81}$$

Detection of the specimen image depends on the relative intensity differences, and therefore on the amplitudes, of the particle and surround (P and S) waves. If the amplitudes of the particle and surround waves are significantly different in the intermediate image plane, then the specimen acquires a considerable amount of contrast and is easily visualized in the microscope eyepieces. Otherwise, the specimen remains transparent and appears as in an ordinary brightfield microscope.

Images produced by phase contrast microscopy are relatively simple to interpret when the specimen is thin and distributed evenly on the substrate. When thin specimens are examined using positive phase contrast optics, they appear darker than the surrounding medium when the refractive index of the specimen exceeds that of the medium. It should also be noted that numerous optical artifacts are present in all phase contrast images, and large extended specimens often present significant fluctuations in contrast and image intensity. Symmetry can also be an important factor in determining how both large and small specimens appear in the phase contrast microscope. Sensible interpretation of phase contrast images requires careful examination to ensure that artifacts are not incorrectly assigned to important structural features.

2.3.5.11 Polarization Microscopy

Polarized light microscopy provides all benefits of brightfield microscopy but offers a wealth of further information not available with any other optical technique. For example, it can distinguish between isotropic and anisotropic materials. This is because isotropic materials have the same optical properties in all directions, only one refractive index, and no restriction on the vibration direction of light passing through them. In anisotropic materials, in contrast, optical properties vary with the orientation of incident light with the crystallographic axes. They demonstrate a range of refractive indices, depending both on the propagation direction of light through the substance and on the vibrational plane coordinates. More importantly, anisotropic materials act as beam splitters and divide light rays into two parts. The technique of polarizing microscopy exploits the interference of the split light rays, as they are re-united along the same optical path, to extract information about these materials.

The wave model of light describes light waves vibrating at right angles to the direction of travel of light, with all vibration directions being equally probable. This is "common" light. It can be converted into plane-polarized light by passing through a polarizing filter. Here only light with one specific vibration plane passes through. There are two polarizing filters in a polarizing microscope – the polarizer and analyzer. The polarizer is situated below the specimen stage – usually with its permitted vibration direction fixed in the East–west direction. The analyzer, usually aligned North–south, is placed above the objectives and can be moved in and out of the light path. When both the analyzer and polarizer are in the optical path, their permitted vibration directions are positioned at right angles to each other. In this configuration, the polarizer and analyzer are said to be crossed, with no light passing through the system and a dark field of view present in the eyepieces. But if there is a birefringent material on the specimen stage, the plane of the polarized light passing through the polarizer is turned to a certain extent. Consequently, there arises some light having a polarization plane which again can pass through the analyzer. A (partially) bright and (potentially) colored picture of the sample can be seen in the field of view.

Polarization colors result from the interference of the two components of light split by the anisotropic specimen. The two components of light travel at different speeds through the specimen and have different refractive indices, or refringences. The faster beam emerges first from the specimen with an optical path difference (OPD). It may be regarded as a "winning margin" over the slower one. The analyzer recombines only components of the two beams traveling in the same direction and vibrating in the same plane. The polarizer ensures that the two beams have the same amplitude at the time of recombination for maximum contrast: there is constructive and destructive interference of light in the analyzer, depending on the OPD on the specimen and the wavelength of the light, which can be determined from the order of polarization color(s).

Superimposed on the polarization color information is an intensity component. As the specimen is rotated relative to the polarizers, the intensity of the polarization colors varies cyclically, from zero (extinction) up to a maximum after 45° and back down to zero after a 90° rotation. Whenever the specimen is in extinction, the permitted vibration directions of light passing through are parallel with those of either the polarizer or analyzer. This can be related to geometrical features of the specimen, such as fiber length, film extrusion direction, and crystal faces. In crossed polarizers, isotropic materials can be easily distinguished from anisotropic materials as they remain permanently in extinction (remain dark) when the stage is rotated through 360°.

Polarized light microscopy is thus used to study composites such as cements, ceramics, mineral fibers, and polymers, and crystalline or highly ordered biological molecules such as DNA, starch, and wood. The technique can be used both qualitatively and quantitatively and is an outstanding tool for materials science. During the solidification of polymer melts there may be some organization of the polymer chains, a process that is often dependent upon the annealing conditions. When nucleation occurs, the synthetic polymer chains often arrange themselves tangentially and the solidified regions grow radially. These can be seen in crossed polarized illumination as white regions with the black extinction crosses. When these spherulites impinge, their boundaries become polygonal. In other cases, polymers can undergo lyotropic or thermotropic liquid crystalline phase transitions, which can often be observed and recorded in a polarized light microscope.

In summary, polarizing microscopy provides a vast amount of information about the composition and three-dimensional structure of a variety of samples. The technique can reveal information about thermal history and the stresses and strains to which a specimen was subjected during formation. Polarizing microscopy is a relatively inexpensive and well accessible investigative and quality control tool.

2.3.5.12 Scanning Electron Microscopy (SEM)

In the scanning electron microscope (SEM), an image is formed by a very fine electron beam which is scanned across the surface of a sample in a series of lines and frames called a raster: at any given moment, the specimen is bombarded with electrons over a very small area. These electrons may be elastically reflected with no loss of energy (backscattered electrons), they may be absorbed and give rise to secondary electrons of very low energy (together with X-rays), they may be absorbed and give rise to the emission of visible light, and they may give rise to electric currents within the specimen. All these effects can be used to produce images. The contrast in the image is determined by the sample morphology. A high-resolution image can be obtained because of the small diameter of the primary electron beam.

For backscattered electrons, the contrast in the produced image is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are emitted from a depth in the sample, the resolution in the image is not as good as for secondary electrons. Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The emitted X-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis (energy dispersive X-ray spectroscopy or EDS). EDS can provide rapid qualitative or even quantitative analysis of elemental composition with a sampling depth of 1–2 μm. X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface.

By far the most common technique in SEM, however, is image formation by means of the low-energy secondary electrons. The primary electrons enter a surface with an energy of 0.5–30 keV, and generate many low-energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). The secondary electrons are selectively attracted to a grid held at a low (50 V) positive potential with respect to the specimen. Behind the grid is a disc held at about 10 kV positive with respect to the specimen. The disc consists of a layer of scintillant coated with a thin layer of aluminum. The secondary electrons pass through the grid and strike the disc, causing the emission of light from the scintillant. The light is led down a light pipe to a photomultiplier tube which converts the photons of light into a voltage. The strength of this voltage depends on the number of secondary electrons that are striking the disc. Thus, the secondary electrons produced from a small area of the specimen give rise to a voltage signal of a particular strength. The voltage is led out of the microscope column where it is processed and amplified to generate a point of brightness on a cathode ray tube (or television) screen. An image is built up simply by scanning the electron beam across the specimen in exact synchrony with the scan of the electron beam in the cathode ray tube.

The SEM does not contain objective, intermediate and projector lenses to magnify the image as in the optical microscope. Instead magnification results from the ratio of the area scanned on the specimen to the area of the television screen. Increasing the magnification in an SEM is therefore achieved quite simply by scanning the electron beam over a smaller area of the specimen. Scanning electron microscopy (SEM) is the best known and most widely-used of the surface analytical techniques. High-resolution images of surface topography, with excellent depth of field are produced using a highly-focused electron beam.

Samples suitable for SEM measurements include most solids which are stable under vacuum (metals, ceramics, polymers, minerals). Samples must be less than 2 cm in diameter. Non-conducting samples are usually coated with a thin layer of carbon or gold in order to prevent electrostatic charging.

