Consideration of the Asymptotic Behavior of the Reciprocal Light Scattering Function for Polymer Molecular Weight Distribution Moment Determination[1a]

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ABSTRACT: The possible use of the reciprocal light scattering function's asymptote to determine distribution moments in polydisperse polymers is examined. Computations are made for Gaussian coils of polymers having molecular weight distributions of the Schulz–Zimm form. Caution is advised in applying the concept to scattering data since in most instances the asymptote lies well off the scattering envelope in experimentally accessible ranges of the scattering parameters.

The possible use of the reciprocal light scattering intensity function asymptote to determine the M_n of a polydisperse polymer and to determine an essentially polydispersity-independent value of R^2/M of the polymer coils (assumed to have Gaussian segment distributions) was proposed 15 years ago.[2] The proposal prompted one of us to make computations on the basis of the Schulz–Zimm distribution function[3] to inspect the validity of the approach for such distributions. The results were incorporated in a short manuscript which was not submitted for publication at that time. Recently a more complete consideration of the nature of the total reciprocal scattering intensity curves of polydisperse polymers has appeared.[4] The 1954, manuscript complements this material with numerical results based on the Schulz–Zimm distribution function which was not applicable[4] to the isotactic polypropylenes studied.

The use of various experimental methods to obtain molecular weight distribution information appears to be experiencing a resurgence of interest and activity. The use of the reciprocal light scattering intensity asymptote as one of several methods was discussed in a recent talk.[5] It now seems desirable to present the results of our 1954 calculations to reinforce admonition against indiscriminate or injudicious application of the method. The original manuscript is unchanged except for journal reference assignments, and inclusion of $z = {}^1/_4$ and ${}^1/_2$ data and asymptotic slope data in Table I.

Approach and Calculations

Benoit[2] has focused attention on the possible use of the entire reciprocal scattering intensity curve obtained in light-scattering experiments to determine the relation of the various dimension and molecular weight averages which depend upon different moments of the molecular weight distribution of a polymer. Both the limiting tangent and the asymptote to the reciprocal intensity curve have been utilized to evaluate molecular weights and mean square radii of cellulose nitrate samples.[6,7] The difficulties encountered in treating light-scattering data on molecularly disperse materials justify a consideration of the merits and regions of applicability of the tangential and asymptotic extrapolations.

Considering polymer molecules in dilute solution to be *approximated by Gaussian chains*, the reciprocal intensity function of light scattered from solutions in the limit of zero polymer concentration is given by[2,3,6,7]

$$(Kc/I_\theta)_{c=0}^{\text{obsd}} = P^{-1}(\theta, z)/\overline{M}_w \qquad (1)$$

I_θ is the intensity of the excess scattered light from a solution of polymer concentration c observed at an angle θ from the direction of the incident beam. K, the optical constant, is determined by the wavelength and state of polarization of the light used, by the refractive index of the solution and by the refractive index increment of the polymer–solvent pair. M_w signifies the weight-average molecular weight of the polymer. The reciprocal scattering factor, $P^{-1}(\theta, z)$, is a function of the observation angle, θ, of the molecular weight heterogeneity of the polymer, and of the molecular dimensions of the polymer chains relative to the wavelength of light within the solution.

As $P^{-1}(\theta, z) \rightarrow 1$, eq 1 reduces to the limiting tangential form[2,3]

$$(Kc/I_\theta)_{c=0}^{\text{tan}} = (1/\overline{M}_w)(1 + \bar{u}_z/3) \qquad (2)$$

as $P^{-1}(\theta) \rightarrow \infty$, eq 1 approaches the asymptotic form[2,3]

$$(Kc/I_\theta)_{c=0}^{\text{asym}} = (1/2\overline{M}_n)(1 + \bar{u}_n) \qquad (3)$$

where $\bar{u}_z$ and $\bar{u}_n$ are, respectively, the z and number averages of the quantity

$$\bar{u} = (16\pi^2/\lambda^2)R^2 \sin^2(\theta/2) \qquad (4)$$

where λ is the wavelength of the light in the solution

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(6) H. Benoit, A. M. Holtzer, and P. Doty, *J. Phys. Chem.*, **58**, 635 (1954).
(7) A. M. Holtzer, H. Benoit, and P. Doty, *ibid.*, **58**, 624 (1954).

