The Molecular Weight Average Obtained by Combining Quasielastic Light-Scattering and Intrinsic Viscosity Measurements

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Synopsis

For "monodisperse," randomly coiled macromolecules, we find that the molecular weight, intrinsic viscosity, and diffusion coefficient are accurately related by

$$[\eta]M_{D,\eta} = 3.0 \times 10^{-27}(D_t^0\eta_0/T)^{-3}(\text{erg}/^\circ\text{K})^3/\text{g}$$

This equation holds for denatured proteins in $6M$ GuHCl(aq) as well as for narrow polystyrene fractions in tetrahydrofuran. For a Schulz distribution of molecular weights, the weight measured from combining diffusion and viscosity data is closely approximated by

$$M_{D,\eta} = M_w^{0.425}M_z^{0.575}$$

These equations are verified with measurements of wide molecular distributions of polystyrene in toluene and data from the literature. These relations provide a rapid, nondestructive method to determine a well-specified molecular weight average of small quantities of polymers in a wide diversity of solvents using quasielastic light scattering techniques to evaluate polymer diffusion coefficients.

INTRODUCTION

With the development of simple, rapid, but accurate procedures for measuring polymer diffusion coefficients in solution using quasielastic laser light-scattering techniques,[1] a reexamination of the usefulness of the Mandelkern–Flory (MF) method[2] for molecular weight determination from a combination of diffusion and viscosity measurements becomes a worthwhile proposition. For many of the novel polymers currently being synthesized, which often have complex chemical composition and are soluble only in unconventional solvents, the MF theory offers a possible easy route to molecular weight determination. However, synthetic polymers are invariably polydisperse, and one must address the question of how variability in molecular weight distribution affects the molecular weight determined by the MF method. More specifically, can one accurately define a particular molecular weight average measured from diffusion and viscosity analysis that is insensitive to the polymer–solvent system or degree of polydispersity? An approach to this problem is discussed in the following paper.

The method is tested using polystyrene samples of different polydispersities which were independently characterized.

BACKGROUND

According to Flory's treatment of the solution hydrodynamics of flexible polymer coils,[3] the intrinsic viscosity is related to the radius of gyration of the polymer by the equation

$$M[\eta] = 6^{3/2}\Phi_0\alpha_\eta^3\langle R_g^2\rangle^{3/2} \qquad (1)$$

where Φ_0 is a constant which depends on the hydrodynamic model, α_η is the polymer chain expansion parameter as measured by intrinsic viscosity, and $\langle R_g^2\rangle$ is the mean-square radius of gyration. Similarly, the translational diffusion coefficient at zero concentration may be written

$$D_t^0 = \frac{kT}{f_0} = \frac{kT}{6^{1/2}P_0\eta_0\alpha_f\langle R_g^2\rangle^{1/2}} \qquad (2)$$

where P_0 is a frictional constant, η_0 is the solvent viscosity, and α_f is the expansion parameter obtained in a frictional coefficient measurement. According to subsequent modifications of the Flory theory, α_η and α_f are not quite identical.[4] Combination of these equations leads to the Mandelkern-Flory equation[2]

$$M[\eta] = \Phi_0(P_0)^{-3}(\alpha_\eta/\alpha_f)^3k^3(D_t^0\eta_0/T)^{-3} \qquad (3)$$

Application of this expression to molecular weight determination is based on the premise that the parameter

$$\beta = \frac{\Phi_0^{1/3}\alpha_\eta}{P_0\alpha_f(100)^{1/3}} \qquad (4)$$

is insensitive to polymer–solvent interaction. The earliest experimental evidence that eq. (4) is indeed insensitive to these parameters was given by Vallet.[5]

THE MF EQUATION IN POLYDISPERSE SYSTEMS

To apply eq. (3) to molecular weight determination for most synthetic polymers, we must consider the effect of polydispersity on intrinsic viscosity and diffusion coefficient measurements. As is well known, v1] defines a viscosity-average molecular weight M_η through the Mark–Houwink equation which depends on the polymer–solvent interaction:

$$[\eta] = K_\eta M_\eta{}^a \qquad (5)$$

A similar relation can be defined for the diffusion coefficient:

$$D_t^0 = K_D M_D{}^{-b} \qquad (6)$$

where $3b = a + 1$. However, the problem of suitably defining a diffusion coefficient average from the experimental optical mixing spectrum must be solved. By suitable spectral analysis procedures,[6] it is possible to obtain a z-average diffusion coefficient $(D_t^0)_z$ and parameters related to the breadth and shape of the molecular weight distribution. To obtain the latter requires light scattering data of high precision.[7] The z-average diffusion coefficient cannot be related

to a well-defined molecular weight average in any simple way unless one assumes a specific functional form for the distribution of molecular weights.

