MOLECULAR WEIGHT DETERMINATION

Introduction

This article discusses the theory and methods for the determination of molecular weight averages and molecular weight distributions of oligomeric and polymeric materials. The more important methods are described in greater detail in separate articles (see CHROMATOGRAPHY, SIZE EXCLUSION; FRACTIONATION; CHARACTERIZATION OF POLYMERS).

Molecular Weight Averages and Distributions

Most polymeric materials are comprised of mixtures of molecules of various sizes. This distribution of molecular weights is a result of the statistical nature of the polymerization process (1). A complete description of the molecular weight distribution of a homopolymer is necessary to understand its physical, rheological, and mechanical properties. Structural variations, such as chain branching, and copolymer or higher mer polymers with various degrees of structural randomness further complicate a complete description of the molecular ensemble. Copolymers and higher mer polymers also need to be characterized for molecular composition as a function of molecular weight. Block copolymers and polymer mixtures also offer significant challenges to evaluate their molecular weight distribution. Failure mechanisms and practical lifetimes of polymeric materials may also be established through molecular weight measurements.

Most classical techniques for molecular weight determination are only capable of yielding one of the molecular weight averages of the distribution. These traditional methods are used nowadays only on a limited basis, and only a limited number of commercial instrumentation is available.

These averages are defined in terms of the molecular weight $M_i$ and the number of moles $n_i$ or the weight $w_i$ of the component molecules. The molecular weight averages are defined by equations 1-4.

Number-average molecular weight:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i/M_i}$$ (1)

Weight-average molecular weight:

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$ (2)

z-Average molecular weight:

$$\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}$$ (3)

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(z + 1)-Average molecular weight:

\[ \bar{M}_{z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3} = \frac{\sum w_i M_i^3}{\sum w_i M_i^2} \]  

(4)

Viscosity-average molecular weight:

\[ \bar{M}_v = \left[ \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a} = \left[ \frac{\sum w_i M_i^a}{\sum w_i} \right]^{1/a} \]  

(5)

Equation 5 is an important practical molecular weight average derived from viscometry. To calculate this average, the exponent \( a \) and the constant \( K \) of the Mark–Houwink relationship relating intrinsic viscosity \( [\eta] \) to molecular weight must be known.

\[ [\eta] = KM^a \]  

(6)

The value of \( a \) lies between 0.5 and 1.0 for random coils, depending on the solvent employed to determine the relationship of the intrinsic viscosity to molecular weight. For rigid rod molecules, the value of \( a \) is expected to be \( \sim 1.8 \). With these limits for \( a \), it may be seen that \( \bar{M}_v \) is always larger than \( \bar{M}_n \) but can equal \( \bar{M}_w \) when the upper limit of \( a \) is reached for random coils.

If molecular weight is considered a continuous variable, the molecular weight distribution may be described by a set of moments \( \mu_r \) given by the integrals

\[ \mu_r = \int_0^\infty M^r f(M) \, dM \]

where \( r = 0, 1, 2, 3, \) etc; \( f(M) \) is the number-density distribution; and \( f(M) \, dM \) is the number of moles of molecules with molecular weight between \( M \) and \( (M + dM) \).

The average molecular weights are defined as

\[ \bar{M}_n = \frac{\mu_1}{\mu_0} \]
\[ \bar{M}_w = \frac{\mu_2}{\mu_1} \]
\[ \bar{M}_z = \frac{\mu_3}{\mu_2} \]
\[ \bar{M}_{z+1} = \frac{\mu_4}{\mu_3} \]

Molecular weight averages can be determined from these moments (2).
Molecular Weight Distribution Functions

Various mathematical functions have been employed to describe the distribution of molecular weights. Some of the more common functions are shown in Table 1 in terms of the mole fraction $X$. Further details are available (3).

**Width of Molecular Weight Distributions.** The width of the Gaussian distribution function may be expressed in terms of the standard deviation of the mole fraction MWD function $\sigma_n$ or the mass fraction MWD function $\sigma_w$:

\[
\sigma_n = (\bar{M}_w \bar{M}_n - \bar{M}_n)^{0.5}
\]

\[
\sigma_w = (\bar{M}_z \bar{M}_w - \bar{M}_w)^{0.5}
\]

The standard deviation is an absolute measure of the width for the Gaussian function only. Widths of molecular weight distribution for other functions have to be calculated for each case from the distribution function itself.

The relationships between molecular weight averages and parameters in the molecular weight distribution functions are as follows: which leads to

\[
\exp(\sigma_w)^2 = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\bar{M}_z}{\bar{M}_w}
\]

Thus the ratios of two adjacent averages are constant.