TABLE I

THE RECIPROCAL SCATTERING FUNCTION $P^{-1}(\theta, z)$, THE RATIO q OF $P^{-1}(\theta, z)$ TO THE ASYMPTOTE ORDINATE, AND THE RATIO A OF THE $P^{-1}(\theta, z)$ SLOPE TO THE ASYMPTOTIC SLOPE AT VARIOUS VALUES OF THE DISTRIBUTION BREADTH PARAMETER z AND OF THE SCATTERING VARIABLE u

u	$P^{-1}(\theta, z)$	q	A	$P^{-1}(\theta, z)$	q	A
		$z = 0.25$			$z = 0.50$	
0.00	1.000	2.500	1.200	1.000	1.500	1.111
0.25	1.148	2.286	1.174	1.138	1.428	1.098
0.50	1.294	2.126	1.156	1.275	1.373	1.087
0.75	1.437	2.000	1.139	1.410	1.330	1.079
1.0	1.579	1.900	1.127	1.544	1.295	1.072
1.5	1.858	1.749	1.108	1.811	1.243	1.061
2	2.133	1.641	1.094	2.075	1.205	1.053
3	2.675	1.495	1.075	2.598	1.155	1.041
4	3.209	1.402	1.063	3.117	1.123	1.034
6	4.263	1.290	1.047	4.146	1.085	1.025
10	6.340	1.183	1.031	6.185	1.051	1.016
		$z = 2$			$z = 4$	
0.00	1.000	0.750	0.889	1.000	0.625	0.800
0.25	1.112	0.787	0.900	1.101	0.681	0.819
0.50	1.225	0.816	0.910	1.205	0.726	0.836
0.75	1.339	0.840	0.918	1.310	0.763	0.850
1.0	1.455	0.859	0.926	1.417	0.794	0.864
1.5	1.688	0.889	0.938	1.636	0.840	0.886
2	1.923	0.910	0.947	1.860	0.874	0.904
3	2.400	0.938	0.960	2.319	0.916	0.930
4	2.882	0.954	0.969	2.788	0.941	0.948
6	3.857	0.972	0.980	3.747	0.967	0.968
10	5.828	0.987	0.989	5.704	0.986	0.986
		$z = 10$			$z = \infty$	
0.00	1.000	0.550	0.727	1.000	0.500	0.667
0.25	1.092	0.618	0.751	1.085	0.576	0.694
0.50	1.188	0.674	0.773	1.173	0.639	0.719
0.75	1.286	0.720	0.793	1.265	0.692	0.743
1.0	1.386	0.758	0.811	1.359	0.736	0.766
1.5	1.593	0.816	0.843	1.556	0.803	0.806
2	1.807	0.858	0.869	1.762	0.852	0.840
3	2.252	0.910	0.908	2.195	0.911	0.892
4	2.712	0.940	0.934	2.650	0.943	0.926
6	3.663	0.969	0.964	3.598	0.973	0.964
10	5.617	0.988	0.986	5.556	0.990	0.988

and R^2 is the mean-square radius of a molecule of molecular weight M.

Zimm[3] approximated the weight distribution of a heterogeneous polymer by the relation

$$w(M) = m^{z+1}M^z e^{-mM}/\Gamma(z + 1) \quad (5)$$

where z is a breadth of distribution parameter related to m and M by

$$m = z/\bar{M}_n = (z + 1)/\bar{M}_w = (z + 2)/\bar{M}_z \quad (6)$$

Using eq 1, 2, 3, and 5, the ratios of $(Kc/I_\theta)_{c=0}^{\text{cor t}}$ and $(Kc/I_\theta)_{c=0}^{\text{cor a}}$ to $(Kc/I_\theta)_{c=0}^{\text{obsd}}$ were calculated as functions of $\bar{u}_w$ and z, and representative curves were constructed.[3] Following the procedure of Zimm we have recalculated the factor

$$q = (Kc/I_\theta)_{c=0}^{\text{cor a}}/(Kc/I_\theta)_{c=0}^{\text{obsd}} \quad (7)$$

and also have calculated a slope ratio

$$A = (\text{slope of } P^{-1}(\theta, z))/(\text{slope of asymptote } (\theta, z)) \quad (8)$$

The results are presented in Table I for distributions conforming to eq 5 and having $z = 1/4$, $1/2$, 2, 4, 10 and ∞.