The Schulz distribution function is a unimodal distribution formula with two adjustable parameters which successfully describes the molecular weight distributions obtained in a variety of condensation and addition polymerizations[8] as well as in certain fractionation by precipitation procedures.[8] The Schulz function defines the concentration $C(M)dM$ of molecules with molecular weight in the range M to $M + dM$ by

$$C(M)dM = y^{h+1}M^h e^{-yM}dM/\Gamma(h + 1)$$

where the adjustable parameters h and y are related through the number- and weight-average molecular weights: $M_n = h/y$, and $M_w/M_n = (h + 1)/h$. Using this distribution, Ford et al. showed[9] that it is possible to relate the z-average diffusion coefficient to a diffusion-average molecular weight M_D:

$$M_D = \frac{1}{y}\left[\frac{\Gamma(h + 2)}{\Gamma(h + 2 - b)}\right]^{1/b} \tag{7}$$

where y and h are parameters used in defining the Schulz distribution and b is the exponent in eq. (6). Similarly, one may write

$$M_\eta = \frac{1}{y}\frac{\Gamma(h + 1 + a)}{\Gamma(h + 1)} \tag{8}$$

Rewriting eq. (2) for polydisperse samples in terms of the constants of eqs. (5) and (6) gives

$$M_{D,\eta}[\eta] = 100\beta^3 k^3(D_t^0\eta_0/T)^{-3}g^{-1} = K_\eta K_D{}^3/D_t^{03} \tag{9}$$

where

$$M_{D,\eta} = M_D{}^{a+1}/M_\eta{}^a$$

For a Schulz distribution eqs. (7) and (8) indicate

$$M_{D,\eta} = \frac{1}{y}\frac{\Gamma(h + 1)}{\Gamma(h + 3b)}\frac{\Gamma(h + 2)}{\Gamma(h + 2 - b)} \tag{10}$$

An alternative way of deriving eq. (10) is implicit in the analysis of Johnsen[10] who used the Schulz function to evaluate polydispersity corrections to $[\eta]$ and $(D_t^0)_z$ which would enable correct comparison of hydrodynamic radii deduced by either quantity when working with polydisperse samples.

Before we can apply eq. (9) to molecular weight determination of unknown polymers, two steps are necessary. We must first determine the hypothetically system-insensitive constant of proportionality β by an experimental route. Secondly, it would be a significant advantage to find a numerical approximation for eq. (10) that is simply and directly related to conventional molecular weight averages (rather than the Schulz parameters h and y), is accurate over a wide range of polydispersities, and at the same time is insensitive to the nature of polymer–solvent interactions reflected in the parameter b.

To determine the β value of eq. (4), two substantially different relatively monodisperse systems were used. Data for globular proteins denatured in $6M$ guanidine hydrochloride and $0.1M$ mercaptoethanol at 25°C and for polystyrene samples with 1.06 polydispersity in tetrahydrofuran at 30°C were analyzed.
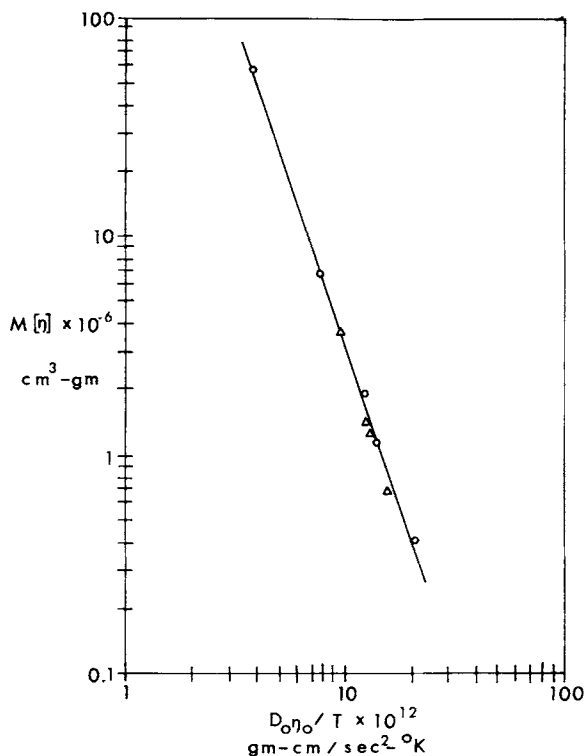
Fig. 1. Product $M[\eta]$ as a function $D_t^0 \eta_0/T$. The straight line shows the best fit to a cubic relation between the two quantities. The slope of the line implies $\beta = 2.3 \times 10^6$.