**Poisson distribution function.**

The ratio of the weight-average to number average molecular weight is given by

\[
\frac{\bar{M}_w}{\bar{M}_n} = 1 + \left(1 - \frac{1}{\bar{M}_n}\right) - \left(1 - \frac{1}{\bar{M}_n}\right)^2
\]

### Table 1. Molecular Weight Distribution Functions

<table>
<thead>
<tr>
<th>Name</th>
<th>Function</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>$X(M) = \frac{1}{\sigma_n(2\pi)^{1/2}} \exp\left[\frac{(M - M_m)^2}{2\sigma_n^2}\right]$</td>
<td>$M_m$ = median value equal to $\bar{M}_n$</td>
</tr>
<tr>
<td>Log-normal</td>
<td>$X(M) = \frac{1}{\sigma_n(2\pi)^{1/2}} \exp\left[\frac{(\ln M - \ln M_m)^2}{2\sigma_n^2}\right]$</td>
<td>$M_m$ = geometric mean</td>
</tr>
<tr>
<td>Poisson$^a$</td>
<td>$X(M) = \frac{\nu^{M-1}}{\Gamma(M)} \exp(-\nu)$</td>
<td>$\nu = \bar{M}_n - 1$</td>
</tr>
<tr>
<td>Flory–Schulz$^b$</td>
<td>$X(M) = \frac{\beta^{k+1} M_k^{\beta+1} \bar{M}_n^k}{\Gamma(k+1)} \exp(-\beta M)$</td>
<td>$k = \text{degree of coupling}$</td>
</tr>
</tbody>
</table>

$a$ $\Gamma(M) = \gamma$-function.

$b$ $\Gamma(k + 1) = \gamma$-function.
Gaussian distribution function
mole-fraction distribution function median value $\bar{M}_n$
mass-fraction distribution function median value $\bar{M}_w$

Log-normal distribution function
mass-fraction distribution function median value $\bar{M}_m$

$$\bar{M}_n = M_m \exp\left(\frac{\sigma_w^2}{2}\right)$$
$$\bar{M}_w = M_m \exp\left(3\frac{\sigma_w^2}{2}\right)$$
$$\bar{M}_z = M_m \exp\left(5\frac{\sigma_w^2}{2}\right)$$

and therefore depends only on $\bar{M}_n$.

Flory–Schulz distribution function
The molecular weight averages this function are related by

$$\frac{\bar{M}_n}{k} = \frac{\bar{M}_w}{k+1} = \frac{\bar{M}_z}{k+2}$$

where $k$ is the coupling constant, defined as the number of independently growing chains required to form one dead chain.

Polydispersity
Traditionally, polydispersity $Q$ has been defined as

$$Q = \frac{\bar{M}_w}{\bar{M}_n} = U + 1$$

where $U$, the molecular inhomogeneity, has a numerical value of one less than $Q$. The width of molecular weight distributions increases with increasing $Q$ and $U$. Except for the Gaussian distribution function, the standard deviation is only a relative measure of distribution width (4,5).

Determinations of Molecular Weight

Several books have been published since this article was last written (6–9).

Number-Average Molecular Weight.

End-Group Analysis. In end-group analysis the concentration of an end group is measured by a suitable technique, and then, from the known structure of the polymer, the value for $\bar{M}_n$ may be calculated (10–15). In condensation polymers one end of the polymer should have a specific group that can be titrated by appropriate means. Polysterse (13), polyamides (13), and polyurethanes (16) have been subjected to this analysis. Polyethers have been analyzed by hydroxyl-group titrations similar to those used for polyesters or by reaction with excess phenyl isocyanate followed by reaction with excess di-n-butylamine; the latter was back-titrated with perchloric acid (17). Nonaqueous titrations (18) have been used to
characterize polysulfones with $\bar{M}_n$ values of up to 25,000. Potentiometric titration in aqueous and nonaqueous media have been used to determine molecular weights of acrylamide and acrylonitrile polymers (19). Spectrophotometric analyses have also been widely utilized (14), notably uv–visible, infrared techniques, and NMR (20). Examples include the determination of phenolic end groups in polymers by uv spectroscopy (21) and potentiometric titration (18). Infrared spectroscopy has been used (22) to estimate carboxyl groups in the presence of carbonyl groups by reaction of the former with SF$_4$; the resulting thionyl halides were quantitatively measured. NMR spectroscopy ($^1$H) has been used to characterize $\bar{M}_n$ of hydroxyl end-capped polystyrenes (A. D. Edwards and M. J. R. Loadman, Malaysian Rubber Producers Research Association, unpublished data, 1976). Reaction of the single proton on the hydroxyl group yields a trimethylsilyl group containing nine protons. The enhanced sensitivity allows determination of $\bar{M}_n$ values of up to 80,000. A similar method has been reported for hydroxy-terminated polybutadienes (23), polyester polyurethanes (24), epoxides (25), and other polymers (26–28). Acid end groups in polyethylene terephthalate have been characterized (29) by reaction with hexafluoroisopropanol and $^{19}$F NMR.

