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:

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

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
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 $w_i$ ($= n_i \cdot M_i$).

$$W_i = \frac{w_i}{\sum_{i=1}^{\infty} w_i}$$  \hspace{1cm} (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:
\[ M_n = \frac{\sum_{i=1}^{\infty} n_i M_i}{\sum_{i=1}^{\infty} n_i} \quad (2.17) \]

\( n_i \) 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 \( M_w \) \((w = \text{average weight})\) is defined as:

\[ M_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} n_i M_i^2}{\sum_{i=1}^{\infty} n_i M_i} \quad (2.18) \]

\( M_w \) 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:

\[ M_z = \frac{\sum_{i=1}^{\infty} z_i M_i}{\sum_{i=1}^{\infty} z_i} = \frac{\sum_{i=1}^{\infty} w_i M_i^2}{\sum_{i=1}^{\infty} w_i M_i} \quad (2.19) \]

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, \( M_\eta \):

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

The exponent \( a \) can be determined experimentally from the relation between the intrinsic viscosity, \([\eta]\), and the molecular weight, \( M \) (Mark-Houwink-Kuhn relation):
\[ [\eta] = K \cdot M^a \]  \hspace{1cm} (2.21)

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

\[ M_n \leq [\eta] \leq M_w \leq M_Z \]  \hspace{1cm} (2.22)

Identity is only given for monodisperse samples, i.e., polymers whose macromolecules have all the same molar mass. Moreover, \([\eta]\) 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:

\[ PDI = \frac{M_w}{M_n} \]  \hspace{1cm} (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, \(P_w\):

\[ P_w = \frac{\sum_{i=1}^{i=\infty} w_i P_i}{\sum_{i=1}^{i=\infty} w_i} \]  \hspace{1cm} (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 $M = M_i$:

$$J_w(M) = \sum_{M=M_i}^{M=M_0} w_i \cdot \Delta M$$  \hspace{1cm} (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 $\Delta M$ which are equal to the integer multiple of the molecular weight of the repeating unit, $M_0$, in the case of homopolymers:

$$J_w(M) = \int_{M_0}^{M_i} w(M) dM$$  \hspace{1cm} (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:

$$W = \int_{0}^{\infty} w(M) dM = 1$$  \hspace{1cm} (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 $M$:

$$w(M) = \frac{dJ_w(M)}{dM}$$  \hspace{1cm} (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 polymerization 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 polyoxymethylene) 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 $\Pi_{os}$. The value of $\Pi_{os}$ 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 $\Pi_{os}$ and the hydrostatic pressure generated by the diluted polymer solution

$$\Pi_{os} = \rho g \Delta h$$  \hspace{1cm} (2.29)

where $\rho$ is the density of the solvent and $g$ is the acceleration of gravity. Following van’t Hoff, it is

$$\Pi_{os} V = nRT$$  \hspace{1cm} (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:

$$\Pi_{os} = \frac{m}{V} \frac{RT}{M_n} = \frac{cRT}{M_n}$$  \hspace{1cm} (2.31)

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

$$\frac{\Pi_{os}}{c} = \frac{RT}{M_n} + A_2 \cdot c$$  \hspace{1cm} (2.32)

Thus, the osmotic pressure is first measured at different polymer concentrations, $\Pi_{os}/c$ 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 $\vartheta$ 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:

$$\frac{p_1}{p_{1,0}} = x_1 = 1 - x_2$$ \hspace{1cm} (2.33)

The relative decrease of the vapor pressure is:

$$\frac{\Delta p_1}{p_{1,0}} = 1 - \frac{p_1}{p_{1,0}} = x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$ \hspace{1cm} (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 $\Delta T^*$. 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 $\Delta T^*$ 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 $\Delta T$ is measured instead of $\Delta T^*$, and vapor pressure osmometry needs calibration despite the fact that it is – at least in principle – an absolute method). Introduction of the Clausius Clapeyron relation leads to:

$$\frac{\Delta T}{c} = K \cdot \frac{1}{M_n}$$ \hspace{1cm} (2.35)

with
$$K = \frac{\text{const.} \cdot RT^2}{L_1 \rho_s} \quad (2.36)$$

K being a constant which is usually determined experimentally during cell calibration. $L_1$ is the heat of evaporation of the solvent, $\rho_s$ 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 $c$:

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

Experimentally, $\Delta T$ is determined for approx. five different polymer concentrations. After several minutes, a constant temperature difference $\Delta T$ 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. $\Delta T$ 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 $c \rightarrow 0$. $M_n$ 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 $\mu$ which is proportional to the absolute value $E$ of the electric field vector of the light wave. The polarizability $\alpha$ 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 surroundings: 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, \( \frac{dn}{dc} \), of the dissolved substance in the solution. For much diluted solutions \((c \to 0)\), the scattering intensity caused by the dissolved molecules, \( R_\theta \), is given by:

\[
R_\theta = R_{\theta, \text{solution}} - R_{\theta, \text{solvent}} = \frac{I_\theta r^2}{I_0} = \frac{4\pi^2 n_0^2 f \cdot p \left( \frac{dn}{dc} \right)^2}{\lambda^4 N_L} \cdot c \cdot M
\]

or

\[
K_c \frac{R_\theta}{R_\theta} = \frac{1}{M_w}
\]

Here, \( I_0 \) is the intensity of the incident light, \( I_\theta \) the scattered light intensity at a scattering angle \( \theta \), \( r \) is the distance between sample and detector, \( n_0 \) is the refractive index of the solvent, \( f \) a depolarization factor (\( \approx 1 \)), \( p \) a polarization factor (\( \approx 1 \)), and \( \lambda \) is the wavelength of the light. \( K \) can be calculated for known values of \( \frac{dn}{dc} \), \( n \) and \( \lambda \). Hence, the molecular weight \( M \) of the dissolved material can be determined by measuring \( R_\theta \) 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:

\[
R_\theta = K \sum c_i M_i = K_c M_w
\]

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 \( \theta = 0^\circ \) and has a maximum at \( \theta = 180^\circ \).

This internal interference is described by the particle form factor, \( P_\theta \). It allows the direct calculation of the radius of gyration, \( \sqrt{\langle s^2 \rangle} \), of the macromolecules and thus provides information about their chain conformation:

\[
P(\theta)^{-1} = 1 + \frac{16\pi^2 n_0^2 \langle s^2 \rangle}{3\lambda^2} \sin^2 \frac{\theta}{2}
\]
Because all the above deductions are valid for infinite low polymer concentrations but practical measurements have to be carried out at finite values of $c_i$, 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:

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

(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, $Kc/R_\theta$ is plotted versus $\sin^2(\vartheta/2) + kc$ (with $k$ an arbitrary constant) and then simultaneously extrapolated to $c \to 0$ and $\vartheta \to 0$ (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) derivative. It shows clearly the different chain lengths as well as the patterns of the end groups.
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 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

![Mass Spectrum of a Side-Chain Substituted Poly(p-phenylene)](image)
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:

\[
K_r = F \frac{dx}{dt}
\]  
(2.43)

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

\[
D = \frac{RT}{F \cdot N_t}
\]  
(2.44)

the Svedberg equation of sedimentation is obtained:

\[
M_{s,D} = \frac{s \cdot RT}{D \cdot (1 - \frac{1}{C_1} \cdot \frac{V}{C_2})}
\]  
(2.45)

If (1) the diffusion coefficient \( D \) of the polymer in the used solvent, (2) the specific volume \( V \) of the dissolved polymer, and (3) the density of the solvent \( \rho_{solvent} \) 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 \( c \to 0 \) is called sedimentation constant \( s_0 \):

\[
\frac{1}{s} = \frac{1}{s_0} (1 + k_s c)
\]  
(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 \( D_0(c_0) \) (“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, \( \bar{M}_v \), and the number average, \( \bar{M}_n \), 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:

\[
M = \frac{dc/dx}{\omega^2 xc} \frac{RT}{(1/s_{0\text{,meniscus}})}
\]  

(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 \( c \to 0 \). 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:

\[
M_w = \frac{c_b - c_m}{\omega^2 (x_b^2 - x_m^2) + c_0} \frac{2RT}{(1/s_{0\text{,meniscus}})}
\]  