These measurements have been discussed previously.[11,12] Each infinite dilution diffusion coefficient is extrapolated from diffusion coefficients at four or five different concentrations at or below 10 mg/ml. The total light scattered was constant to within 1%, and a total of 1024 400-point frequency spectra were collected for each sample in less than 3 min.

The data from the two relatively monodisperse systems are displayed in Figure 1. The line gives the best least-squares fit to the data according to eq. (9). This line implies that $\beta = (2.27 \pm 0.09) \times 10^6$, which is significantly below theoretically predicted results for flexible coils of 2.7×10^6. The low value of β, in fact, is consistent with predicted values for solid spherical particles; but since each homologous series of polymers follow eq. (6) with a value of b between 0.5 and 0.6, obviously a solid spherical model is not satisfactory either.[11,12]

The accuracy with which eq. (9) predicts molecular weight depends on the accuracy in measurements of D_t^0 and $[\eta]$. We have determined that the accuracy of our D_t^0 measurements are 3%, of the solvent viscosity, 0.5%, and of the intrinsic viscosity, 2%. This leads to a 13% instrumental uncertainty in our molecular weight determinations. Using the accuracies cited by some workers,[7] we conclude that state-of-the-art equipment could decrease the overall instrumental uncertainty to 3%.

In earlier work,[11] we calculated the variation of $M_{D,\eta}/[(M_w M_z)^{1/2}]$ as a function of b and h. In order to define a more system-insensitive numerical approximation to $M_{D,\eta}$, applicable to wide polydispersity, we set the geometric mean
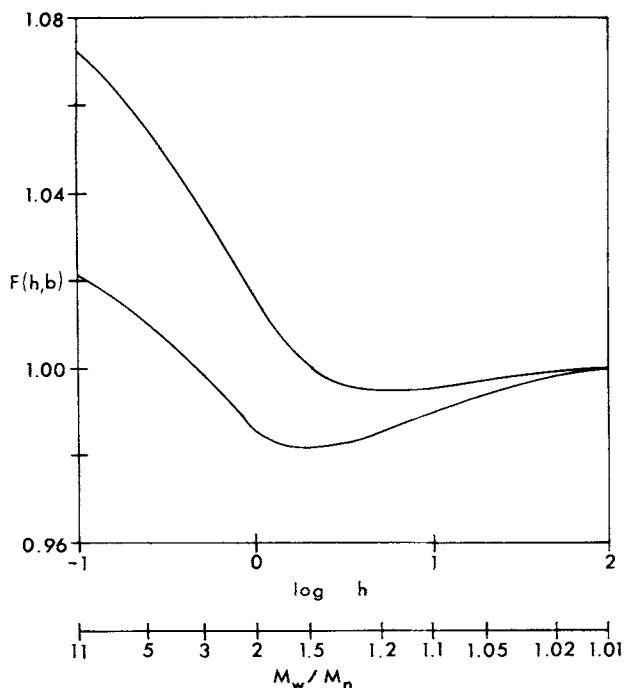
Fig. 2. For a Schulz distribution, $F(h,b) = M_{D,\eta}/M_w{}^{0.425}M_z{}^{0.575}$ is shown as a function of width parameter h or polydispersity M_w/M_n. The upper curve corresponds to $b = 0.6$ and the lower one, to $b = 0.5$.

of $M_{D,\eta}$ for the extreme b values and polydispersity of 2 equal to the weighted average of M_w and M_z:

$$\begin{array}{cc} b = 0.5 & b = 0.6 \end{array}$$
$$\frac{[M_{D,\eta}|h = 1.0 M_{D,\eta}|h = 1.0]^{1/2}}{M_w{}^m M_z{}^{1-m}} = 1 \tag{11}$$

and find $m = 0.425$. In Figure 2, $M_{D,\eta}/M_w{}^m M_z{}^{1-m}$ is plotted for $0.5 < b < 0.6$ and $0.1 < h < 100$. The upper limit of the range corresponds to $b = 0.5$. Note that the deviation of $M_{D,\eta}$ from the respective average $M_w{}^{0.425}M_z{}^{0.575}$ is never more than 7%, even for values of polydispersity as large as 11.