A light-scattering study[8] was made on carefully fractionated linear poly(vinyl acetates) in methyl ethyl ketone using vertically polarized 5461-Å incident light. The data obtained may profitably be examined with respect to the shape of the $(Kc/I_\theta)_{c=0}^{\text{obsd}}$ *vs.* $\sin^2(\theta/2)$ curves over the range of angles 30–145°. Figure 1 presents the observed curve (upper curve with extrapolated experimental data as open circles) for poly(vinyl acetate) fraction 2-2 ($\bar{M}_w = 3.0 \times 10^6$). Owing to the reasonable sharpness of the fraction the curve exhibits considerable positive curvature. Four "asymptotes" were calculated based on distributions corresponding to eq 5 assuming successively $z = 2$, 4, 10 and ∞. The procedure used in the calculations was that proposed by Zimm.[3] An "asymptote" was guessed. The intercept obtained was then multiplied by $2z/(z + 1)$ and this product divided into the $(Kc/I_\theta)_{c=0}^{\text{obsd}}$ values to determine $P^{-1}(\theta, z)$. From Table I q values were obtained, and $(Kc/I_\theta)_{c=0}^{\text{cor a}}$ was calculated by eq 7 for each experimental point. A plot of these calculated points would then yield a better

(8) A. R. Shultz, *J. Amer. Chem. Soc.*, 76, 3422 (1954).

approximation to the intercept and the process was repeated until the calculated curve yielded the approximated intercept. Calculated "asymptotes" (Figure 1), assuming $z = 2$ and 4, retain positive curvature. The "asymptote" obtained assuming $z = \infty$ exhibits slight, although nearly imperceptible, negative curvature. The true asymptote, represented by the solid straight line, was calculated by setting z equal to 10. The limiting tangent corresponding to $z = 10$ is also shown in Figure 1.

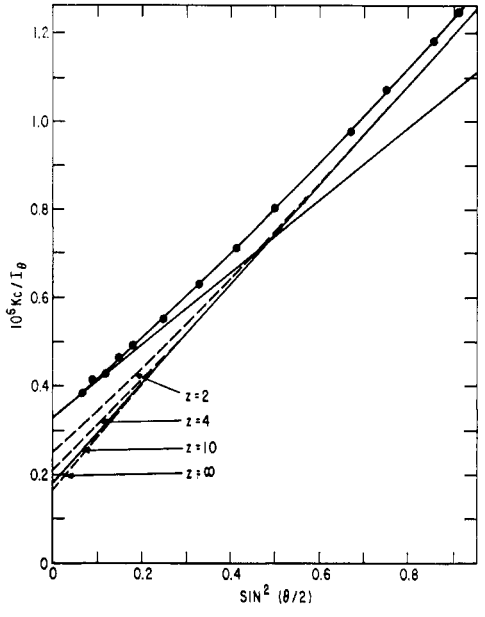

Figure 1. Computed "asymptotes" for the extrapolated light-scattering curve $(Kc/I_\theta)_{c=0}^{obsd}$ *vs.* $\sin^2(\theta/2)$ for poly(vinyl acetate) fraction 2–2 in methyl ethyl ketone. The solid curve corresponding to $z = 10$ is a straight line and the true asymptote. The limiting tangent is also shown for $z = 10$.

From Figure 1 we may conclude that the number-average molecular weights for poly(vinyl acetate) fraction 2–2 in MEK obtained with 5461-Å light from the intercepts of calculated "asymptotes" are quite sensitive to the degree of heterogeneity assumed for the polymer. As shown, the $\bar{M}_n$ range from 3.0×10^6 for $z = \infty$ to 2.0×10^6 for $z = 2$. M_w values calculated by $\bar{M}_w = \bar{M}_n(z + 1)/z$ are essentially constant and equal to an $\bar{M}_w$ of 3.0×10^6. It is true that the "asymptotes" obtained assuming considerably incorrect degrees of molecular weight heterogeneity are nonlinear and thus unacceptable; however, the detection of this deviation from linearity depends upon precise scattering data at angles in the range 0–90°.

