

branched), and on the extent to which it is swollen by the solvent. An average radius of gyration can be determined from the angular dependence of the intensities of scattered light.

We saw in Section 3.2.3 that the light scattered from large particles is less intense than that from small scatterers except at zero degrees to the incident beam. This reduction in scattered light intensity depends on the viewing angle (cf. Fig. 3-3b), on the size of the solvated polymer, and on its general shape (whether it is rodlike, a coil, and so on). A general relation between these parameters can be derived [3], and it is found that the effects of molecular shape are negligible at low viewing angles. The relevant equation (for zero polymer concentration) is

$$\lim_{c \rightarrow 0} \frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} \left(1 + \frac{16\pi^2}{3\lambda^2} r_g^2 \sin^2 \frac{\theta}{2} + \dots \right) \quad (3-31)$$

The limiting slope of the zero concentration line of the plot of Kc/R_θ against $\sin^2 \theta/2$ (Fig. 3-4) gives $(16\pi^2/3\lambda^2 \bar{M}_w) r_g^2$. The mutual intercept of the zero concentration and zero angle lines gives \bar{M}_w^{-1} , and the limiting slope of the zero angle line can be used to obtain the second virial coefficient as indicated by Eq. (3-20).

For a polydisperse polymer, the average molecular weight from light scattering is \bar{M}_w , but the radius of gyration which is estimated is the z average.

3.3 DILUTE SOLUTION VISCOSIMETRY

The viscosity of dilute polymer solutions is considerably higher than that of the pure solvent. The viscosity increase depends on the temperature, the nature of the solvent and polymer, the polymer concentration, and the sizes of the polymer molecules. This last dependence permits estimation of an average molecular weight from solution viscosity. The average molecular weight which is measured is the viscosity average \bar{M}_v , which differs from those described so far in this text. Before viscosity increase data are used to calculate \bar{M}_v of the solute it is necessary, however, to eliminate the effects of solvent viscosity and polymer concentration. The methods whereby this is achieved are described in this section.

The procedures outlined below do not remove the effects of polymer-solvent interactions, and so \bar{M}_v of a particular polymer sample will depend to some extent on the solvent used in the solution viscosity measurements (Section 3.3.1).

Solution viscosity measurements require very little investment in apparatus and can be carried out quite rapidly with certain shortcuts described in Section 3.3.4. As a result, this is the most widely used method for measuring a polymer molecular

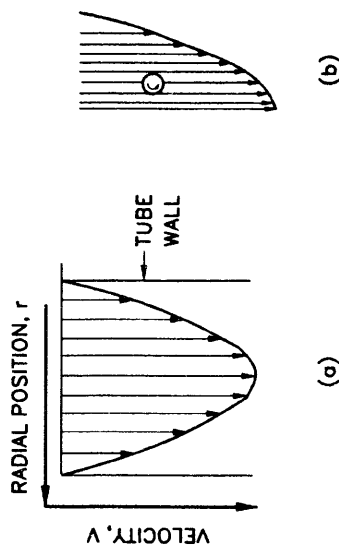


Fig. 3-5. (a) Variation of the velocity of laminar flow with respect to the distance r from the center of a tube. (b) Sphere suspended in a flowing liquid.

weight average. Solution viscosities are also used, without explicit estimation of molecular weights, for quality control of some commercial polymers, including poly(vinyl chloride) and poly(ethylene terephthalate).

We first consider briefly why a polymer solution would be expected to have a higher viscosity than the liquid in which it is dissolved. We think initially of a suspension of solid particles in a liquid. The particles are wetted by the fluid, and the suspension is so dilute that the disturbance of the flow pattern of the suspending medium by one particle does not overlap with that caused by another. Consider now the flow of the fluid alone through a tube which is very large compared to the dimensions of a suspended particle. If the fluid wets the tube wall its velocity profile will be that shown in Fig. 3-5a. Since the walls are wetted, liquid on the walls is stationary while the flow rate is greatest at the center of the tube. The flow velocity v increases from the wall to the center of the tube. The difference in velocities of adjacent layers of liquid (velocity gradient $= dv/dr$) is greatest at the wall and zero in the center of the tube.