We, therefore, conclude from the above that the appropriate form of the MF equation for molecular weight determination in polydisperse systems is

$$M_{D,\eta}[\eta] = 3.0 \times 10^{-27}(D_t^0 \eta_0/T)^{-3}(\mathrm{erg}/°\mathrm{K})^3/\mathrm{g} \tag{12}$$

with

$$M_{D,\eta} \approx M_w{}^{0.425}M_z{}^{0.575} \tag{13}$$

RESULTS

To test the usefulness of eqs. (12) and (13), we studied two broad molecular weight determinations of polystyrene dissolved in toluene at 25°C and also analyzed the data of Johnsen[10] for a polydisperse polystyrene sample at 25°C in four different solvents made up of ethyl acetate and ethanol. The two samples

we measured were provided by the Dow Chemical Company and had been characterized by analytical gel permeation chromatography to indicate polydispersities (M_w/M_n) of 2.5 and 4.6. Intrinsic viscosity measurements were made by Lenora A. Griffin while a participant in the N.S.F. Student Science Training Program EPP 75-05603.

Since the above discussion depends on z-average diffusion coefficients which are evaluated by spectral analysis in the high-frequency limit,[9] the spectrum was fitted from the first to the twelfth half-width.[11,12] Using these values to extrapolate to D_t^0, the $M_{D,\eta}$ values determined for the two samples by eq. (12) are 3.43×10^5 and 4.16×10^5. The values of $M_w^{0.425}M_z^{0.575}$ computed for the two samples from the reported GPC molecular weight averages using eq. (13) agree with these results to within 4% on the sample with polydispersity of 2.5 and to within 10% on the sample with a polydispersity of 4.6. Both these comparisons are within our experimental uncertainty.

Johnsen[10] studied a polystyrene sample approximating a Schulz distribution with 1.46 polydispersity in ethyl acetate–ethanol solutions ranging from 0% to 10.66% in ethanol. It is concluded that β varies by 15% over this range in solvent composition; however, on the basis of the large uncertainties associated with the presented diffusion coefficients extrapolated to zero concentration, this conclusion does not seem definitively established. If we interpret Johnsen's data using eq. (12), the apparent molecular weight varies between 3.40×10^5 and 2.25×10^5, the mean being 2.74×10^5. In only one system were the data of sufficient quality to have four diffusion constants within 5% of their best straight-line fit. This measurement produces a molecular weight average of 2.50×10^5. The values of h and y for the sample studied by Johnsen[10] lead to a molecular weight determination of $M_w^{0.425}M_z^{0.575} = 2.64 \times 10^5$. In the systems studied, the agreement between the predictions of eqs. (12) and (13) is within the uncertainty limits consistent with a 7% uncertainty in diffusion coefficient. Judging from the quality of the concentration extrapolations, this degree of uncertainty cannot be excluded.

DISCUSSION AND CONCLUSIONS

We have proposed that application of the MF method combining a z-average D_t^0 and $[\eta]$ determines a molecular weight average which closely approximates that deduced by eq. (13), irrespective of polymer–solvent combination. Data are presented for solutions of polydisperse polystyrenes in toluene which support this contention. Our arguments, however, are based on the two assumptions that the polymer has a unimodal molecular weight distribution and that individual macromolecules approximate spherical symmetry. In addition, to establish the universal reliability of eq. (13), it would be advantageous to study other polymer–solvent combinations which include bimodal distributions. A particularly fruitful group of systems for the implementation of the procedure described above are the block copolymers in dilute solution recently discussed by Wang.[13]

Quasielastic laser light scattering permits rapid determination of the diffusion coefficient. Current developments in the determination of intrinsic viscosity from single concentration measurements[14] suggest that intrinsic viscosity can be measured with equal speed. The result is that from two rapid measurements

the molecular weight can be quickly calculated for an unknown polymer–solvent combination. If more information, such as a Mark–Houwink relation, is known, it is in addition possible to deduce a measure of polydispersity. However, we have previously proposed more accurate methods for evaluating molecular weight averages and polydispersity parameters in these systems.[12]

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