In certain cases extremely high sensitivity may be attained with radioactive labeling (30). Using radiolabeled ($^{35}$S) bisulfite initiator, the number-average molecular weight of Teflon samples was determined in the range of 389,000–8,900,000 (31). This is a particularly useful technique for insoluble polymers.

**Measurement of Colligative Properties.** Colligative properties are those that depend on the number of species present rather than on their kind (32,33). From thermodynamic arguments it may be shown that for very dilute ideal solutions

$$\ln a_1 = -X_2$$

where $a_1$ is the activity of the solvent and $X_2$ is the mole fraction of solute. From this relationship the solute molecular weight may be calculated if the weight fraction $w_2$ is known.

$$x_2 = \frac{n_2}{n_1} = \frac{w_2M_1}{M_2w_1}$$

This equation demonstrates that the activity, measurable by several methods, is proportional to the number of solute molecules. Thus in the case of polydisperse solutes, the number-average molecular weight is the average determined. At higher concentrations and molecular weights, the solutions become nonideal, and higher powers of the solute concentration are introduced into the equations. Measurements of several solute concentrations are required, and appropriate extrapolation techniques must be used.

**Lowering of Vapor Pressure.** The partial vapor pressure $p_1$ of solvent 1 over a solution is lower than the vapor pressure over the pure solvent $p_1^0$. This is expressed by Raoult’s law:

$$P_1 = X_1p_1^0$$
where \( X_1 \) is the mole fraction of the solvent.

For a binary solution containing a mole fraction \( X_2 \) of solute then,

\[
X_2 = \frac{p_1 - p_1^0}{p_1^0} = \frac{\Delta p_1}{p_1^0} \tag{7}
\]

For a dilute solution,

\[
X_2 = \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1} \tag{8}
\]

Combining equations 7 and 8 yields

\[
M_2 = \frac{w_2 M_1}{w_1} \frac{p_1^0}{\Delta p_1}
\]

The unknown molecular weight of solute \( M_2 \) may be calculated from the lowering of the vapor pressure caused by the addition of \( w_2 \) grams of solute to form a binary solution; \( \bar{M}_n \) values of up to 1000 may be determined (34–37).

A variation of this technique, the isopiestic method (38–40), was devised to avoid the difficulty of accurately determining the small difference in vapor pressure caused by the addition of solute. In this method (41) two limbs of a container joined by a common vapor space are filled, one with a reference solution of known weight concentration \( w_s \) and molecular weight \( M_s \) and the other with the unknown solution of known weight concentration \( w_2 \) and unknown molar concentration. The apparatus is immersed in a constant-temperature bath controlled to \( \pm 0.001 \) °C; the absolute temperature is not important. Distillation of the solvent continues until the vapor pressures above the solutions in each limb are equal, and thus the solutions contain equal mole fractions of solute. At equilibrium, which may require several weeks, the final volumes \( V_s \) and \( V_2 \) of the known and unknown solutions are read from the calibrations on each limb.

\[
\bar{M}_n = \frac{w_2 M_s V_s}{V_2 w_s}
\]

\( \bar{M}_n \) values of up to 20,000 have been determined by this method.

**Ebulliometry.**  
Ebulliometry (34,42–47) is another technique for determining the depression of the solvent activity by the solute. In this case the elevation of the boiling point is determined. The boiling-point elevation \( \Delta T_b \) is measured with sensitive thermocouples or matched thermistors in a Wheatstone bridge. The molecular weight \( \bar{M}_n \) is calculated from

\[
\bar{M}_n = \frac{K_b c}{\Delta T_b}
\]

where \( c \) is the concentration of solute in g/1000 g of solvent and

\[
K_b = \frac{RT_b^2 M}{1000 \Delta H_v} \tag{9}
\]
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Fig. 1. (a) Ebulliometer design for molecular weight determination of up to \( M_n = 100,000 \). A denotes ebulliometer cooler; B, boiler; C, Cottrell pump; D, adiabatic jacket cooler; M, thermopile; N, upper thermopile weldings; P, thermopile terminals connected with detector; Q, adiabatic jacket boiler; R, platinum resistance; T, lower thermopile weldings; and V, vacuum jacket circulated by solvent vapor. (b) Complete ebulliometer with adiabatic jackets and insulating apparatus (50). Courtesy of Huethig and Wepf Verlag.

is the molal ebullioscopic constant. \( M \) is the molecular weight of the solvent and \( T_b \) its boiling point; \( \Delta H_v \) is the molar latent heat of vaporization of the solvent.

