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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

$$[\eta] = KM^a \quad (1)$$

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

$$\bar{M}_v = \left(\sum_i w_i M_i^a / \sum_i w_i \right)^{1/a} \quad (2)$$

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:

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

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 $\Phi^{1/3}p^{-1} = \text{constant}$, originally assumed to be universal. A similar equation was derived for oblate and prolate ellipsoids (2). The equations may be generalized to

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

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,

$$s = \bar{s}_w = \frac{\sum_i w_i s_i}{\sum_i w_i} \quad (5)$$

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

$$[\eta] = [\bar{\eta}]_w = \frac{\sum_i w_i [\eta]_i}{\sum_i w_i} \quad (6)$$

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

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

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

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

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

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)

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

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 ($a = 2$):

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

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

$$(\bar{M}_{s_w})_{\text{rod}} = (\bar{M}_\eta)_{\text{rod}} = (\bar{M}_z \bar{M}_w)^{0.5} \quad (11)$$

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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