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Direct Determination of Viscosity-Average Molecular Weight in the Theta State

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LETTER TO THE EDITOR

Direct Determination of Viscosity-Average Molecular Weight in the Theta State

The intrinsic viscosity$[\eta]$ is related to molecular weight M via the modified Staudinger equation

$$[\eta] = KM^a \tag{1}$$

where K and a are constants for a given polymer–solvent system and temperature. Thus for the calculation of molecular weights from intrinsic viscosities, a calibration is necessary. It is well known that for this purpose the molecular weight should be measured as a viscosity average $\bar{M}_v$, which is defined by

$$\bar{M}_v \equiv \left(\sum_i w_i M_i^a \Big/ \sum w_i\right)^{1/a} \tag{2}$$

It is generally assumed that there is no direct experimental method for the determination of viscosity-average molecular weights. Instead of using viscosity-average molecular weights in the calibration of Eq. (1), calibration is carried out either with sharp fractions using the weight-average molecular weight $\bar{M}_w$ or the viscosity-average molecular weight is calculated for each sample via $\bar{M}_w$, $\bar{M}_n$, and a, assuming a definite type of distribution function.

There is, however, a method which gives directly the viscosity average molecular weight in the theta state ($a = 0.5$) for random coils and for stiff rods ($a = 2$). Mandelkern and Flory (*1*) have shown that the sedimentation coefficient s (at infinite dilution) and intrinsic viscosity $[\eta]$ can be combined to calculate the molecular weight for random coils:

$$\bar{M}_{s\eta} = \frac{N_A \eta_1}{\Phi^{1/3} p^{-1}(1 - {}^*v_2 \rho_1)} s^{3/2} [\eta]^{1/2} \tag{3}$$

where N_A = Avogadro's number, η_1 = viscosity of the solvent, ρ_1 = density of the solvent, ${}^*v_2$ = partial specific volume of the solute, and $\Phi^{1/3}p^{-1}$ = constant, originally assumed to be universal. A similar equation was derived for oblate and prolate ellipsoids (2). The equations may be generalized to

$$\bar{M}_{s\eta} = A_{s\eta}K_{s\eta}s^{3/2}[\eta]^{1/2} \tag{4}$$

where $K_{s\eta}$ is a physical constant, depending on constants like N_L, $^*v_2$, ρ_1, etc., and $A_{s\eta}$ is a model constant, depending on the model used (for a review see Ref. *4*).

s is an average quantity for a polydisperse sample and may be measured, e.g., as a weight average,

$$s = \bar{s}_w = \sum_i w_i s_i \Big/ \sum_i w_i \tag{5}$$

The intrinsic viscosity $[\eta]$ is determined as a weight average, too (Philippoff's rule):

$$[\eta] = [\bar{\eta}]_w = \sum_i w_i[\eta]_i \Big/ \sum_i w_i \tag{6}$$

The molecular weight dependence of the sedimentation coefficient s_i of molecular homogeneous fractions i is given by

$$s_i = K_s M_i^{\gamma} = K_s M_i^{(2-a)/3} \tag{7}$$

whereas the corresponding relationship for the intrinsic viscosity is expressed by Eq. (1).

Combining Eqs. (1) and (4) to (7), we arrive at

$$\bar{M}_{s_w\eta_w} = A_{s\eta}K_{s\eta}K_s^{3/2}K_\eta^{1/2}\left(\frac{\sum\limits_i w_i M_i^{(2-a)/3}}{\sum\limits_i w_i}\right)^{3/2}\left(\frac{\sum\limits_i w_i M_i^{a}}{\sum\limits_i w_i}\right)^{1/2} \tag{8}$$

It has been shown (*3*) by dimensional analysis that the product of physical constants $K_{s\eta}K_s^{3/2}K_\eta^{1/2} = 1$. For the theta state ($a = 0.5$) we get therefore, from Eq. (8)

$$(\bar{M}_{s_w\eta_w})_\theta = A_{s\eta}\left(\frac{\sum\limits_i w_i M_i^{0.5}}{\sum\limits_i w_i}\right)^2 = A_{s\eta}(\bar{M}_\eta)_\theta \tag{9}$$

where the averaging is identical with that of the viscosity average molecular weight $(\bar{M}_\eta)_\theta$ in the theta state. For arbitrary solvents, the approximation $\bar{M}_{s\eta} \approx 0.9\bar{M}_w$ was assumed so far (5). A similar identity exists for a stiff rod ($a = 2$):

$$(\bar{M}_{s_w\eta_w})_{\text{rod}} = A_{s\eta}\left(\frac{\sum_i w_i M_i^2}{\sum_i w_i}\right)^{0.5} = (\bar{M}_\eta)_{\text{rod}} \tag{10}$$

In the case of stiff rods, the sedimentation constant is independent of the molecular weight and thus $\bar{s}_n = \bar{s}_w = \bar{s}_z = \cdots$. As has already been shown by Schumaker (6), the resulting average is also given by the geometric average of weight and z average:

$$(\bar{M}_{s\eta_w})_{\text{rod}} = (\bar{M}_\eta)_{\text{rod}} = (\bar{M}_z\bar{M}_w)^{0.5} \tag{11}$$

The identical averaging of the sedimentation/viscosity molecular weight and the viscosity molecular weight in the theta state allows a more exact proof of the numerical value of the Mandelkern-Flory constant ($\Phi^{1/3}p^{-1}$) than hitherto was possible and thus a test of the influence of theta solvents on the Fox-Flory constant Φ without corrections for effects of polymolecularity. On the other hand, the model constant $A_{s\eta}$ must not necessarily equal 1. Because no relevant data could be found in the literature, an experimental test of the influence of different parameters on $\Phi^{1/3}p^{-1}$ has been started.

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