Figure 2 presents $(Kc/I_\theta)_{c=0}^{obsd}$ values (open circles) plotted against $\sin^2(\theta/2)$ for three poly(vinyl acetate) fractions in MEK at 25°. Calculated points on the limiting tangents and asymptotes (solid circles) assumed $z = 10$ for each fraction. These limiting tangents and asymptotes are satisfactorily linear. The weight-average molecular weights of PVA·1–2, 2–2 and 4–2 are 3.46×10^6, 3.02×10^6 and 1.74×10^6 according to the limiting tangent intercepts. The number-average molecular weights, calculated from the asymptote intercepts, are 2.96×10^6, 2.77×10^6, and 1.53×10^6 in good agreement with the expected values $\bar{M}_n = z\bar{M}_w/(z + 1) = (10/11)\bar{M}_w$. Application of eq 2 to the limiting tangent slope-to-intercept ratios yields root-mean-square z-average radii, $(\overline{R_z^2})^{1/2}$ (equal to the root-mean-square z-average end-to-end distance of the Gaussian chains divided by $6^{1/2}$) of 905, 854 and 616 Å for 1–2, 2–2 and 4–2, respectively. From the slope-to-intercept ratios of the asymptotes (*cf.* eq 3) we find the corresponding $(\overline{R_n^2})^{1/2}$ to be 815, 782 and 550 Å. Ignoring the correction which should be made due to the molecular weight dependence of expansion of the polymer chains relative to their unperturbed dimensions,[8] the ratio $(\overline{R_z^2}/\overline{R_n^2})^{1/2}$ should be $[(z + 2)/z]^{1/2} = 1.094$ for the assumed molecular weight distributions. The observed ratios 1.11, 1.09 and 1.12 are in reasonable agreement with this prediction.

The most important possible use of the asymptote to the reciprocal intensity curve is the determination of a unique value for the ratio $\overline{R^2}/\bar{M}$ essentially unencumbered by molecular weight heterogeneity.[2,3,6,7] Thus, assuming Gaussian chains, eq 3 states that the slope of the asymptote is proportional to $\overline{R^2}/\bar{M}$ in which the same moment of the molecular weight distribution enters into the averaging of the mean-square radius and the molecular weight over the distribution. Figure 1 reveals that for values of z in the range 2 to ∞ the calculated "asymptotes" for fraction

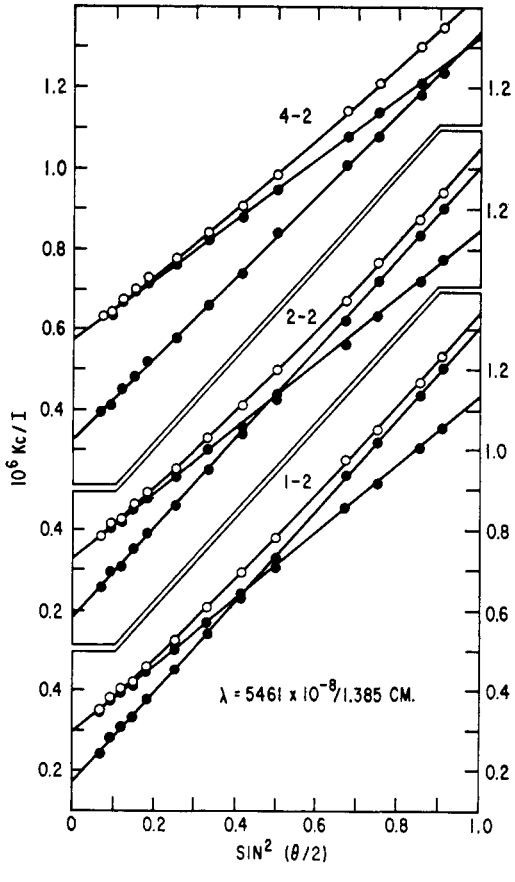

Figure 2. Scattering curves for three poly(vinyl acetate) fractions (1–2, 2–2, and 4–2) in methyl ethyl ketone. Open circles are the extrapolated experimental points. Solid circles are the corresponding points on the limiting tangents and asymptotes computed on the assumption of a Schulz–Zimm distribution function with breadth parameter $z = 10$.