When one layer of fluid moves faster than the neighboring layer, it experiences a retarding force F due to intermolecular attractions between the materials in the two regions. (If there were no such forces the liquid would be a gas.) It seems intuitively plausible that the magnitude of this force should be proportional to the local velocity gradient and to the interlayer area A . That is,

$$F = \eta (dv/dr) A \quad (3-32)$$

where the proportionality constant η (eta) is the coefficient of viscosity or just the viscosity. During steady flow the driving force causing the fluid to exit from the tube will just balance the retarding force F . A liquid whose flow fits Eq. (3-32) is called a Newtonian fluid; η is independent of the velocity gradient. Polymer solutions which are used for molecular weight measurements are usually Newtonian. More concentrated solutions or polymer melts are generally not Newtonian in the

sense that η may be a function of the velocity gradient and sometimes also of the history of the material.

Now consider a particle suspended in such a flowing fluid, as in Fig. 3-5b. Impingement on the particle of fluid flowing at different rates causes the suspended entity to move down the tube and also to rotate as shown. Since the particle surface is wetted by the liquid, its rotation brings adhering liquid from a region with one velocity into a volume element which is flowing at a different speed. The resulting readjustments of momenta cause an expenditure of energy which is greater than that which would be required to keep the same volume of fluid moving with the particular velocity gradient, and the suspension has a higher viscosity than the suspending medium.

Einstein showed that the viscosity increase is given by

$$\eta = \eta_0(1 + \omega\phi) \quad (3-33)$$

where η and η_0 are the viscosities of the suspension and suspending liquid, respectively, ϕ is the volume fraction of suspended material, and ω (omega) is a factor which depends on the general shape of the suspended species. In general, rigid macromolecules, having globular or rodlike shapes, behave differently from flexible polymers, which adopt random coil shapes in solution. Most synthetic polymers are of the latter type, and the following discussion focuses on their behavior in solution.

The effects of a dissolved polymer are similar in some respects to those of the suspended particles described earlier. A polymer solution has a higher viscosity than the solvent, because solvent which is trapped inside the macromolecular coils cannot attain the velocities which the liquid in that region would have in the absence of the polymeric solute. (Appendix 3A provides an example of an industrial application of this concept.) Thus the polymer coil and its enmeshed solvent have the same effect on the viscosity of the mixture as an impenetrable sphere, but this hypothetical equivalent sphere may have a smaller volume than the real solvated polymer coil because some of the solvent inside the coil can drain through the macromolecule.

The radius of the equivalent sphere is considered to be a constant, while the volume and shape of the real polymer coil will be changing continuously as a result of rotations about single bonds in the polymer chain and motions of the segments of the polymer. Nevertheless, the time-averaged effects of the real, solvent-swollen polymer can be taken to be equal to that of equivalent smaller, impenetrable spherical particles.

For spheres and random coil molecules, the shape factor ω in Eq. (3-33) is 2.5 and this equation becomes

$$\eta/\eta_0 - 1 = 2.5\phi \quad (3-34)$$

If all polymer molecules exist in solution as discrete entities, without overlap, and

each solvated molecule has an equivalent volume V and molecular weight M (the polymer is monodisperse), then the volume fraction ϕ (phi) of solvent-swollen polymer coils at a concentration c (g cm^{-3}) is