2.3.5.13 Scanning Transmission Electron Microscopy (STEM)

In a scanning transmission electron microscope (STEM) the objective lens focuses the electron beam onto an atomic-scale sample volume. All scattered electrons can then be collected by a variety of detectors placed behind the specimen. An image is generated simply by moving the focused beam step by step over the specimen. Hence a STEM image may be considered as a collection of individual scattering experiments. Various types of signals discriminated in scattering angle and/or energy loss yield different structural and chemical information and may be captured simultaneously in different channels. This simultaneous and controlled acquisition of information lends itself to quantitative analyses that are difficult to realize with other instruments. In addition, as there is no limitation of the solid angle and the energy loss interval over which the scattered electrons may be collected, 60–100% of them contribute to the image. This provides a unique opportunity to image even beam-sensitive biomolecules at low dose.

Elastically scattered electrons are collected by an annular detector and provide the elastic dark-field signal. A spectrometer deflects those electrons that have lost energy at a larger angle than the unscattered electrons, thus facilitating the acquisition of the inelastic dark-field signal. The coherent bright-field signal arising from unscattered and low-angle elastically scattered electrons is collected through a small aperture placed on the optical axis. The various signals can be collected in parallel and processed online as the probe is scanned over the sample.

2.3.5.14 Transmission Electron Microscopy (TEM)

In transmission electron microscopy (TEM), a beam of highly focused and highly energetic electrons is directed toward a thin sample (<200 nm) which might be prepared from solution as thin film (often cast on water) or by cryocutting of a solid sample. The incident electrons interact with the atoms in the sample, producing characteristic radiation. Information is obtained from both deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons.

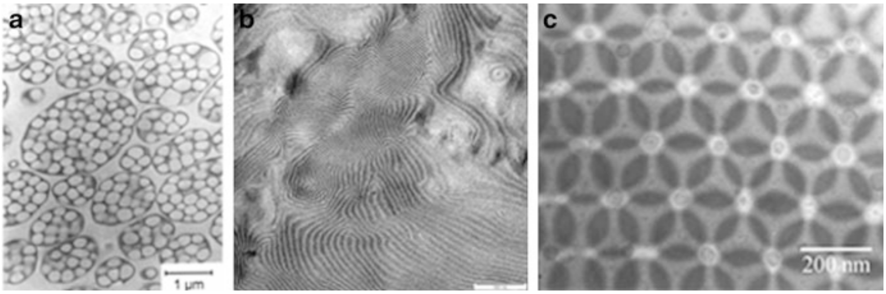


Fig. 2.20 TEM-pictures of multiphasic materials (**a**) Micromorphology of high impact polystyrene. White: Polystyrene, black: Polybutadiene (see Sect. 5.5.2.4). (**b**) Lamellar micromorphology of an AB diblock copolymer (see Sect. 3.4.2.1). (**c**) Quasi crystalline order of polystyrene particles in an "artificial opal"

Because the electron beam passes through the sample, transmission electron microscopy reveals the interior of the specimen. It is sensitive toward the internal structure of the material (size, shape, and distribution of phases within the material), its composition (distribution of elements, including segregation if present), and the crystalline structure of the phases and the character of crystal defects.

A typical electron microscope at an accelerating voltage of 75 kV works with electrons having a wavelength less than 5 pm. This makes the theoretical resolution about hundred thousand times better than that of light. Unfortunately, this theoretical resolution has never come even close to being attained. The basic drawback is that magnetic fields cannot be manipulated, shaped, and grouped the way it is possible with glass lenses: as a result, electron microscopes must use very small apertures which seriously attenuates the resolution, about 100 times. Nevertheless, excellent information can be achieved in polymer science, for example, for multiphasic polymer blends and composites (Fig. 2.20).

2.3.5.15 Scanning Probe Microscopy

Around 1980 a new method of microscopy known as scanning probe microscopy (SPM) was invented. Within the past 10 years, applications have been increasing exponentially in fields like surface physics and chemistry, biology and optics. SPM is also beginning to emerge as a useful and popular technique for R & D and quality control in several industries.

Probe microscopes are characterized by two common features. On the one hand, a sharp, tiny probe gets very close to the sample and feels the surface by monitoring some kind of interaction between the probe and the surface, which is very sensitive to distance. On the other hand, the sample is scanned in a raster fashion with near atomic accuracy, and the variation in the interaction is translated into a topographic map of the surface.

Among the family of SPMs the two most commonly used are Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). In STM, a sharp metallic probe and a conducting sample are brought together until their electronic wave functions overlap. By applying a potential bias between them, a tunneling current is produced. The probe is mounted on a piezoelectric drive that scans the surface. Combining the piezoelectric drive with a feedback loop allows imaging of the surface in either a constant current or a constant-height mode. In AFM, the probe tip is attached to a cantilever with a small spring constant. The probe is much like a spring which changes dimension upon experiencing a force and the interaction that will be monitored is the repulsion between two atoms when they are brought extremely close to each other. The forces acting on the probe tip deflect the cantilever and the tip displacement is proportional to the force between the surface and the tip. The resultant bending of the AFM cantilever is measured optically by the deflection of the reflected laser beam. The most important advantage that AFM has over STM is that the former is not limited to conducting samples, so materials can often be imaged "as is" with essentially no sample preparation as long as the surface roughness is not too high. While the technique of AFM is maturing, many AFM modes have appeared for special purposes. The most common techniques are contact mode, non-contact mode, and tapping mode.

In the *contact mode* the tip scans the sample in close contact with the surface. The force on the tip is repulsive with a mean value of 10^{-9} N. This force is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. In contact mode AFM the deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value, the feedback amplifier applies a voltage to the piezo to raise or lower the sample relative to the cantilever in order to restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface. It is displayed as a function of the lateral position of the sample.

Problems with contact mode are caused by excessive tracking forces applied by the probe to the sample. The effects can be reduced by minimizing tracking force of the probe on the sample. Moreover, under ambient conditions, sample surfaces are covered by a layer of adsorbed gases consisting primarily of water vapor and nitrogen which is 10–30 monolayers thick. When the probe touches this contaminant layer, a meniscus forms and the cantilever is pulled by surface tension toward the sample surface. The magnitude of the force depends on the details of the probe geometry, but is typically on the order of 100 nN. This meniscus force and other attractive forces may be neutralized by operating with the probe and part or the entire sample totally immersed in liquid.

An attempt to avoid these problems is the *non-contact mode*. This technique is used in situations where tip contact might alter the sample in subtle ways. In this mode the tip hovers 50–150 Ångstrom above the sample surface. Attractive Van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Unfortunately the attractive forces from the sample are substantially weaker than the forces used by contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Van der Waals forces which may extend only a nanometer from the sample surface. In general, the fluid contaminant layer is substantially thicker than the range of the Van der Waals force gradient and therefore, attempts to image the true surface with non-contact AFM fails as the oscillating probe becomes trapped in the fluid layer or hovers beyond the effective range of the forces it attempts to measure.

Tapping mode is a key advance in AFM. This potent technique allows high-resolution topographic imaging of sample surfaces that are easily damaged, loosely hold to their substrate, or difficult to image by other AFM techniques. Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces, and other difficulties that plague conventional AFM scanning methods by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever's resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude (typically greater than 20 nm) when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000–500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features.

