# The Effect of Polydispersity on Rayleigh Line-Broadening Measurements of Diffusion Constants of Random-Coil Macromolecules

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ABSTRACT: Detailed numerical calculations have been made based on a theory by Pecora for the spectrum of light scattered from dilute solutions of random-coil polymers with molecular weights given by the Schulz distribution function. These calculations show that the spectra for samples of moderate molecular weight with relatively broad molecular weight distributions will be nearly Lorentzian, with half-widths that are nearly proportional to the square of the scattering vector $\kappa^2$. The ratio of the apparent diffusion constant to the diffusion constant of a monodisperse polymer with the same molecular weight as the weight-average molecular weight is computed as a function of $z$, $\alpha$, and $x$, the parameters which influence this ratio. Experimental spectra of NBS-706 polystyrene in cyclohexane at 35.0° and in 2-butanone at 25.0° are in accord with these predictions of theory.

In an earlier paper[2] the effect of increasing molecular weight on the shape and angular dependence of the half-wdith of the spectrum of light scattered from dilute solutions of polystyrene in a $\Theta$ solvent was reported. Two deviations from the predictions of the theory which deals only with translational motion were found. The spectrum became increasingly non-Lorentzian with increasing molecular weight, and simultaneously the half-width of the spectrum began to deviate from proportionality to the square of the magnitude of the scattering vector $\kappa^2$. Two possible causes for this deviation are the increasing polydispersity with increasing molecular weight and the increasing contributions to the scattering from intramolecular motions.

In order to facilitate making the distinction between these two causes, an experimental study has been made of the effects of polydispersity alone on the spectral shape and its angular dependence. Measurements were performed on solutions of NBS-706 polystyrene in cyclohexane at 35.0° and in 2-butanone at 25.0°. This well-characterized polymer has a broad molecular weight distribution near a most-probable distribution, yet nearly all species present in high enough quantity to scatter appreciably are below the molecular weight at which intramolecular contributions would be expected to influence the spectrum.

## Theory

If the effects of translation alone on the spectrum are considered, the light from a dilute solution of random-coil molecules having a Schulz distribution of molecular weights is given by[3]

$$\omega S_{0z}(x,\delta,\alpha) = \frac{\delta(z+1)^{z+1}}{xz!\zeta^{z+1-\alpha}} \int_0^\infty \left\{\mathrm{erf}\left[\frac{1}{2}\left(\frac{tx}{\zeta}\right)^{1/2}\right]\right\}^2 \times \frac{t^{z+\alpha}}{[t^{2\alpha}+\delta^2\zeta^{2\alpha}]} e^{-t}\mathrm{d}t \qquad (1)$$

Here $z$ is a parameter characterizing the Schulz distribution function and $\zeta$, $x$, and $\delta$ are given respectively by

$$\zeta = z + 1 + x^2/6 \qquad (2)$$

$$x = \kappa^2 nb^2/6 \qquad (3)$$

$$\delta = \kappa^2 D_w/\omega \qquad (4)$$

where $\kappa^2$ is the magnitude of the scattering vector and $\omega$ is the angular frequency variable used in specifying the spectral distribution. The dependence of the translational diffusion coefficient $D$ on molecular weight has been assumed in deriving eq 1 to be

$$D = CM^{-\alpha} \qquad (5)$$

where $C$ and $\alpha$ are characteristic of the polymer–solvent pair at the temperature of measurement. $D_w$ is the diffusion constant of the species with molecular weight equal to the weight-average molecular weight for the distribution considered. The combined parameters $nb^2/6$ may be conveniently set equal to $\langle s^2\rangle_w$, the mean-square radius of gyration of the species with molecular weight equal to the weight-average molecular weight.

Equation 1 arises from considering the distribution of diffusion coefficients arising from the distribution of molecular weights, then weighting the contribution from each species according to its scattering power. The resulting spectrum is a distribution of Lorentzians, each with different half-width and amplitude, as is readily seen by rearranging eq 1 to the form

$$S_{0z} = \frac{(z+1)^{z+1}}{xz!\zeta^{z+1}} \int_0^\infty \left\{\mathrm{erf}\left[\frac{1}{2}\left(\frac{tx}{\zeta}\right)^{1/2}\right]\right\}^2 \times t^z e^{-t}\left[\frac{\dfrac{\kappa^2 D_w\zeta^\alpha}{t^\alpha}}{\omega^2 + \left(\dfrac{\kappa^2 D_w\zeta^\alpha}{t^\alpha}\right)^2}\right]\mathrm{d}t \qquad (6)$$

The first factor in the integrand is a distribution function for Lorentzian form which it multiplies. As Pecora has pointed out,[3] this spectrum is not itself Lorentzian, nor would its half-width in general be proportional to $\kappa^2$.