The ebullioscopic constant may be evaluated directly from equation 9 and thus provides an absolute method. However, the value for \( K_b \) is often determined by using a high purity solute of known molecular weight.

Currently, a sensitivity of \( 1 \times 10^{-5} \)°C or \( 2.4 \times 10^{-6} \)°C is attainable using a 160-junction thermocouple (48) or thermistors (49), respectively. The upper limit of molecular weight, which may be determined by this method, also depends on the solvent and solution nonideality. With careful measurements and good ebulliometer design, \( M_n \) values of up to 100,000 may be determined on isotactic polypropylene (50). The apparatus employed is shown in Figure 1. This technique has been applied to aqueous solutions (51). An ebulliometer of simple design having a temperature sensitivity of \( 50 \times 10^{-6} \)°C has recently been reported (52). A rotating ebulliometer attempts to overcome the superheating problem (53). Errors in the methods for treating ebullioscopic data to obtain molecular weight have been discussed (54).

Cryoscopy. The freezing point of a solution is depressed below that of the pure solvent by an amount proportional to the mole fraction of solute. The value
for $\bar{M}_n$ is obtained from

$$\bar{M}_n = \frac{K_c c}{\Delta T_b}$$

where $c$ is the concentration of solute in g/1000 g of solvent and

$$K_f = \frac{RT_m^2 M}{1000 \Delta H_{fus}}$$

is the molal cryoscopic constant; $M$ is the molecular weight of the solvent and $T_m$ its melting point; $\Delta H_{fus}$ is the molar latent heat of fusion of the solvent.

Some materials, such as camphor, have very large cryoscopic constants and may be used to increase the sensitivity of the method. The method is used to determine $\bar{M}_n$ of polymers (55–59), such as polyesters (60) and ethylene-vinyl acetate copolymers (61).

A novel variation of this technique (62) involves depression of the first-order, nematic–isotropic melting transition of $N$-(p-ethoxybenzylidene)-p-n-butylaniline. Polystyrene and poly(ethylene oxide) are soluble in both phases, and $\bar{M}_n$ values of up to $10^6$ have been studied.

**Vapor-Pressure Osmometry.** When a drop of solution is exposed to pure solvent vapor, the solvent vapor condenses onto the droplet, because the solute lowers the vapor pressure of the drop (63–68). The heat of condensation causes the temperature of the drop to rise, until theoretically the solution vapor pressure is increased to equal that of the solvent. In practice this does not occur, but a state of equilibrium is reached, where the heat losses from the droplet are matched by the heat of condensation (GB/T 6579-86). The temperature increase is proportional to the number of moles of solute present. A standardized method is available (H. Knauer, Berlin, unpublished data).

The design of a commercial instrument is given in Figure 2 (H. Knauer, Berlin, unpublished data). The temperature stability needed is 0.001°C. In another design, by Wescan Instruments, Inc., small platinum mesh screens ensure that a constant amount of solvent or solution is present on the thermistor. The resistance value $\Delta R$, which is proportional to the temperature difference, is measured with a bridge circuit in all instruments. A calibration curve of $\Delta R$ vs molality $m$ is determined by employing a solute of known molecular weight. After several minutes $\Delta R$ reaches a constant value; the calibration curve is often highly linear, but may not go through the zero point (66).

$$\Delta R = a + bm$$

The number-average molecular weight of the unknown sample may then be calculated from equation 10:

$$\bar{M}_n = \frac{bc}{\Delta R - a} \quad (10)$$
where $c$ is the concentration of solute in g/1000 g of solvent. In older osmometers the calibration curve depended on the material used to perform the calibration. For the Wescan instrument and another research vapor-pressure osmometer (69), both based on the same design (70), the calibration constant was independent of the material. These instruments have determined polystyrene $M_n$ values of 400,000 (71), 100,000 (72), and 100,000 (69); polyolefins have been characterized at 140°C (73) and styrene/methylmethacrylate copolymers (32). For higher molecular weight solutes, the virial coefficients become important. In this case $\Delta R/c$ must be plotted against $c$ in order to extrapolate the $\Delta R/c$ value to infinite dilution. When the plot is not linear, it is necessary to plot $(\Delta R/c)^{1/2}$ vs $c$ to obtain a linear extrapolation to infinite dilution.