In addition to these topographic measurements, AFM can also provide much more information. The AFM can also record the amount of force felt by the cantilever as the probe tip is brought close to – and even indented into – a sample surface and then pulled away. This technique can be used to measure the long-range attractive or repulsive forces between the probe tip and the sample surface, elucidating local chemical and mechanical properties like adhesion and elasticity, and even thickness of adsorbed molecular layers or bond rupture lengths. Phase images allow to distinguish between softer and harder domains on the sample surface.

Studies on fundamental interactions between surfaces extend across physics, chemistry, materials science, and a variety of other disciplines. With a force sensitivity on the order of a few pico-Newtons, AFMs are excellent tools for probing these fundamental force interactions. Force measurements in water revealed the benefits of AFM imaging in this environment due to the lower tip-sample forces. Some of the most interesting force measurements have also been performed with samples under liquids where the environment can be quickly changed to adjust the concentration of various chemical components. In liquids, electrostatic forces between dissolved ions and other charged groups play an important role in determining the forces sensed by an AFM cantilever.

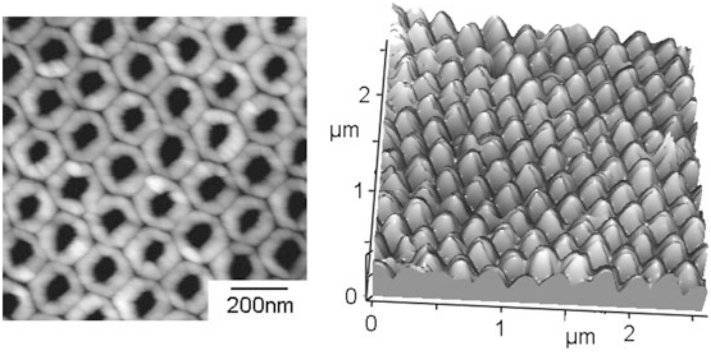


Fig. 2.21 AFM pictures of (*left*) a porous crystal made from a core-shell latex: the crystalline lattice of the SiO_2 appears *grey* while the nanopores are black; (*right*) surface of a dried core-shell latex

Insulators, organic materials, biological macromolecules, polymers, ceramics, and glasses are some of the many materials which can be imaged in different environments, such as liquids, vacuum, and low temperatures. The materials being investigated include thin and thick films, coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors (Fig. 2.21). AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, polishing, and any nano- and mesostructures in multiphase systems. By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-Newton scale.

2.3.6 Mechanical Measurements

The determination of the mechanical characteristics of a polymer serves ultimately to establish its usefulness and applicability as an industrial material. Although at first sight such measurements are of a purely applied character, some methods of investigation yield data that are not only useful for engineering practice, but also allow deductions about composition, structure, and state of aggregation of the polymeric material. Thus, they supplement the methods of characterization of polymers discussed in Sects. 2.3.1, 2.3.2, and 2.3.3. The following mechanical properties can, in this sense, serve for the physical characterization of a polymer in the solid state: strength and elongation, stiffness (modulus of elasticity), brittleness and toughness, and hardness. They are collected in Table 2.10 and discussed separately in Sects. 2.3.6.1, 2.3.6.2, 2.3.6.3, and 2.3.6.4.

For analytical purposes and an initial characterization, quick tests (duration minutes to few hours) are sufficient. However, the estimation of the usefulness as an industrial material needs long-term testing (months to years) in different environments (air, water, solvents, etc.). The numerous other tests employed in

Table 2.11 List of the most important mechanical properties for the characterization of a polymer

Property	Symbol	Units
Tensile strength (yield strength)	σ_B	N/mm^2
Tensile strength at break	σ_R	N/mm^2
Elongation at yield	ε_B	%
Elongation at break	ε_R	%
Modulus of elasticity or Young's modulus	E	$(J/m)/mm^2$ or N/mm^2
Impact strength	a_n	$N \cdot mm/mm^2 = N/mm$
Notched impact strength	a_k	$N \cdot mm/mm^2 = N/mm$
Ball hardness	H	N/mm^2

engineering practice to determine mechanical (and other) properties, as well as the special methods for testing rubbers, films, fibers, foams, coatings, and adhesives, will not be dealt with here.

The results of mechanical tests on polymers can obviously only be compared with one another when they are obtained at the same temperature, since the physical properties of polymers change markedly with temperature (see Sect. 1.4.3). Furthermore, the manner of preparation and pretreatment (conditioning) of the test specimen is decisive for the reliability and reproducibility of mechanical tests on polymers. For the determination of constants that are characteristic of the material, it should be as isotropic as possible, that is, exhibit the same characteristics in all directions, and therefore be free of internal stress; in addition, the temperature and humidity should be held constant for all measurements. While the latter conditions are relatively easy to fulfill, the preparation of completely stress-free and therefore isotropic test specimens is quite difficult to achieve for the reasons already given (see Sect. 1.4.3). Flow orientation in test specimens is especially liable to occur in thermoplastic materials (less so in thermosetting polymers), and in extreme cases can lead to values of tensile strength or impact strength that are two or three times as high when measured in the flow direction compared with those perpendicular to this direction. Possible ways of suppressing the anisotropy have been suggested in the literature. Test specimens can be fabricated either directly by injection or compression molding or casting (thermosetting plastics) in suitable forms, or by milling, sawing or punching of sheets of the polymer.

Because of reasons mentioned above the preparation, the dimensions, and the pretreatment of the test specimen have been standardized (DIN standard or ASTM standard). The important characteristic values of technical polymers are listed in databases (Campus, Polymat) (Table 2.11).

2.3.6.1 Stress–Strain Measurements

In a stretching experiment a test specimen is placed under tension, causing the length to increase and the cross-section to decrease, until finally it breaks. For these stress–strain measurements the test specimen has shoulders at both ends, such that the break occurs in the desired place, namely at the position of lowest cross-section.

The specimen is held at its broader parts in the clamps of the testing machine. The machine then pulls the clamps apart at constant speed, whereby a force is transmitted to the test specimen. The latter is plotted continuously against the change of length by means of a coupled recorder. The maximum tension P_{max} during the experiment is not always the same as the tension at break.

The prevailing tension divided by the smallest cross-section F_0 of the test specimen at the beginning of the experiment gives the corresponding stress σ, which is thus the tension per unit cross-section (1 mm^2). The ultimate tensile strength σ_B is obtained by dividing the maximum load P_{max} by the initial cross-section F_0 measured in N/mm^2 or MPa:

$$\sigma_B = \frac{P_{max}}{F_0} \tag{2.82}$$

The elongation e is generally understood to be the extension with respect to the original length. The elongation at yield is accordingly the extension, $\Delta l = l - l_0$, at maximum load P_{max} divided by the initial length l_0:

$$\varepsilon_B = \frac{\Delta l}{l_0} \cdot 100\,[\%] \tag{2.83}$$

From the values of the yield strength and the corresponding elongation one thus obtains a measure of the ultimate load that can be carried by the material. However, it is very much more informative for the characterization of a polymer to observe not just the values of yield strength σ_B and elongation at yield ε_B, but the whole stress–strain experiment shown graphically as a plot of stress s_B against ε (stress–strain diagram). The point in the stress–strain curve where deviation from linearity sets in is called the proportionality limit. This means that Hooke's law is no longer obeyed beyond this point. The position of the proportionality limit depends very much on temperature. Polymers may be divided into three main categories according to the shape of such a stress–strain diagram (see Fig. 2.22).