2–2 for $\sin^2(\theta/2) > 0.7$ all have slopes practically equal to that of the true asymptote. Also, the slope of a straight line approximating $P^{-1}(\theta, z)$ for $\sin^2(\theta/2) > 0.7$ is nearly equal to that of the asymptote in this case. If one first ascertains that the experimental $(Kc/I_\theta)_{c=0}^{obsd}$ lie near the asymptote, the slope of $P^{-1}(\theta, z)$ in that region may be used to obtain a value of $\overline{R^2}/\bar{M}$.

Conclusions

In conclusion, it is advisable to be very cautious in using the extrapolated asymptote to obtain $\bar{M}_n$. For distributions having $\bar{M}_n$ differing from $0.5\bar{M}_w$ and $P^{-1}(\theta, z)$ less than 4 at $\sin^2(\theta/2) = 1$ the experimentally observed $(Kc/I_\theta)_{c=0}$ lie appreciably off the asymptote. If $P^{-1}(\theta, z)$ considerably exceeds 4 in the region studied, the experimental points will lie near the asymptote, but the large slope of the asymptote under such conditions will make the long extrapolation to $\sin^2(\theta/2) = 0$ somewhat precarious. When large Gaussian chains are studied with light of short wavelength leading to $P^{-1}(\theta, z)$ values of approximately 3 or greater, a straight line approximating $P^{-1}(\theta, z)$ in this region (*i.e.*, $P^{-1}(\theta, z) \geq 3$) will have a slope nearly equal to the asymptotic slope. Such a line may then be used to calculate the ratio $\overline{R^2}/\bar{M}$ which will be independent of the molecular weight distribution except for corrections arising from the molecular weight dependence of R^2/M due to osmotic expansion of the coils.

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Photophysical Processes in Polymers. II. Intramolecular Triplet Energy Transfer in Styrene–1-Vinylnaphthalene Copolymers[1]

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ABSTRACT: Electronic energy transfer in copolymers of styrene and 1-vinylnaphthalene has been studied by means of delayed emission spectra run in a rigid glass at 77°K. Relative to the equivalent mixtures of polystyrene and poly(1-vinylnaphthalene), the copolymers excited by light absorbed by polystyrene show quenching of phosphorescence from the styrene-derived segments and sensitization of phosphorescence from the 1-vinylnaphthalene-derived segments. It is concluded that triplet energy has been transferred intramolecularly from the styrene- to the 1-vinylnaphthalene-derived portions of the chain. In effect, the 1-vinylnaphthalene segments not only act as detectors of intermolecular energy transfer in polystyrene, but play the role of "energy sinks" in the copolymer, thereby behaving as inhibitors to photodegradation of the copolymer. From the ratios of delayed fluorescence to phosphorescence from the 1-vinylnaphthalene-derived segments, it is concluded that these segments are distributed randomly rather than as blocks in the copolymer chains.

Polymers subjected to degrading ultraviolet light are generally protected by the incorporation of additives which act as absorbers of the offending radiation. The effect is to prevent, by optical filtering, absorption of the radiation by the polymer. In practice, however, part of the light is absorbed by the polymer, and in time the additives may themselves become ineffective through photolysis. In addition, a portion of the energy absorbed by the additives may in certain cases be transferred intermolecularly to the polymer.[2] The net effect is that the polymer is still subject to photodegradation, and its mechanism, both in the presence and in the absence of protective agents, will remain a subject of interest.

Once a bond has been broken at any point in a polymer molecule, overt degradation has begun. Methods of inhibition based on the control of subsequent processes are likely to be inefficient at best. On the other hand, if the energy of the absorbed photon can be dissipated before bond dissociation occurs, inhibition of the photodegradation process will have been effected. This necessitates a knowledge of the photophysical processes which take place between the event of photon absorption and bond dissociation.

Photophysical processes in small molecules have been under intensive investigation.[3] In polymer molecules the same processes undoubtedly take place, but an additional degree of freedom is provided by the chain itself. An analogy might be drawn to crystals in which exciton migration along chains of small molecules or atoms can occur.[4,5] From the standpoint of polymer photolysis, it is of particular interest to know whether energy is delocalized along a polymer chain.

(1) Paper I: R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, in press. These papers were presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, and the 157th National Meeting, Minneapolis, Minn., April 1969.

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