$$\phi = LcV/M \quad (3-35)$$

where L is Avogadro's number. The two preceding equations yield

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{2.5LV}{M} \quad (3-36)$$

In the entity on the left-hand side of Eq. (3-36), the contribution of the polymer solute to the solution viscosity is adjusted for solvent viscosity since the term in parentheses is the viscosity increase divided by the solvent viscosity. The term is also divided by c to compensate for the effects of polymer concentration, but this expedient is not effective at finite concentrations where the disturbance of flow caused by one suspended macromolecule can interact with that from another solute molecule. The contributions of the individual macromolecules to the viscosity increase will be independent and additive only when the polymer molecules are infinitely far from each other. In other words, the effects of polymer concentration can only be eliminated experimentally when the solution is very dilute. Of course, if the system is too dilute, $\eta - \eta_0$ will be indistinguishable from zero. Therefore, solution viscosities are measured at low but manageable concentrations and these data are used to extrapolate the left-hand side of Eq. (3-36) to zero concentration conditions. Then

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \lim_{c \rightarrow 0} \frac{2.5LV}{M} \quad (3-37)$$

The term in brackets on the left-hand side of Eq. (3-37) is called the *intrinsic viscosity* or *limiting viscosity number*. It reflects the contribution of the polymeric solute to the difference between the viscosity of the mixture and that of the solvent. The effects of solvent viscosity and polymer concentration have been removed, as outlined earlier. It now remains to be seen how the term on the right-hand side of Eq. (3-37) can be related to an average molecular weight of a real polymer molecule. To do this we first have to express the volume V of the equivalent hydrodynamic sphere as a function of the molecular weight M of a monodisperse solute. Later we substitute an average molecular weight of a polydisperse polymer for M in the monodisperse case.

If radius of gyration (Section 3.2.6) of a solvated polymer coil is r_g , then the radius of the equivalent sphere r_e will be Mr_g , where H is a fraction which allows for the likelihood that some of the solvent inside the macromolecular volume can drain through the polymer chain. Intuitively, we can see that the solvent deep inside the polymer will move with about the same velocity as its neighboring polymer chain segments while that in the outer regions of the macromolecule will

be able to flow more in pace with the local solvent flow lines. Values of H have been calculated theoretically [4]. Since r_g can be measured directly from light scattering experiments (Section 3.2.6) it is possible to determine H by measuring $[\eta]$ and r_g in the same solvent. Data from a number of different investigators show that H is 0.77 [5].

Under theta conditions the polymer coil is not expanded (or contracted) by the solvent and is said to be in its unperturbed state. The radius of gyration of such a macromolecule is shown in Section 4.4.1 to be proportional to the square root of the number of bonds in the main polymer chain. That is to say, if M is the polymer molecular weight and M_0 is the formula weight of its repeating unit, then

$$r_e = H r_g \propto H (M/M_0)^{1/2} \quad (3-38)$$

Since the volume of the equivalent sphere equals $\frac{4}{3}\pi r_e^3$, then Eqs. (3-37) and (3-38) show that the intrinsic viscosity of solutions of unsolvated (unperturbed) macromolecules should be related to M by

$$[\eta] = \frac{10\pi}{3} L H^3 r_g^3 \propto \frac{10\pi L H^3}{3(M_0)^{3/2}} M^{1/2} \quad (3-39)$$

The intrinsic viscosity in a theta solution is labeled $[\eta]_\theta$. Equation (3-39) can thus be expressed as follows for theta conditions:

$$[\eta]_\theta = K_\theta M^{0.5} \quad (3-40)$$

Flory and Fox [4] have provided a theoretical expression for K_θ which is in reasonable agreement with experimental values.

In a better solution than that provided by a theta solvent the polymer coil will be more expanded. The radius of gyration will exceed the r_g which is characteristic of the bulk amorphous state or a theta solution. If the polymer radius in a good solvent is α_η times its unperturbed r_g , then the ratio of hydrodynamic volumes will be equal to α_η^3 and its intrinsic viscosity will be related to $[\eta]_\theta$ by

$$[\eta]/[\eta]_\theta = \alpha_\eta^3 \quad (3-41)$$

or

$$[\eta] = K_\theta \alpha_\eta^3 M^{0.5} \quad (3-42)$$

The lower limit of α_η is obviously 1, since the polymer is not soluble in media which are less hospitable than theta solvents. In a good solvent $\alpha_\eta > 1$ and increases with M according to $\alpha_\eta = \lambda M^\Delta$, where λ and Δ are positive and $\Delta = 0$ under theta conditions [6, 7]. Then

$$[\eta] = \lambda^3 K_\theta M^{(0.5+\Delta)} = K M^a \quad (3-43)$$

where K and a are constants for fixed temperature, polymer type, and solvent.