However, for the case where $x$ is small, the variation of the half-width will still be proportional to $\kappa^2$ even though the spectrum is non-Lorentzian. This can be seen from eq 6. For small values of the argument $u$ the error function can be expanded in series to give[4]

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(1) Author to whom correspondence should be addressed.

(2) T. F. Reed and J. E. Frederick, *Macromolecules*, **4**, 72 (1971).

(3) R. Pecora and Y. Tagami, *J. Chem. Phys.*, **51**, 3298 (1969). Note that typographical errors occur in eq 5 of this reference; these have been corrected in eq 1 of the present work.

(4) M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, U. S. Government Printing Office, Washington, D. C., 1964.

TABLE I

($D_c/D_w$) AS A FUNCTION OF $z$, $\alpha$, AND $x$

| $x$ | $\alpha$ | $z$ = 0.5 | 1 | 2 | 3 | 4 | 5 | 7 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 0.01 | 0.5 | 0.77 | 0.81 | 0.86 | 0.89 | 0.91 | 0.93 | 0.94 | 0.96 |
| | 0.75 | 0.63 | 0.69 | 0.77 | 0.81 | 0.84 | 0.87 | 0.90 | 0.92 |
| | 1.0 | 0.50 | 0.57 | 0.66 | 0.72 | 0.77 | 0.80 | 0.84 | 0.88 |
| 0.1 | 0.5 | 0.78 | 0.82 | 0.87 | 0.90 | 0.91 | 0.93 | 0.94 | 0.96 |
| | 0.75 | 0.64 | 0.70 | 0.77 | 0.82 | 0.85 | 0.87 | 0.90 | 0.92 |
| | 1.0 | 0.50 | 0.57 | 0.67 | 0.73 | 0.77 | 0.80 | 0.84 | 0.88 |
| 0.2 | 0.5 | 0.78 | 0.83 | 0.87 | 0.90 | 0.92 | 0.93 | 0.94 | 0.96 |
| | 0.75 | 0.65 | 0.71 | 0.78 | 0.82 | 0.85 | 0.87 | 0.90 | 0.93 |
| | 1.0 | 0.51 | 0.58 | 0.67 | 0.73 | 0.78 | 0.81 | 0.85 | 0.88 |
| 0.3 | 0.5 | 0.79 | 0.83 | 0.88 | 0.90 | 0.92 | 0.93 | 0.95 | 0.96 |
| | 0.75 | 0.66 | 0.71 | 0.78 | 0.83 | 0.86 | 0.88 | 0.91 | 0.93 |
| | 1.0 | 0.52 | 0.59 | 0.68 | 0.74 | 0.78 | 0.81 | 0.85 | 0.89 |
| 0.4 | 0.5 | 0.80 | 0.84 | 0.88 | 0.91 | 0.92 | 0.94 | 0.95 | 0.96 |
| | 0.75 | 0.67 | 0.72 | 0.79 | 0.83 | 0.86 | 0.88 | 0.91 | 0.93 |
| | 1.0 | 0.53 | 0.60 | 0.69 | 0.75 | 0.78 | 0.81 | 0.85 | 0.89 |
| 0.5 | 0.5 | 0.81 | 0.84 | 0.89 | 0.91 | 0.93 | 0.94 | 0.95 | 0.96 |
| | 0.75 | 0.67 | 0.73 | 0.79 | 0.84 | 0.86 | 0.88 | 0.91 | 0.93 |
| | 1.0 | 0.54 | 0.61 | 0.69 | 0.75 | 0.79 | 0.82 | 0.86 | 0.89 |
| 0.7 | 0.5 | 0.82 | 0.86 | 0.90 | 0.92 | 0.93 | 0.94 | 0.96 | 0.97 |
| | 0.75 | 0.69 | 0.74 | 0.81 | 0.84 | 0.87 | 0.89 | 0.91 | 0.94 |
| | 1.0 | 0.56 | 0.62 | 0.71 | 0.76 | 0.80 | 0.82 | 0.86 | 0.90 |
| 1.0 | 0.5 | 0.85 | 0.87 | 0.91 | 0.93 | 0.94 | 0.95 | 0.96 | 0.97 |
| | 0.75 | 0.72 | 0.77 | 0.83 | 0.86 | 0.88 | 0.90 | 0.92 | 0.94 |
| | 1.0 | 0.59 | 0.65 | 0.73 | 0.78 | 0.81 | 0.84 | 0.87 | 0.90 |