The first group comprises materials whose stress–strain curve is very steep and almost linear, and flattens only slightly near the break point (curve I in Fig. 2.22). Like metals, these materials deform only to a small extent at relatively high loads. Amongst these may be numbered all thermosets, some thermoplastics such as polystyrene and poly(methyl methacrylate) as well as high modulus/high strength fibers, i.e., substances that are only slightly elastic and rather brittle.

The second group exhibits the phenomenon of drawability. This manifests itself in the stress–strain behavior (curve II in Fig. 2.22) as follows: At first these materials behave in a similar way to those of curve I. The proportionality limit lies at low values, and the deformation with increasing load is also quite small. Then, suddenly, a large extension occurs, even though the load remains constant or becomes smaller. The material begins to flow and the stress–strain curve sometimes runs nearly parallel to the abscissa. The point at which the flow begins is called the

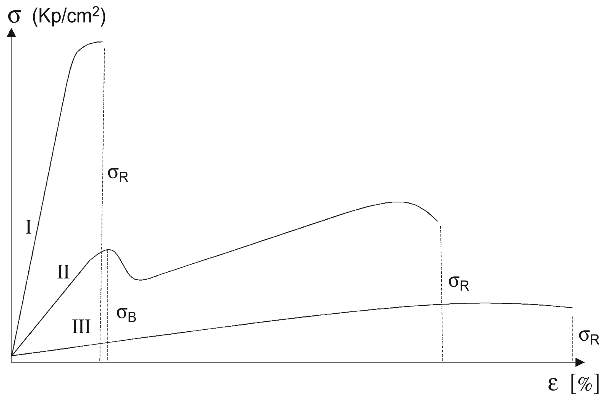


Fig. 2.22 Stress–strain diagram for various types of polymers (for explanation, see text): σ_B = yield strength; σ_R = tensile strength at break

upper yield point. The stress at this point is called the yield strength σ_B although the specimen has not broken. When all the macromolecules have been brought into a new (orientated) position by the flow process, the flow ceases and the stress increases again until finally the sample breaks. This phenomenon is used in the production of drawn fibers and films (see Sect. 2.4.2). The stress σ at this point is called the tensile strength at break σ_R, associated with the elongation at break ε_R. Many thermoplastics belong to this group, such as polyolefins, Nylon-6 and Nylon-6,6, and poly(ethylene terephthalate).

The third group comprises materials that show relatively large deformations even at low loads. In the stress–strain diagram (curve III in Fig. 2.22) there is no sudden drop in the stress, i.e., no flow limit. Furthermore, in the middle range the curve is not quite as flat as the curve for drawable materials (group II), i.e., the increase in strength resulting from reorientation of the macromolecules is a gradual one. A further increase in load leads eventually to failure. The stress at this point is called the tensile strength at break σ_R and the corresponding elongation at break ε_R. To this group belong all plasticized thermoplastics (e.g., soft PVC) as well as rubbers (elastomers).

Finally, the modulus of elasticity E (Young's modulus), which is a measure of the stiffness of the polymer, can be calculated from the stress–strain diagram. According to Hooke's law there is a linear relation between the stress σ and the strain ε:

$$\sigma = \varepsilon \cdot E \tag{2.84}$$

so that the elastic modulus is given simply by the slope of the stress/strain curve in the linear region, i.e., below the proportionality limit. Thus,

$$E = \frac{stress}{relative\ change\ of\ length}\left[\frac{N/mm^2}{mm/mm}\right] = \left[\frac{N}{mm^2}\right] = [MPa] \tag{2.85}$$

Hence, the elastic modulus corresponds in principle to the force per square millimeter that is necessary to extend a rod by its own length. Materials with low elastic modulus experience a large extension at quite low stress (e.g., rubber, $E \cong 1$ N/mm^2). On the other hand, materials with high elastic modulus (e.g., polyoxymethylene, $E \cong 3500$ N/mm^2) are only slightly deformed under stress. Different kinds of elastic modulus are distinguished according to the nature of the stress applied. For tension, compression, and bending, one speaks of the intrinsic elastic modulus (E modulus). For shear stress (torsion), a torsion modulus (G modulus) can be similarly defined, whose relationship to the E modulus is described in the literature.

In polymers the time dependence of an E modulus plays a more important role than in metals. If polymers are loaded with a constant stress they undergo a deformation ε, which increases with time. This process is named creep. Conversely, if a test specimen is elongated to a certain amount and kept under tension, the initial stress σ decreases with time. This decay is called stress relaxation. As a consequence of this time dependency of σ and ε it is important to state the conditions under which the elastic modulus was determined.

2.3.6.2 Dynamic-Mechanical Measurements

In dynamic-mechanical measurements the test specimen is not destroyed. The measurements are called dynamic because the mechanical properties are determined under oscillatory conditions. Of the numerous methods of measurement the oscillatory torsion experiment, using the so-called torsion pendulum, is one of the most widely used. In this test the specimen, having the form of a strip, is clamped firmly at the upper end, while an oscillating disc is fastened to the lower end. The turning motion of this disc can be followed optically and continuously recorded. A thermostatted chamber that can be heated or cooled surrounds the test specimen. After imparting an initial impulse to the torsion pendulum the decay of oscillation with time can be analyzed to yield two pieces of information. The vibration period allows the calculation of the torsion modulus (G modulus), which is a measure of the rigidity. From the decrease of amplitude with time one obtains a measure of the "internal mechanical absorption", called the mechanical loss factor δ (or logarithmic decrement). From such measurements it is possible to make valuable deductions about the molecular motions, not only about the motions of chain segments within a macromolecule (micro-Brownian motion), but also concerning the motions of the entire macromolecule relative to others (macro-Brownian motion).

Since these processes are strongly dependent on temperature, it is appropriate to carry out torsion-oscillation experiments over a wide range of temperature, and to plot the values for the modulus and d against temperature (see Fig. 2.23).

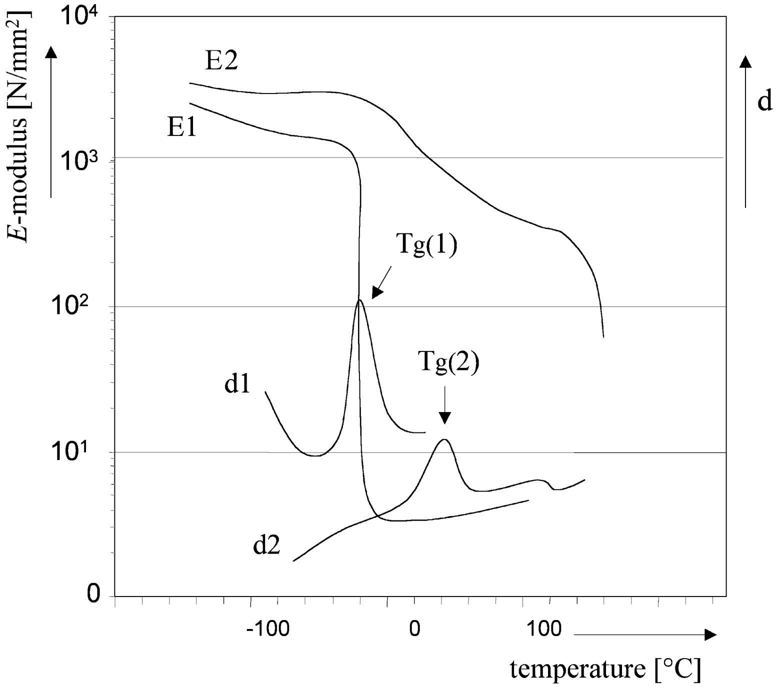


Fig. 2.23 Dependence of the elastic modulus E and the mechanical loss factor d on temperature for various polymers. Curves 1: elastomer (statistical copolymer of ethylene and propylene); curves 2: isotactic polypropylene (semicrystalline)

Besides temperature, frequency plays an important role, lying in the region from 1 to 1000 Hz; it is held constant during the measurement. An absorption maximum in the *d* curve corresponds to an inflection point in the modulus curve. Such diagrams are especially useful in determining the positions of softening point (glass transition temperature), melting point, melting range, and transition points, as well as indicating the influence of temperature on stiffness (*G* modulus or *E* modulus). If more absorption maxima occur, they are called α-, β-, γ-processes (the α-value being the absorption at the highest temperature).