**Membrane Osmometry.** Membrane osmometry is a well-established technique (68,74–81). Commercial instrumentation is available (Gonotec GmbH, Knauer). A standardized method is available (GB/T 6596-86). The main problem is membrane permeation by lower molecular weight species (82). Improvements in membranes with well-defined, low molecular weight cutoffs can be expected as a consequence of the renewed interest in membrane-separation techniques (83,84) (see **Membrane Technology**). Membrane osmometry has been applied to a wide variety of polymers, including operation at high temperatures for polymers difficult to dissolve. Comb-like polymers have been characterized and the results compared with those from gel permeation chromatography (GPC) (85). Preliminary results of an online osmometer for GPC detection have been described (86,87). The upper limit for molecular weight determination is ca $1 \times 10^6$. The lower limit
depends on the molecular weight distribution, i.e., the details of the composition of the low molecular weight tail. In most cases the concentration dependence of osmotic pressure $\Pi$ must be determined and $\Pi/c$ extrapolated to zero concentration by plotting $\Pi/c$ vs $c$, or $(\Pi/c)^{1/2}$ vs $c$.

**Viscosity-Average Molecular Weight.** The viscosity of dilute polymer solutions may be related to the molecular weight of the polymer by the appropriate calibration (see Viscometry). The polymer is usually separated into narrow molecular weight distribution fractions, which are characterized by absolute molecular weight methods. The molecular weight is related to the intrinsic viscosity $[\eta]$ by the Mark–Houwink relationship (eq. 6).

The intrinsic viscosity is obtained using viscometer types of viscometer tubes and plotting the reduced or inherent viscosity of a series of polymer solutions with various concentrations against the solution concentration. Extrapolation to zero concentration yields the intrinsic viscosity. The technique has found widespread application (88–92), and compilations of Mark–Houwink constants are available (93). A novel method to determine intrinsic viscosity using a flow piezoelectric quartz crystal has been developed (94). Static and continuous measurements of intrinsic viscosity using a differential viscometer (Viscotek) have been reviewed (95). If the Mark–Houwink constants are determined using narrow molecular weight distribution materials, the average molecular weight obtained from equation 6 is the viscosity-average molecular weight $\bar{M}_v$. The range of molecular weights that may be characterized is very large. Special precautions are required for extremely high molecular weight samples to avoid degradation during the solution process or the measurement (96). Dilute solution viscometry for measurement of molecular weight, branching, and other physical parameters have been reviewed (97). A method to calculate the viscosity average molecular weight from GPC for a polymer with unknown Mark–Houwink constants has been reported (98).

**Weight-Average Molecular Weight.**

**Light Scattering.** Laser Light Scattering (qv) is a technique (99–106) widely used to characterize polymeric materials. Standardized methods are available (ASTD D4001 and GB/T 6598-86). Commercial instrumentation is available to measure the light-scattering properties of polymer solutions and the refractive index increment (107). Older instrumentation includes the Brice Phoenix Photometer, the Sofica Light Scattering Photometer, as well as the Chromatix product. Wyatt Technology and Malvern Instruments currently produce instruments. Lasers are used as light sources to measure scattering at small angles to the beam. This is important since the data obtained must be extrapolated to zero concentration and zero scattering angle using Zimm plots (108). The weight-average molecular weight is determined by this technique, and the molecular weights accessible range from a few hundred to several million. The solutions employed must be free of dust and are usually subjected to filtration or centrifugation. Solutions of high molecular weight degradable polymers are the most difficult to clarify. The solvent is selected to give a reasonable difference in refractive index with the solute. The technique has been applied to determine the molecular weight of difficultly soluble polymers such as polyethylene (109,110) and of polytetrafluoroethylene and its copolymers with ethylene (111–113). Copolymers with homogeneous distribution of monomer units in the polymer chain may be analyzed by the same methods as homopolymers. If the composition varies as a function of molecular weight, the analysis is more complicated (114). Terpolymers have also been considered (115).
True molecular weights and heterogeneity of styrene-butyl acrylate copolymers have been determined using static low angle laser light scattering (LALLS) and GPC/LALLS (116) and styrene–polydimethylsiloxane block copolymers (117) using GPC/LALLS. Multi-angle laser light scattering (MALLS) has been used as a GPC detector to characterize molecular weight, molecular size, and branching of organic and water soluble polymers (118).

Dynamic light scattering (119) has been used to determine the number average molecular weight (120) and molecular weight distribution of polymers in solution (121–123). There are several mathematical approaches to determine the molecular weight distribution from PCS data. Comparisons with GPC and numerical simulation have been made (124). The resolution of bimodal distributions has been demonstrated (125).

Pulse-induced critical scattering (126,127), although not utilized as a method for molecular weight characterization, may be a sensitive procedure for detecting small differences in molecular weight distribution.

X-ray (128) and neutron scattering (qv) (129,130) may also be used to determine weight-average molecular weights. The main drawback is the greater expense and the lack of suitable facilities.