Equation (3-43) is the Mark-Houwink-Sakurada (MHS) relation. It appeared empirically before the underlying theory which has just been summarized.

To this point we have considered the solution properties of a monodisperse polymer. The MHS relation will also apply to a polydisperse sample, but M in this equation is now an average value where we denote \bar{M}_v the viscosity average molecular weight. Thus, in general,

$$[\eta] = K \bar{M}_v^a \quad (3-44)$$

The constants K and a depend on the polymer type, solvent, and solution temperature. They are determined empirically by methods described in Sections 3.3.2 and 3.4.3. It is useful first, however, to establish a definition of \bar{M}_v analogous to those which were developed for \bar{M}_w , \bar{M}_n , and so on in Chapter 2.

3.3.1 Viscosity Average Molecular Weight \bar{M}_v

We take the Mark-Houwink-Sakurada equation (Eq. 3-44) as given. We assume also that the same values of K and a will apply to all species in a polymer mixture dissolved in a given solvent. Consider a whole polymer to be made up of a series of i monodisperse macromolecules each with concentration (weight/volume) c_i and molecular weight M_i . From the definition of $[\eta]$ in Eq. (3-37),

$$\eta_i/\eta_0 - 1 = c_i [\eta_i] \quad (3-45)$$

where η_i is the viscosity of a solution of species i at the specified concentration, and $[\eta_i]$ is the intrinsic viscosity of this species in the particular solvent. Recall that

$$c_i = n_i M_i \quad (3-46)$$

where n_i is the concentration in terms of moles/volume. Also,

$$[\eta_i] = K M_i^a \quad (3-44a)$$

and so

$$\eta_i/\eta_0 - 1 = n_i K M_i^{a+1} \quad (3-47)$$

If the solute molecules in a solution of a whole polymer are independent agents, we may regard the viscosity of the solution as the sum of the contributions of the i monodisperse species that make up the whole polymer. That is,

$$\left| \frac{\eta}{\eta_0} - 1 \right|_{\text{whole}} = \sum_i \left(\frac{\eta_i}{\eta_0} - 1 \right) = K \sum_i n_i M_i^{a+1} \quad (3-48)$$

From Eq. (3-37),

$$[\eta] = \lim_{c \rightarrow 0} \frac{1}{c} \left(\frac{\eta}{\eta_0} - 1 \right)_{\text{whole}} = \lim_{c \rightarrow 0} \frac{K}{c} \sum_i n_i M_i^{a+1} \quad (3-49)$$

However,

$$c = \sum_i c_i = \sum_i n_i M_i \quad (3-50)$$

and so

$$[\eta] = \lim_{c \rightarrow 0} \left(K \sum_i n_i M_i^{a+1} / \sum_i n_i M_i \right) \quad (3-51)$$

with Eq. (3-44),

$$[\eta] = K \bar{M}_v^a = \lim_{c \rightarrow 0} \left(K \sum_i n_i M_i^{a+1} / \sum_i n_i M_i \right) \quad (3-52)$$

Then, in the limit of infinite dilution,

$$\bar{M}_v = \left[K \sum_i n_i M_i^{a+1} / \sum_i n_i M_i \right]^{1/a} \quad (3-53)$$