$$\operatorname{erf}(u) = (2/\pi^{1/2})(u - {}^1/_3u^3 + \ldots) \tag{7}$$

If only the first term of this expression is used to expand the error function in the integrand of eq 6, then only a dependence on $t$ remains in the integrand excepting a very weak dependence on $x$ through the parameter $\zeta$. When the distribution function depends on $t$ alone the relative amplitudes of the Lorentzians in the distribution do not change with $x$. Accordingly, a variation in the scattering angle does not change the relative amplitudes of the Lorentzian components. It may be readily shown that when the relative amplitudes do not change, the angular dependence of the half-width of curves which are the sums of Lorentizians must be the angular dependence of the individual Lorentzians. Since the half-widths of Lorentzians arising from translation are proportional to $\kappa^2$, the half-width of the composite curve is also proportional to $\kappa^2$ under conditions where the approximation made above in eq 7 is valid. This proportionality to $\kappa^2$ holds independent of the shape of the composite spectrum.

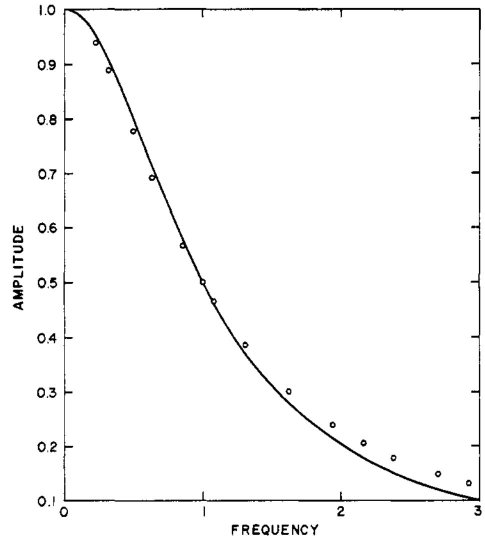

Figure 2. Calculated light spectrum for a polydisperse sample with $z = 1$, $\alpha = 0.75$, and $x = 0.1$: —, Lorentzian; O, spectrum for polydisperse sample. Frequency units are arbitrary.

The exact shape of the spectral distribution predicted by eq 1 varies with $z$, $\alpha$, and $x$. The effect of changing each of these parameters over the range shown in Table I was determined by numerical calculation as described by Pecora.[3] Varying $\alpha$ has the effect shown in Figures 1–3, where $\alpha$ has been given the values 0.5, 0.75, and 1.0 while $x$ remains constant at 0.1. These curves are computed with $z$ equal to 1.0, which corresponds to the relatively broad most probable distribution of molecular weights. It is apparent that for $\alpha$ = 0.5 the spectral shape is very similar to a single Lorentzian, whereas for larger values of $\alpha$ there are greater deviations from this form. An experimental spectrum similar to that

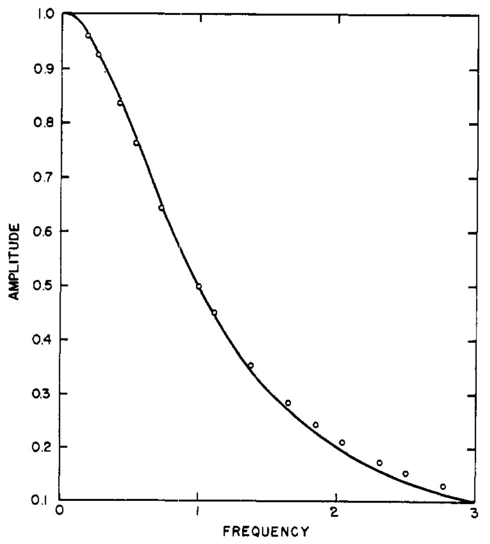

Figure 1. Calculated light spectrum for a polydisperse sample with $z = 1$, $\alpha = 0.5$, and $x = 0.1$: —, Lorentzian; O, spectrum for polydisperse sample. Frequency units are arbitrary.