The value of the modulus and the shape of the modulus curve allow deductions concerning not only the state of aggregation but also the structure of polymers. Thus, by means of torsion-oscillation measurements, one can determine the proportions of amorphous and crystalline regions, crosslinking and chemical non-uniformity, and can distinguish *random* copolymers from *block* copolymers. This procedure is also very suitable for the investigation of plasticized or filled polymers, as well as for the characterization of mixtures of different polymers (polymer blends).

Curve E1 in Fig. 2.22 corresponds to an elastomer (statistic copolymer from ethylene and propylene), characterized by a low value of the elastic modulus over a wide temperature range and a sudden increase at low temperature corresponding to the transition from the elastic to the brittle (glassy) state at the glass transition temperature $T_g(1)$ at $-50°C$.

In contrast, the curve E2 (isotactic polypropylene) is characteristic for partially crystalline polymers. The modulus is three decades higher than in an elastomer. At the glass transition temperature [$T_g(2) \sim 0°C$] the decay of the E modulus is small; it does not drop to the lower level of the molten state before the melting point.

The corresponding curves for the mechanical loss factor d show the following characteristics: The transition to the glassy state for elastomers is seen in curve 1 as a characteristic "mechanical absorption". On the other hand, two absorption maxima are visible in the curve for the partially crystalline polymer d2. The first one at 10°C indicates the glass transition, the second one at about 145°C is coherent with the crystalline melting point.

2.3.6.3 Impact Strength and Notched Impact Strength

Besides the test methods in which the load is applied over a relatively long period and the deformation rate is small (as in stress–strain and hardness measurements), there are other methods of interest in which the material is placed suddenly under high stress. Such measurements include that of impact strength, which gives an idea of the brittleness and toughness of the material. For this purpose, the test specimen is broken by means of a weighted pendulum, the energy of fracture ($N \cdot mm = mJ$) being measured. The impact strength is given by the fracture energy divided by the area of cross-section and has the units $N \cdot mm/mm^2 = mJ/mm^2$. The test specimens may be either smooth or notched rectangular bars; accordingly one speaks of (normal) impact strength (a_n) and of notched impact strength (a_k). The notched impact method is simply a variant of the normal impact test, the specimen being notched in a V-shape before the test. On impact the shear is thereby concentrated at a particular point on the test bar.

There are two principle methods for measuring impact and notched impact strength, which in practice differ only in the way in which the test bar is held. In the *Charpy method* the test piece is suspended at both ends and is struck in the center by a weighted pendulum. In the *Izod method* the test piece is clamped at one end only and is struck at the free end by the pendulum.

2.3.6.4 Hardness

Hardness is defined as the resistance that one body offers against penetration by another. Hence, to judge the hardness of a material one measures the force that is required to obtain a certain depth of penetration. This force or depth of penetration is dependent not only on temperature but also on many factors not characteristic of the material, such as the form of the penetrating body (ball or needle) and the time factor. Unfortunately, there is no universal hardness test and numerous methods are in use, many of which do not cover the entire range of possible hardness and can, therefore, not be used on all polymers. These methods can be divided into two groups: in one group the depth of penetration is measured after removal of the load (e.g., Brinell test); in the other the depth of penetration is measured under full load. The latter methods are the most suitable for thermoplastics, thermosets, and elastomers. A very popular method is the ball hardness test: a steel ball (diameter 5 mm) is pressed into the sample (4-mm-thick plate) with constant force and the depth of penetration measured after 10 s and after 60 s loading. Since the area of deformation must be taken into account, ball hardness has the dimensions N/mm^2. The hardness values measured with different methods cannot be interconverted because each of these gives different results. For example, according to the Brinell method a rubber is very hard, because the permanent deformation is measured. In contrast, the ball pressure method points out the soft character of the polymer because the permanent and elastic deformation is simultaneously measured.

The hardness of a polymer can also be estimated from the modulus of elasticity *E* (high *E* modulus indicates high hardness). The advantage here is that every region of elasticity and every degree of hardness can be detected with a single kind of measurement (determination of stress–strain-behavior or torsional oscillation).

2.4 Correlations of Structure and Morphology with the Properties of Polymers

It is one of the advantages of polymers versus low-molecular-weight compounds that their properties do not only depend on the chemical composition alone. Macromolecules can differ from each other also in molecular weight, molecular-weight distribution, branching, crosslinking, stereoregularity, etc. Each of these parameters has an influence on the properties in solution and in bulk. Nearly all properties are dependent on the molecular weight. Some values increase more or less steadily with growing chain length, e.g., solution viscosity, others increase very fast from oligomers to polymers and then reach a plateau, in particular, many mechanical properties.

It is important to mention that the structure/properties relationships which will be discussed in the following section are valid for many polymer classes and not only for one specific macromolecule. In addition, the properties of polymers are influenced by the morphology of the liquid or solid state. For example, they can be amorphous or crystalline and the crystalline shape can be varied. Multiphase compositions like block copolymers and polymer blends exhibit very often unusual meso- and nano-morphologies. But in contrast to the synthesis of a special chemical structure, the controlled modification of the morphology is mostly much more difficult and results and rules found with one polymer are often not transferable to a second polymer.

2.4.1 Structure/Properties Relationships in Homopolymers

2.4.1.1 Correlations with Solution Properties

The solubility of polymers is determined by the interactions between macromolecules and the molecules of the solvent. But the prediction of the solubility of a macromolecule and hence the correlation to its chemical (and morphological) structure is much more complicated than for a low-molecular-weight compound. Nevertheless, some general rules do exist:

- A decisive and general role is played by the molecular weight: the higher the molecular weight, the lower is the solubility of the polymer and the higher is the solution viscosity at given conditions.
- Amorphous polymers dissolve much easier than crystalline ones. The latter are often soluble at elevated temperatures only, i.e., near the crystallite melting point T_m.
- Polar groups in a macromolecule mostly enhance solubility.
- Short chain branches increase solubility.
- Macromolecules with polar and stiff main chains (e.g., cellulose, polyaramides) are often only soluble via complexation.
- Crosslinking reduces the solubility dramatically. Medium or highly crosslinked polymers do not dissolve at all but form more or less swollen gels, depending on the degree of crosslinking.

In a similar way, some general rules can be derived for the viscosity of polymer solutions:

- The solution viscosity increases strongly with the molecular weight.
- Branched polymers show lower solution viscosities than linear ones with the same molecular weight.
- The degree of stereoregularity is in general only of very small influence on the solution viscosity for polymers with the same molecular weight.
- The stiffness of the main chain of a polymer is of great importance for the solution viscosity: the stiffer the chain is, the higher is the viscosity for polymers with the same molecular weight (see Sect. 2.3.3.3.1 for the dependency of K and a in the viscosity equation on the shape of macromolecules in solution).