(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 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:

\[
\frac{c}{c_0} = \exp \left( -\frac{(x - x_0)^2}{2\sigma^2} \right) \tag{2.49}
\]

with

\[
\sigma^2 = \frac{RT}{Mv(\frac{dp}{dx})_x x_0^2 x_0^2} \tag{2.50}
\]

where \(x_0\) is the distance between the center of the Gauss curve and the rotor axis, and \((dp/dx)_{x0}\) 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 $\eta_{rel}$:

$$\frac{t}{t_0} = \eta_{rel} \quad (2.51)$$

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, $\eta_{sp}$, which is a dimensionless quantity:

$$\frac{t - t_0}{t_0} = \eta_{sp} \quad (2.52)$$

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 $\eta$ and $\eta_0$ are represented in a good approximation by the elution times $t$ and $t_0$. It follows that:

$$\frac{t - t_0}{t_0} = \eta_{sp} \approx \frac{\eta - \eta_0}{\eta_0} \quad (2.53)$$

If this value is divided by the concentration $c$ of the polymer in solution, one obtains the reduced specific viscosity, $\eta_{red}$:

$$\frac{\eta_{sp}}{c} = \eta_{red} \quad (2.54)$$

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
concentrations). Then, the limiting value (intrinsic viscosity, Staudinger index or limiting viscosity number) \([\eta]\) 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:

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

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

Since \(\eta_{sp}\) is dimensionless, \([\eta]\) 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:

\[
[\eta] = K \cdot M^a
\]  

\(M\) 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 concentrations.
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:

$$\log[\eta] = \log K + a \cdot \log M$$  \hspace{1cm} (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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>$K_m$ (10$^3$ ml/g)</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (atactic)</td>
<td>Toluene</td>
<td>25</td>
<td>7.5</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>28</td>
<td>108.0</td>
<td>0.479</td>
</tr>
<tr>
<td>Poly(α-methylstyrene)</td>
<td>Toluene</td>
<td>25</td>
<td>7.06</td>
<td>0.744</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>34.5</td>
<td>73.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>Cyclohexane</td>
<td>25</td>
<td>40.0</td>
<td>0.72</td>
</tr>
<tr>
<td>Polybutadiene (98% cis)</td>
<td>Toluene</td>
<td>30</td>
<td>30.5</td>
<td>0.725</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>Toluene</td>
<td>25</td>
<td>50.2</td>
<td>0.667</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>27</td>
<td>30.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>Acetone</td>
<td>25</td>
<td>21.4</td>
<td>0.68</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Water</td>
<td>25</td>
<td>20.0</td>
<td>0.76</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Acetone</td>
<td>25</td>
<td>5.5</td>
<td>0.73</td>
</tr>
<tr>
<td>Polycyanonitrile</td>
<td>DMF</td>
<td>20</td>
<td>17.7</td>
<td>0.78</td>
</tr>
<tr>
<td>Polycrylamide</td>
<td>Water</td>
<td>30</td>
<td>6.31</td>
<td>0.8</td>
</tr>
<tr>
<td>Poly(ethylene glycol terephthalate)</td>
<td>o-chlorophenol</td>
<td>25</td>
<td>17.0</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Tetrachloroethane</td>
<td>50</td>
<td>13.8</td>
<td>0.87</td>
</tr>
<tr>
<td>Polycarbonate from bisphenol A</td>
<td>Chloroform</td>
<td>25</td>
<td>12.0</td>
<td>0.82</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>o-chlorophenol</td>
<td>25</td>
<td>168.0</td>
<td>0.62</td>
</tr>
<tr>
<td>Poly(phenylene ether)</td>
<td>Toluene</td>
<td>25</td>
<td>28.5</td>
<td>0.68</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td>Toluene</td>
<td>25</td>
<td>18.7</td>
<td>0.66</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>Dichloromethane</td>
<td>20</td>
<td>24.7</td>
<td>0.704</td>
</tr>
</tbody>
</table>
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.
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 M1 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 M1 to mark M2 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 \( \eta_{sp}/c \) 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
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 $\eta_{\text{sp}}/c$ 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 weight.
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., $M_n$, $M_w$, $M_z$. 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. 10–10⁵ 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.

Fig. 2.16 Behavior of a polyelectrolyte in dilution viscometry 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.
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, $V_e$:

$$V_e = V_0 + V_i \quad (2.58)$$

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:

$$V_e = V_0 + K_d \cdot V_i \quad (2.59)$$

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 $V_i$ 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:

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

(2.60)

A universal calibration is therefore possible for SEC by plotting \( [\eta] \cdot M \) 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: simplistically, 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 \( \chi \) exceeds a critical value \( \chi_c \). The critical value of \( \chi_c \) decreases with increasing molecular weight of the polymer.