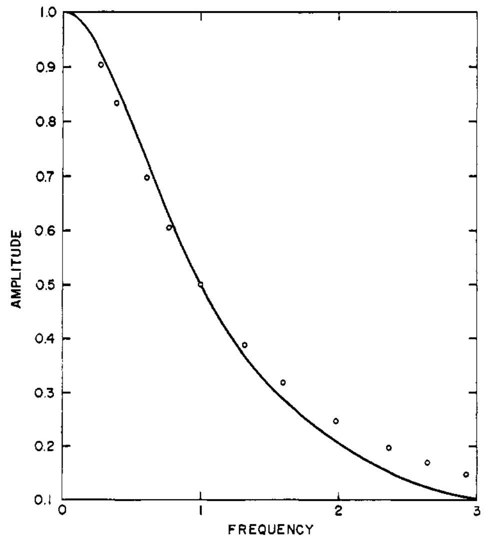

Figure 3. Calculated light spectrum for a polydisperse sample with $z = 1$, $\alpha = 1.0$, and $x = 0.1$: —, Lorentzian; O, spectrum for polydisperse sample. Frequency units are arbitrary.

shown in Figure 1 would probably be indistinguishable from a single Lorentzian. With values of $z$ greater than unity, the effect of varying $\alpha$ on the spectral shape is sharply diminished. This is to be expected, since as $z$ is increased the distribution of molecular weights becomes narrower and the spectrum tends toward the single Lorentzian shape characteristic of a monodisperse material. Computation of spectra for several values of $x$ showed that the shape of the spectrum was practically independent of $x$ for $x \leq 1.0$. This implies that for a sample with values of $z$, $x$, and $\alpha$ in the range considered in Table I, the spectral shape will be independent of angle. Such behavior contrasts with the characteristic effect of intramolecular motions on the spectrum; in cases where intramolecular motions contribute the spectrum changes shape significantly with angle.[2,3]

Although an experimental spectrum for a polydisperse sample may appear to be nearly Lorentzian in form and to have a half-width proportional to $\kappa^2$, the diffusion constant $D_c$ calculated from this half-width bears no obvious relation to the diffusion constant of any particular species in the distribution. A relationship may be established by numerical computation, however. For given values of $z$, $\alpha$, and $x$, calculations using eq 1 were made of the spectrum as a function of $\kappa^2$ for fixed values of $\langle s^2 \rangle_w$ and $D_w$. These calculations were performed on an IBM 360/50 computer using a 24-point Gaussian–Laguerre quadrature formula.[5] A value of $D_c$ was computed from the half-width of the composite spectrum obtained, and the ratio $D_c/D_w$ was calculated. Values of $D_c/D_w$, the ratio of the diffusion constant calculated from the half-width of the composite curve to that of the species of weight-average molecular weight, are summarized in Table I as a function of $z$, $x$, and $\alpha$. The ratio is seen to approach unity with increasing $z$ (decreasing polydispersity) and to decrease with increasing $\alpha$ (better solvent). To the extent that the integrand of eq 1 is independent of $x$, the ratios given in Table I should be independent of $x$. An influence of $x$ is shown, however; the variation of the ratio with $x$ shows the amount of deviation of the proportionality of the half-width to $\kappa^2$ to be expected with increasing $x$.

It should be noted that in the derivation of eq 1 the assumption is implicitly made that the mean-square radius of gyration $\langle s^2 \rangle$ for a random-coil macromolecule is proportional to $M$, the molecular weight. This is very satisfactory for a $\Theta$ solvent, but in good solvents the relationship is more accurately represented by

$$\langle s^2 \rangle \propto M^{1+\epsilon} \tag{8}$$

where $\epsilon$ is zero for a $\Theta$ solvent and becomes greater than zero for better solvents. The upper limit of $\epsilon$ may be estimated from the lattice calculations of Mazur and McCracken,[6] who find the maximum value of the corresponding exponent in the relation between mean-square end-to-end distance and chain length to be 0.2. It is reasonable to expect that $\langle s^2 \rangle$ may depend upon chain length in nearly the same way, and the upper limit of $\epsilon$ should be near 0.2.