Ultracentrifuge. The ultracentrifuge is used to determine molecular weights (131–133). Sedimentation velocity employs a sufficiently high centrifugal field so that the sedimentation rate may be measured. The sedimentation coefficient $S$ is empirically corrected for concentration and pressure effects to give $S_0$, the sedimentation coefficient at zero concentration. The method also requires the measurement of the diffusion coefficient at infinite dilution $D_0$. The molecular weight is calculated from the Svedberg equation

$$
\frac{S_0}{D_0} = \frac{M(1 - \nu \rho)}{RT}
$$

where $\nu$ is the partial specific volume of the solute and $\rho$ the density of the solution. For a polydisperse solute the correct averages for $S$ and $D$ are combined in the Svedberg equation to yield a well-defined average molecular weight. If $D$ is obtained from intensity-fluctuation spectroscopy (134) and combined with the weight average $S$ value, the weight-average molecular weight is obtained. The application of the sedimentation velocity method to calculate molecular weight distribution is extremely complex, but has been successful in special studies (135).

In the sedimentation equilibrium method, a lower centrifugal field is maintained for a period of time in such a way that sedimentation is balanced by diffusion and an equilibrium distribution of polymer is established in the cell. Although $M_w$ and $M_z$ are easily determined, the length of time of the experiment is a disadvantage. In contrast to light scattering, this method is not affected by dust particles, and no calibration is needed. The molecular weight distribution may be obtained from the sedimentation velocity data, but not without mathematical difficulties (136) or requiring additional data at other rotor speeds (137,138). An improved detection system for the analytical ultracentrifuge has been reported (139,140). A new 8-cell rotor that allows increased throughput of samples has been described (141).
Improved data analysis has led to the simultaneous determination of the sedimentation coefficient and diffusion coefficient, and a calculation of the molecular weight from the Svedberg equation (142). The Svedberg method is capable of determining molecular weights of up to $40 \times 10^6$ (96) on an absolute basis. Sedimentation equilibrium in a density gradient has been used to determine the compositional analysis of copolymers, e.g., butadiene-styrene (143).

Munk (144) has recently reviewed the use of sedimentation velocity and sedimentation equilibrium to characterize molecular weight. A new absolute method for the determination of molecular weight distribution based on band sedimentation and LALLS has been applied to water-soluble polymers (145).

**Higher Molecular Weight Averages.** Classical techniques often cannot be used for higher molecular weight averages ($\overline{M}_z, \overline{M}_{z+1}$, etc). These are usually measured by determining the molecular weight distribution by fractionation (qv) or affinity chromatography (qv) and back-calculating the averages from the distribution.

**Determination of Molecular Weight Distribution**

**Fractionation.** Polymers may be separated on the basis of molecular weight by precipitation or phase-separation techniques (146–149). The polymer that is originally in solution separates on the basis of molecular weight when the thermodynamic quality of the solvents is changed, i.e., by changing the solvent composition or temperature. The principal techniques are fractional precipitation and coacervate extraction, both solution-based (Fig. 3). The former is based on the removal of material from the polymer-rich precipitated phase and the latter on the removal of fractions from the polymer-lean solution phase. Computer simulations and experimental results have shown the coacervate extraction technique (150) to yield narrower molecular weight distribution fractions than the fractional precipitation method (151–153).

**Fig. 3.** Successive precipitation (SPF) and solution fractionation (SSF) (coacervate extraction): □, mother solution; □□□, polymer rich phase; and □□□□, polymer-lean phase. Numbers denote fraction numbers (148). Courtesy of Society of Chemical Industry.
To obtain the molecular weight distribution, the fractions of known mass must be characterized by a molecular weight technique. The integral and differential molecular weight distribution may be evaluated using a method (154) that assumes no particular molecular weight distribution function for the fraction or treatments that assume a particular model for the molecular weight distribution of the fractions (155). Fractionation may also be achieved by crystallization from dilute solution (156).

In column fractionation (157,158) the polymer is precipitated onto an inert support, which is placed at the top of a packed column (159). A solvent mixture of increasing solvent power is pumped through the column; a temperature gradient is often maintained. This is known as Baker–Williams fractionation (160). This technique is applicable to all amorphous homopolymers and crystalline homopolymers above the melting point. For copolymers and more complex compositions, the same technique may be employed, but the analysis is considerably more difficult.

Temperature rising elution fractionation (TREF) (161,162) is a useful fractionation technique which gives information on the compositional distribution.

**Chromatography.** The determination of molecular weight distribution and chemical composition by chromatographic techniques has been discussed (163).