2.4.1.2 Correlation with Bulk Properties

Thermal Properties

The thermal properties of polymers include their behavior during heating from the solid amorphous (glassy) or crystalline to the liquid (molten) state, but also their chemical and mechanical stability in the entire range of application.

In industrial practice temperature stability of a polymer means that it is able to maintain its mechanical properties up to a certain temperature and over a certain time period. Depending on the environmental conditions under which the thermal stability is measured one further differentiates between two cases: physical thermostability if the thermal treatment occurs in inert atmosphere and chemical thermostability if the thermal treatment is done, e.g., in the presence of air (thermooxidative stability).

The prediction of the chemical thermostability is based on the rules established for the thermal stability and the reactivity of chemical bonds for low-molecular-weight compounds. Instead, the physical thermostability depends on the transition points of the macromolecules, i.e., the glass transition temperature T_g in case of amorphous polymers, and additionally the crystalline melting point T_m in case of crystalline polymers.

In designing polymers with high physical stability valuable information is obtained from the Gibbs equation:

$$T_m = \frac{\Delta H}{\Delta S}$$

This equation shows that a high melting temperature T_m is obtained by raising the melt enthalpy ΔH and/or a lowering of the melt entropy ΔS. Since T_m and T_g are related via the Boyer/Beaman rule (see Sect. 2.3.4.3), this equation is also valid for the glass transition temperature.

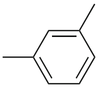
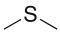
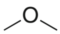
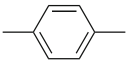
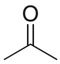
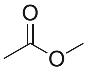
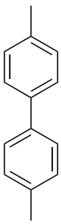
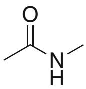
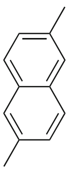
The glass transition temperature T_g increases in the beginning rapidly with the molecular weight and reaches a plateau at high molecular weights. According to Fox and Flory the relation between T_g and the number average molecular weight M_n is given by:

$$T_g = T_{g,\infty} - \frac{K}{M_n}$$

where $T_{g,\infty}$ is the glass transition temperature at very (infinitely) high M_n and K is a constant. But it should be taken into consideration that this proportionality between T_g and M_n is only valid for limited regions of M_n. Crosslinking, stereoregularity (sometimes combined with crystallinity) and chain stiffness in general result in an increase of the glass transition temperature, whereas T_g decreases with branching. Similar rules also hold for the dependencies of the crystallite melting point on the molecular weight, stereoregularity, chain stiffness and branching. Crosslinked polymers in most cases are amorphous and do not crystallize.

The crystallinity and the corresponding density and melting temperature of the crystalline domains of (semi)crystalline polymers depend also on the molecular weight. First, with growing molecular weight the degree of crystallinity increases to a maximum, with further growing the degree of crystallinity drops a little due to changes in the kinetics of crystallization with increasing melt viscosity and the participation of some of the polymer chains in the formation of different crystallites, which hinders the growth of the crystallites. Therefore the rate of crystallization of very high-molecular-weight chains is slower than that of chains with lower molecular weight. This is also the reason why the rate of the growth of spherulites of isotactic polystyrene decreases with increasing molecular weight.

Table 2.12 Selected building blocks for thermally stable polymers

Aromatic units	Temperature-stable bond	Polymer class	Increase of Stiffness of main chain
	 	Polyarylene ether etc. **ΔH** ↑	↓
	 	Aromatic polyesters and polyamides **ΔS** ↓	
		Heterocyclic and ladder polymers **ΔS** ↓	
			

To obtain polymers with high thermal and chemical stability and melting temperatures the following considerations are useful:

- A high melt enthalpy is obtained when the polymer is highly crystalline. The tendency to crystallize is improved when the molecules are linear with a regular chain structure and/or when high intermolecular forces exist. High intermolecular forces are caused through aromatic units, hydrogen bonds, and/or polar groups.
- A low melting entropy is experienced if the intramolecular motions of the polymer are hindered, for example, the free rotation of chain segments. This is preferentially be done by stiffening of the polymer chain. Table 2.12 shows a selection of building blocks for temperature-resistant polymers.

Another thermal property which is of great industrial importance is the melt viscosity, characterized, e.g., by the melt flow index, MFI, or the melt flow rate, MFR (see Sect. 2.3.5.6). The melt viscosity is first of all influenced by the molecular weight according to:

$$MFI \approx {M_w}^{0.75},$$

and by the molecular weight distribution. But branching and crosslinking as well as chemical modifications (e.g., introduction of polar groups) are also factors of influence. A different behavior is experienced with thermotropic liquid crystalline polymers (see Sect. 1.3.4).

Mechanical Properties

The mechanical properties of polymer materials are characterized by the relation between applied mechanical stress and resulting deformation and can be described by a constitutive equation, e.g., in the case of very low deformations by Hooke's law. In its simplest form it gives the deformation of a sample under mechanical stress in form of a stress–strain diagram (see Sect. 2.3.6.1). For such investigations the load is applied over a relatively long time period and besides the tensile modulus of the test specimen the ultimate tensile strength and elongation at which the sample breaks (elongation at break) can be obtained. These values are influenced by many factors like processing conditions (they can cause, e.g., orientation of the macromolecules and inner strain) or content of additives (plasticizers, processing aids, stabilizers).

But for pure homopolymers some general rules can be derived: The tensile strength increases with molecular weight, with crosslinking, and with degree of steric order and stiffness of the main chain, whereas branching results either in increase or dropping of the mechanical strength, depending on the type of branches (number of branches per chain, short or long chain branches, distance of the branch points).

If a polymer material is placed suddenly under high stress, the impact strength can be measured. It provides information on the brittleness or the toughness of a sample. Similar as the tensile strength, the impact strength of homopolymers increases with molecular weight, stereoregularity and stiffness of the main chain, whereas branching shows the same influence as described above for the tensile strength. Remarkable is the effect of crosslinking: Weak crosslinking leads to some increase of impact strength, with stronger crosslinking a reverse tendency is observed and the polymer becomes more and more brittle.

A measure of the stiffness of a polymer is the modulus of elasticity (Young's modulus) E. It can be calculated from the stress–strain curve as the slope in the linear region of Hooke's law. It should be considered that due to the definition $E = \sigma/\varepsilon$ for rubberlike materials which show a rather large extension ε at quite low stress σ, the elastic modulus is lower than in the case of materials which are only slightly deformed under stress. For homopolymers, in general the modulus of elasticity increases with molecular weight, crosslinking, stereoregularity, and

Table 2.13 Correlations of structure with the properties of homopolymers

	Constitutional parameter					
			Crosslinking			
Property	M_w (increasing)	Branching	weak	strong	Stereo-regularity	Stiffness
Solubility	↓↓	↑	↓	↓↓	↓	↓
$\eta_{solution}$	↑	↓	↑	↑↑	→	↑
T_g	↗	↓	↑	↑	↑	↑↑
T_m	↗	↓	→	→	↑	↑
η_{melt}	↑↑	↓	↑	↑↑	→	↑
Tensile Strength	↑	↓↑	↑	↑↑	↑	↑↑
Impact Strength	↑	↓↑	↑	↓	↑	↑
Stiffness	↑	↓	↑	↑↑	↑	↑↑
Hardness	↑	↓	↑	↑↑	↑	↑

stiffness of the main chain, whereas like for tensile and impact strength no simple influence of branching can be predicted.