Alternative definitions follow from simple arithmetic:

$$\bar{M}_v = \left[\sum_i w_i M_i^a \right]^{1/a} \quad (3-54)$$

In terms of moments,

$$\bar{M}_v = [\eta U'_{a+1}]^{1/a} = [w U'_a]^{1/a} \quad (3-55)$$

Note that \bar{M}_v is a function of the solvent (through the exponent a) as well as of the molecular weight distribution of the polymer. Thus a given polymer sample can be characterized only by a single value of \bar{M}_n or \bar{M}_w , but it may have different \bar{M}_v 's depending on the solvent in which $[\eta]$ is measured. Of course, if the sample were monodisperse, $\bar{M}_v = \bar{M}_w = \bar{M}_n = \dots$. In general, the broader the molecular weight distribution, the more \bar{M}_v may vary in different solvents.

Note that Eq. (3-53) defines \bar{M}_n with $a = -1$ and \bar{M}_w with $a = 1$. For polymers that assume random coil shapes in solution, $0.5 \leq a \leq 0.8$, and \bar{M}_v will be much closer to \bar{M}_w than to \bar{M}_n because a is closer to 1 than to -1 . Also, \bar{M}_v is much easier to measure than \bar{M}_w once K and a are known, and it is often convenient to assume that $\bar{M}_v \simeq \bar{M}_w$. This approximation is useful but not always very reliable for broad distribution polymers.

Another interesting result is available from consideration of Eqs. (3-51) and (3-44) which yield

$$[\eta] = \sum_i n_i M_i [\eta]_i / \sum_i n_i M_i \quad (3-56)$$

With Eq. (3-46),

$$[\eta] = \sum_i c_i [\eta]_i / \sum_i c_i = \sum_i w_i [\eta]_i \quad (3-57)$$

This last relation shows that the intrinsic viscosity of a mixture of polymers is the weight average value of the intrinsic viscosities of the components of the mixture in the given solvent. (Compare Eq. 2-13 for the weight average of a molecular size.)

3.3.2 Calibration of the Mark-Houwink-Sakurada Equation

Since \bar{M}_v depends on the exponent a as well as the molecular weight distribution this average molecular weight is not independent of the solvent unless the molecular weight distribution of the polymer sample is very narrow. In the limit of monodispersity w_i in Eq. (3-54) approaches 1 and $\bar{M}_v = \bar{M}_i =$ any average molecular weight of the sample.

The classical method for determining K and a relies on fractionation (p. 455) to divide a whole polymer sample into subspecies with relatively narrow molecular weight distributions. An average molecular weight can be measured on each such subspecies, which is called a *fraction*, by osmometry (\bar{M}_n) or light scattering (\bar{M}_w), and the measured average can be equated to a solvent-independent \bar{M}_v if the distribution of the sample is narrow enough. The intrinsic viscosities of a number of such characterized fractions are fitted to the equation

$$\ln[\eta] = \ln K + a \ln(\bar{M}_v) \quad (3-44b)$$

to yield the MHS constants for the particular polymer-solvent system.

Since actual fractions are not really monodisperse it is considered better practice to characterize them by light scattering than by osmometry because \bar{M}_v is closer to \bar{M}_w than to \bar{M}_n .

Although the initial calibration is actually in terms of the relation between $[\eta]$ and \bar{M}_w or \bar{M}_n , as described, Eq. (3-44) can only be used to estimate \bar{M}_v for unknown polymers. It cannot be employed to estimate \bar{M}_w (or \bar{M}_n as the case may be) for such samples unless the unknown is also a fraction with a molecular weight distribution very similar to those of the calibration samples. An important class of polymers which constitutes an exception to this restriction consists of linear polyamides and polyesters polymerized under equilibrium conditions (Chapter 5). In these cases the molecular weight distributions are always random (Section 5.4.3) and the relation

$$[\eta] = K \bar{M}_n^a \quad (3-58)$$

can be applied. For this group (in which $\bar{M}_w = 2\bar{M}_n$), whole polymers can be used for calibration, and \bar{M}_w and \bar{M}_n can be obtained from solution viscosities. The