**Gel Permeation (Size-Exclusion) Chromatography.** GPC has been in use since the 1960s and has been a most important development in molecular weight determination (164–169). For this technique the polymer must be soluble, and calibration with suitable standards is required. The method is extremely efficient; it requires 0.5–2 h per sample and only a few milligrams of material. Standardized methods are available (GB/T 6599-86, ASTM D5296-97, and A83 ASTM D6747-99). Commercial instrumentation capable of operating up to 150°C is available from Waters and Polymer Laboratories. Detection is normally accomplished by differential refractometry, although uv and ir (170) absorption spectrometry have also been employed. The chromatographic columns are packed with spherical-or irregular-shaped porous beads. The packing may be a crosslinked polymer, a porous glass, or a silica material. The pore size distribution determines the separation range of the columns. Calibration is normally performed using well-characterized narrow MWD standards. Calibration can be performed using broad MWD materials (171). Typical calibration curves (172) are shown in Figure 4. By combining columns in series, a separation range may be achieved covering the molecular weight distribution of the sample. Mathematical treatments of the chromatogram and calibration curve to calculate the molecular weight distribution are given (173). Broadening by the chromatographic process must be calibrated for and corrections applied to produce true molecular weight distributions. Chemimetrics has been applied to GPC calibration equations (174) and helped to establish the best equations. Data reduction in GPC (175) has been described. A new solvent system which allows polyesters and polyamides to be characterized by GPC at room temperature has been developed (176). High speed GPC of low molecular weight polymers has been described (177).

The design and use of a continuous, viscometric detector (178,179) has further advanced the application of the GPC technique, and a commercial viscometric detector is on the market from Viscotek Corp (180,181).
Direct determination of the polymer molecular weight in the detector cell after separation by GPC is possible by LALLS. The technique (182–184) is applicable to the dilute polymer solutions emerging from the chromatographic column; commercial equipment is available, older models (Chromatix KMX6 and LSD100 from LDC/Milton Roy) and newer instruments (Wyatt and Polymer Labs). A review of prior development and a description of a methodology for correcting for dispersion in the concentration detector and the light scattering detector has been published (185). A review of GPC and the application of molecular weight detectors and related separation techniques has been published (186). The characterization of complex polymers by GPC and high performance liquid chromatography (HPLC) has been discussed (187). Quantitative high temperature GPC of polyolefins using refractive index and differential viscometer detection (188) and differential viscometer and light scattering detectors (189) has been reported. This method has been used for on-line molecular weight measurement and branching characterization of water-soluble polymers (185,190). Shear degradation during the chromatographic process may be a problem (191), but can be detected by viscometry and LALLS. A triple detector employing a concentration detector, a viscometer, and a light scattering detector is available (Viscotek). Three detectors, an evaporative light scattering detector to measure concentration, a refractometer, and LALLS, have been used to determine MWD of copolymers (EPM and EPDM) (192). LALLS has proven useful in detecting and eliminating aggregates in dilute polymer solutions which would affect the GPC results (193). Nuclear magnetic resonance,
NMR, has been employed as an on-line detector for GPC (194). Goldwasser (195) developed an analysis which allows the calculation of absolute values for $M_n$ from the combined results from GPC and differential viscometry. Mass spectrometry has been coupled with GPC to characterize a variety of polymers (196–198). A comparison of the most probably peak value of polymer distributions has been evaluated between MALDI MS and GPC (199).

Analyses by GPC of block and statistical copolymers (200,201) and copolymers (202) and polymer mixtures (203) have been reported. Full copolymer characterization by combining GPC-NMR with GPC-MALDI has been demonstrated (204).

Other detectors that are capable of determining the polymer concentration in the effluent are based on dielectric constant (205) and density (206–213). Mass can be determined directly with a piezoelectric quartz sensor having a sensitivity of $10^{-10}$ g (214). A universal mass detector, evaporative light scattering Detector (ELSD) based on the formation of droplets in a nebulizer gas and detection by light scattering using a laser, has been developed and applied to GPC (215). Commercial ELSD units are available from Alltech, Varex Corp., and Polymer Laboratories.

A direct molecular weight method (216) employs the LALLS detector, but uses sedimentation velocity instead of GPC to separate the polymers.

Round robin tests for reproducibility of GPC results have been reported (217). Twenty-four laboratories used calibration standards from two different sources and three test polymers. The results for the three samples varied from 3 to 14% depending on which calibration was used. Similar results for number-average molecular weights have been documented (218). Round robin characterization of polyethylene by high temperature GPC in 15 laboratories has been documented (219).

**High Performance Liquid Chromatography and Supercritical Fluid Chromatography.** For lower molecular weights, HPLC and supercritical fluid chromatography (SFC) (220) offer higher resolution than GPC. Higher molecular weights may produce multiple peaks from monodisperse standards (221). The oligomers are resolved into individual peaks, and molecular weight averages are calculated (222). HPLC is more common and has been applied to phenol-formaldehyde resins (223), polyurethanes (224), polyesters (225), and polycarbonates (226). Since solvent gradients are often used in HPLC the refractometer detector cannot be used, and ultraviolet/visible spectrometers and/or ELSDs must be used. The ELSD may also be used in SFC. SFC can resolve higher oligomers than HPLC. Polystyrene oligomers of up to $n = 50$ may be resolved by SFC; the process requires 18 h (227). Several commercial SFC units are available and their availability should rapidly increase the application of this technique to characterize oligomeric species. A review of supercritical fractionation of polymers and copolymers has been published (228). Mass spectrometry has been used in conjunction with SFC and capillary GPC to characterize polypropylene glycol (229).