Also to the mechanical properties belongs the resistance of a sample against the penetration of another material, what often is described as hardness. The result of the measurement of this property is not only of practical interest and characteristic of the material but also dependant on the temperature, the shape of the penetrating body (e.g., ball or needle) and the rate of penetration. But the hardness of a polymer can also be estimated from the elastic behavior as a high modulus of elasticity indicates high hardness. Therefore, the general correlations of hardness with molecular weight, branching, crosslinking, and chain rigidity are similar to that of the stiffness (see above).

The general correlations of structure and properties of homopolymers are summarized in Table 2.13. Some experiments which demonstrate the influence of the molecular weight or the structure on selected properties of polymers are described in Examples 3.6 (degree of polymerization of polystyrene and solution viscosity), 3.15, 3.21, 3.31 (stereoregularity of polyisoprene resp. polystyrene), 4.7 and 5.11 (influence of crosslinking) or Sects. 4.1.1 and 4.1.2 (stiffness of the main chain of aliphatic and aromatic polyesters and polyamides).

2.4.2 Structure/Properties Relationships in Copolymers

Nearly all structure/properties relationships that were discussed for homopolymers are also valid for copolymers. Additional dependencies exist as a result of the composition and structure of the different types of copolymers.

2.4.2.1 Statistic Copolymers

In the case of statistic copolymers of two monomers (binary copolymers) the glass transition temperature steadily changes with the molar amounts of the two monomers. In many cases, a similar behavior is observed with some mechanical properties (tensile strength, impact strength, stiffness, and hardness) (see Chap. 1). Deviations can occur in copolymers, which contain only a few percent of one comonomer.

2.4.2.2 Alternating Copolymers

As discussed in Sect. 3.4 there are only few examples known of strongly alternating copolymers. They exhibit unusual properties: The radical polymerization of ethylene and tetrafluoroethylene leads to a crystalline material with a remarkable thermal, chemical, and light stability, although it contains 50 mol% ethylene units. Another example is the alternating copolymer of ethylene and norbornene obtained via metallocene-catalyzed polymerization. Whereas random copolymers of these monomers are amorphous thermoplasts, the alternating copolymer is crystalline. Moreover, the crystallites have dimensions below the wavelength of visible light, resulting in a crystalline but still highly transparent thermoplast. In none of these cases, however, general structure/properties relationships could be established, except one: The degree of alternation has to be 100%, because each diad of one monomer is a weak linkage in the polymer chain.

2.4.2.3 Block Copolymers

In general, block copolymers are heterogeneous (multiphase) polymer systems, because the different blocks from which they are built are incompatible with each other, as for example, in diene/styrene-block copolymers. This incompatibility, however, does not lead to a complete phase separation because the polystyrene segments can aggregate with each other to form hard domains that hold the polydiene segments together. As a result, block copolymers often combine the properties of the relevant homopolymers. This holds in particular for block copolymers of two monomers A and B.

The simplest dependency exists between composition and glass transition temperature: Independent from the ratio A/B one finds two values for T_g, one for the block from monomer A and one for the block of B. More complex are the dependencies with the mechanical properties. Here, parameters like the ratio A/B, number of blocks, block length, and alternation of the blocks play a decisive role. This is shown in Examples 3.47 and 3.48 with triblock copolymers of butadiene or isoprene with styrene. If the content of the diene blocks is around 20%, a stiff and elastic, transparent thermoplastic material is obtained. Instead, if the diene content is raised to about 70%, a highly elastic but still rather stiff thermoplastic elastomer is obtained. It has to be stressed that these properties can only be reached, when the polystyrene blocks are the terminal ones.

2.4.2.4 Graft Copolymers

Graft copolymers should in principle exhibit similar structure/properties relationships as block copolymers. The problem is that pure graft copolymers which are not accompanied by large amounts of homopolymers are – with few exceptions – very difficult to synthesize. This is the reason why reliable property data in relation to the structure of graft copolymers only in few cases are available, but these cannot be generalized.

2.4.3 Morphology/Properties Relationships

As already mentioned, the results and rules found in dependencies of properties with the morphology of polymeric materials are in most cases limited to special classes of polymers or even one polymer species only. Therefore, the intention of this subsection can only be to demonstrate the potential and the possibilities which exist to influence the properties of polymers by modification of their morphology. This will be done with relevant examples that are described in detail in Chaps. 3–6.

- By variation of the conditions of crystallization (see Sect. 1.3.3.3) polyethylene can be obtained either as folded lamellae, as extended chain crystals (high strength fiber), or as so-called shish kebabs (fibrils with a morphology similar to cellulose). All these variants differ in properties.
- Addition of small amounts of nucleating agents influence the spherulitic crystallization of polypropylene and improve transparency (Sect. 1.3.3.3 and Example 3.20).
- Under special conditions, stiff macromolecules (rigid rods) are able to self-organize and to form highly ordered domains in solution (polyaramides, Sect. 4.1.2 and Example 4.13) or in the melt (aromatic polyesters, Sect. 4.1.1 and Examples 4.5 and 4.6), which show liquid crystalline behavior. Hence, they can be further oriented in flow direction through external forces (see Sect. 1.3.4). By proper processing, materials with extraordinarily high moduli and tensile strength are obtained. In block copolymers and in polymer blends interesting meso- and nano-morphologies of the dispersed phase are sometimes observed. Variations in structure of the polymers or in phase distribution can lead to changes in properties (Sects. 3.4.2.1 and 5.6 and Example 5.23). The properties of polymers processed out of aqueous dispersions are influenced by the particle size and the particle size distribution (Example 3.47).

2.5 Processing of Polymers

Processing of a polymer can be performed with the polymer in various states of aggregation: in solution, in dispersion, and in the melt. The method chosen will depend on whether the polymer melts without decomposition and whether it is soluble. However, the nature of the application is also decisive. In practice a molded object can be prepared from a thermoplastic only via the melt, while for textile coatings the only feasible method is to process from solution or dispersion. But processing of polymers is not only of industrial interest. A previous processing step is also necessary for many physical and chemical investigations, which only can be done with a well-defined test specimen. Although suitable equipment is available for injection molding and extrusion on the laboratory scale which require amounts of substances in the range of 5–1000 g, the following simpler methods suffice for preliminary investigations.

2.5.1 Size Reduction of Polymer Particles

In many cases polymers are not obtained in a suitable finely divided form during preparation or recovery. It then becomes necessary to reduce the size of the particles before carrying out the processing test or the investigation. Conventional grinding in a mortar is usually ineffective because of the toughness of many polymers, unless the sample is first made brittle by cooling to low temperature with liquid nitrogen. During grinding, the polymer frequently acquires an electrical charge. Moistening the sample with a little ether can prevent this. Grinding can also be done in suitable mills. However, the generation of heat may cause low-melting polymers to begin to flow, leading to the formation of lumps. This can be avoided by the addition of small pieces of dry ice. Especially suitable are cooled analytical mills that have the additional advantage of a small milling volume.

In some cases, a combination of spray precipitation (see Sect. 2.2.5.6) and freeze-drying is recommended. For example, one can spray the polymer solution into a mortar, the bottom of which is covered with pieces of solid carbon dioxide the size of a hazel nut. The pieces are then ground more finely, the mortar placed in a desiccator and evacuated with an oil pump. The polymer solution can also be sprayed into a liquid cooled to low temperature, the liquid being immiscible with the solvent of the polymer, e.g., spraying an aqueous solution into cold ether. The polymer then precipitates in the form of a light flaky snow; decantation of the ether is followed by evacuation as described above.