Liquid adsorption chromatography (LAV) and GPC have been used to determine chemical composition distribution (CCD) and MWD of styrene–methacrylate copolymers (230).

**Thin-Layer Chromatography.** Thin-layer chromatography (TLC) is widely applicable to polymer characterization and has been used to characterize
molecular weight distribution and compositional distribution (231–233). Cellulose nitrate has been fractionated by this method on the basis of molecular weight or nitrogen content (234).

**Mass Spectrometry.** Advances in soft ionization techniques and developments in high resolution mass spectrometers has led to the possibility of determining intact molecular ions up to $1 \times 10^6$ Da and the measurement of the entire MWD (235,236). The application of mass spectrometry techniques to characterize polymer molecular weight distribution has evaluated (237–243). The MWD of polystyrene SRM 1487 and a narrow MND polymethylmethacrylate (MW 6300) determined by MALDI TOF mass spectrometry have been compared with results from the ultracentrifuge and GPC (244).

**Phase-Distribution Chromatography.** A chromatographic fractionation is achieved in this method (245,246), by partitioning a solute between a solvent flowing through a column, packed with a support coated with a thin layer of high molecular weight, non-cross-linked polymer. The temperature of operation is below the $\Theta$-temperature of the solute, and separation efficiency increases sharply with decreasing temperature. A fully automated chromatograph has been designed (247), and applications have been reported (248–250).

**Field–Flow Fractionation.** Field-flow fractionation (FFF) employs a one-phase chromatographic system (251,252). Commercial instrumentation is available from Postnova Analytics and Tecan. Separation occurs in a thin channel containing a single moving fluid. The field applied across the channel may be selected on the basis of the solute. Possible fields include sedimentation, cross-flow, concentration, dielectric, thermal, and magnetic. A book (253) and a review (254) of this technique and its comparison with GPC for the characterization of polymer molecular weights have been published.

Thermal fields have been used for the separation of polymers in organic solvents (255). Methods for calculation of MWD from thermal FFF have been published (256). For aqueous systems a cross-flow of solvent has been used to separate polyelectrolytes (257) and high molecular weight polyacrylamides (258). Water-soluble polymers have also been characterized by this technique (259,260), in conjunction with LALLS detector (261) and MALLS (262). Extremely high molecular weights of up to $10^{12}$ can be determined (263); because no abrupt changes occur in the forces imposed on the polymer molecules, no degradation takes place. Sedimentation fields were investigated (264), and small samples were quickly fractionated. Compositional heterogeneity has been determined by sequential GPC and FFF (265).

**Electrophoresis.** Electrophoresis is widely practiced on biopolymers (266–268) for the determination of molecular weights of proteins and their subunits. Typically, a polyacrylamide bed is used to separate or characterize these solutes under the influence of an electric field, on the basis of charge and molecular size. The proteins are frequently denatured with sodium dodecyl sulfonate (SDS), and these subunit-SDS complexes are separated on the basis of molecular size. A densitometer employing a soft laser scanning device is commercially available to automate the data-reduction process (269).

**Rheological Measurements.** Some polymers are difficult to dissolve. Mechanical spectroscopy or rheological measurements (qv) offer a way to determine the molecular weight distribution of these materials. Mechanical spectroscopy has
been applied to characterize the MWD of polyolefins (270). Rheological data has been used to determine the MWD of polybutadiene and polypropylene (271). Measurements of ethylene–tetrafluorethylene copolymers using dynamic mechanical analysis of the melts showed broader distributions than those determined by high temperature laser light scattering (272).

**Other Techniques.** Atomization of polymer solutions to form single molecules deposited in a solvent-free state on a surface has been demonstrated for a wide variety of polymers (273). The electron microscope is used at 20,000–30,000 × after platinum shadowing to determine size and size distribution (274). The scanning transmission electron microscope is employed for biological macromolecules (275). For extremely high molecular weight polymers hydrodynamic chromatography (HDC) may be a viable technique. Columns are packed with solid spheres and the diameter determines the separation range. Solid particles between 5 and 300 nm may be separated. Columns are available from Polymer Laboratories, and using a high temperature infrared detector cell the composition of polyolefin copolymers can be characterized. A mathematical model for HDC and GPC for porous column packings has been published (276). Methods to characterize insoluble polymers have been discussed (277,278).

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