2.5.2 Melt Processing of Polymers

The processing of polymers in the melt is the method most extensively used in technology. It is an essential requirement that the product does not undergo any significant degradation at the high processing temperature and under shear. The processing temperature must generally be considerably higher than the softening or melting temperature in order to reduce the high viscosity of the polymer melt. In this processing technique the polymer is heated above its melting or softening point, the viscous melt is brought into the desired form by mechanical forces and the formed object is finally cooled. This procedure is very widely applicable and allows the preparation of objects in practically any size or shape, for example, of molded bodies (by pressing, injection molding, or extrusion), of films and sheets (by extrusion and calendering), and of fibers (by extrusion or melt spinning).

Polymers that are difficult to process in the melt, either because the melt viscosity is too high or because they decompose, can often be processed at low temperatures through the addition of a plasticizer, leading to improved flow properties and lower processing temperature.

2.5.2.1 Preparation of Polymer Films from the Melt

Thin polymer films are very suitable for a number of physical investigations (microscopy, spectroscopy, mechanical measurements). They can be prepared in the laboratory as follows: A certain amount of finely powdered polymer is spread on a thin (0.1 mm) aluminum foil (15 $\times$ 15 cm), which is then covered with a second foil and the entirety placed between the plates of a hydraulic press heated to the melting point of the polymer. After pressing for 30–60 s the foil sandwich is removed from the press, and cooled with water or between two metal plates. Finally, the two aluminum foils are pulled carefully away from the thin polymer film. If a certain film thickness is required a suitable template can be laid between the aluminum foils. Optimal conditions, in respect to amount of polymer, press temperature, pressure, and time, must be determined empirically in every case. If the film is opaque, the temperature was probably too low. If it is too thin or contains gas bubbles (decomposition) the temperature was too high. Finally, the rate of cooling can also affect the properties of the film. Sometimes the aluminum foils can only be removed from the polymer film with difficulty; rapid cooling (with water or in a freezer) or prior coating of the aluminum foils with silicone oil or with an aqueous dispersion of poly(tetrafluoroethylene) usually prevents sticking.

If a suitable press is not available, one may improvise as follows: The heating plates of two electric irons are first bored to accept a thermocouple and then connected in parallel to the power supply through a variable transformer. A calibration curve is determined for the temperature attained at different voltages. For the preparation of a film the finely powdered polymer is placed, as described above, between the two hot-plates, which are then pressed together horizontally in a suitable vice. In this arrangement the pressure cannot be measured, but with a little skill the optimum conditions can be found.

2.5.2.2 Preparation of Fibers by Melt-Spinning

The simplest method of melt-spinning is to melt the polymer in a test tube, dip a glass rod in the melt and pull it out slowly. The threads obtained in this manner are short and irregular so that they are not well suited for subsequent investigations.

Much better for melt spinning is the extrusion of a polymer melt through a defined die from which the filament can be drawn to a fiber by stretching, e.g. by using rollers with different velocities. In the simplest case, a very small die can be used and a fiber can be extruded or drawn from a small scale compounder or an extruder. Laboratory spinning devices consisting of a heatable piston with a stamp pressing out a filament through a small die adapted with a drawing unit just requires only a few grams of polymer.

2.5.3 Processing of Polymers from Solution

If suitable equipment for processing the polymer melt is not available, or if the polymer will not melt, or melts only with decomposition, the processing may be carried out from solution. This technique, however, is limited to the fabrication of films, membranes, fibers, coatings, and adhesives.

2.5.3.1 Preparation of Films from Solution

The simplest way of making films in the laboratory is to pour a highly viscous solution of the polymer onto a glass or metal plate and to allow the solvent to evaporate slowly. The polymer film is then carefully peeled off. The following points have to be considered: The solvent should not evaporate too quickly, otherwise the resulting film can wrinkle and tear. If necessary the experiment is carried out in an atmosphere of solvent (use a desiccator). On the other hand, the boiling point should not be too high; otherwise the last residues of solvent are difficult to remove. The concentration of the polymer should be such that the solution can still be poured, but does not run off the glass plate. An approximately 20% solution is usually about right, but the best conditions must be established by experiment. In order to obtain a film of uniform thickness the glass plate must be as level as possible and the polymer solution evenly distributed. This may be achieved most easily with the aid of a glass rod wrapped at both ends with some tape or twine. For more precise work, metal devices with adjustable layer thickness are preferable. When ready the film is lifted at one edge with the aid of a razor blade or small knife and then slowly peeled away from the glass plate. Films can also be made from aqueous polymer dispersions at room temperature if the glass transition temperature of the polymer is not too high.

In an analogous way porous films like asymmetric membranes can be prepared. For this purpose the polymer solution – normally with DMF as solvent – is coated on a glass plate and then the solvent is partially evaporated (for example, in a drying chamber at 80°C for a few minutes). The coated glass plate is cautiously immersed in water, whereby after about 1–5 min an optically opaque film which shows an internal pore structure, detaches from the glass plate. After the exchange of the organic solvent by water, the film is dried and can be used as a separating membrane for, e.g., the deionization of sea water. Appropriate polymers for such membranes are soluble aromatic polyamides, polysulfones, or cellulose derivatives. For an optically clear film, which contains no micropores, the procedure must be repeated with a smaller evaporation time.

2.5.3.2 Preparation of Fibers by Solution Spinning

There are two methods of spinning fibers from solution: dry spinning and wet spinning. In dry spinning the viscous polymer solution is forced through a jet (spinnerette) into a chamber filled with hot air (or hot nitrogen). The solvent is thereby evaporated leaving behind a ready-made thread. This spinning process cannot be conducted in a simple manner and is not readily carried out in the laboratory. On the other hand, wet spinning, in which the polymer solution is injected into a suitable precipitant, by which the polymer coagulates in the form of a thread, is readily conducted on a small scale. The quality of the thread depends very much on the precipitation conditions (precipitant, bath temperature) that must be determined experimentally in each case. The precipitant must be chosen so that complete coagulation does not occur too quickly. If necessary, a solvent/precipitant mixture can be used (e.g., polyacrylonitrile dissolved in DMF, precipitated in DMF/water mixture). For injecting the polymer solution into the precipitant bath, hypodermic syringes are very useful. They allow control of both the thread diameter and rate of spinning in a simple manner (see Example 3.11).

2.5.4 Processing of Aqueous Polymer Dispersions

Aqueous dispersions of polymers with a glass transition temperature near room temperature possess the property of irreversible film formation. If a poly(vinyl acetate) dispersion (solid content about 50 wt.%, see Example 3.4) is spread out in the form of a thin layer on a glass plate and the water is allowed to evaporate at room temperature, then the colloid particles agglomerate irreversibly and build a homogeneous film on the substrate, which cannot be redispersed in water. After removal from the glass plate the self-supporting film has good mechanical properties. The film formation and the properties of the film depend on the chemical composition (glass transition temperature) of the polymer, and also on the size of the colloid particles (see Example 3.48).

The technique of film formation from aqueous polymer dispersions is widely used in the field of paints ("dispersion paints", "latex-paints"), coatings, and adhesives. The equipment is simple: brush, scraper, rake, or roller.

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