TABLE II
EFFECT OF $\epsilon$ ON $(D_c/D_w)$ RATIO FOR $\alpha = 0.75$

| $x$ | $\epsilon$ | $z$: 1 | $z$: 10 |
|---|---|---|---|
| 0.1 | 0.00 | $0.69_8$ | $0.92_3$ |
| | 0.20 | $0.70_0$ | $0.92_3$ |
| | 0.33 | 0.703 | 0.923 |
| 1.0 | 0.00 | $0.76_6$ | $0.94_2$ |
| | 0.20 | $0.79_1$ | $0.94_6$ |
| | 0.33 | 0.807 | 0.949 |

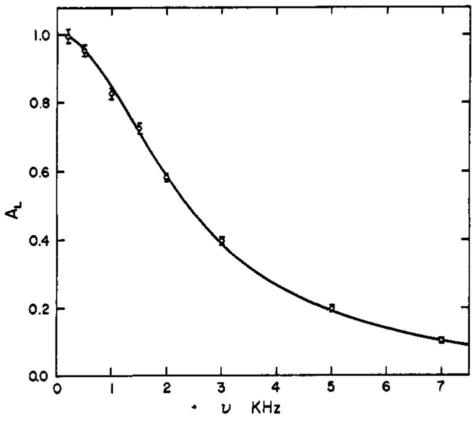

Figure 4. Spectrum of photocurrent due to light scattered from 0.54% NBS-706 polystyrene in cyclohexane at $\theta = 90°$: $\overline{\underline{\Phi}}$, experimental; —, Lorentzian of half-width 2380 Hz. Data were taken at 35.0°.

When the derivation of eq 1 is repeated using eq 8, the result analogous to eq 1 is

$$\omega S_{0z} = \frac{\delta(z+1)^{\alpha+\epsilon}}{xz!} \int_0^\infty \left[\operatorname{erf}\left(\frac{1}{2}\sqrt{x\left(\frac{t}{z+1}\right)^{1+\epsilon}}\right)\right]^2 \times \left[\frac{t^{z+\alpha-\epsilon} \exp\left\{\frac{-x}{6}\left(\frac{t}{z+1}\right)^{1+\epsilon}\right\}}{t^{2\alpha} + \delta^2(z+1)^{2\alpha}}\right] e^{-t}\mathrm{d}t \tag{9}$$

In order to evaluate the effect of $\epsilon$ on the shape and breadth of the spectrum, eq 9 was used to calculate spectra for a few values of $z$, $\alpha$, and $\epsilon$. As before, the calculation was performed on an IBM 360/50 computer using a 24-point Gaussian–LaGuerre quadrature formula. Spectra computed for $\epsilon = 0.0$ agreed to four significant figures with those computed using eq 1. The results are given in Table II, which gives computed values of the ratio $D_c/D_w$ as a function of $z$, $x$, and $\epsilon$ while $\alpha$ is held constant at 0.75. The greater the value of $\alpha$ chosen, the greater will be the influence of the parameter $\epsilon$; the value of 0.75 chosen here for $\alpha$ is near the largest observed experimentally for random-coil polymers. Values of $\epsilon$ as high as 0.33 were taken, although this seems much higher than is likely to be observed experimentally. As is shown in Table II, the effect of $\epsilon$ is negligible except for highly polydisperse (low $z$) samples at high values of molecular weight or scattering angle (high $x$).

## Experimental Section

The solution of 0.45 wt % NBS-706 polystyrene was prepared in spectral grade cyclohexane as previously described.[2] This polymer, originally prepared by thermal polymerization, has a distribution of molecular weights near to a most probable distribution. The distribution is thus adequately represented by the Schulz distribution incorporated in the derivation of eq 1 with the parameter $z$ set equal to unity. The number-average molecular weight of the polymer determined by osmotic pressure measurements is given by the National Bureau of Standards as 136,500 and the ratio of weight-average to number-average molecular weights as determined by fractionation is given as 2.1:1. The weight-average molecular weight measured by light scattering is given as 257,800, and the weight average measured by sedimentation equilibrium is given as 288,100.

A typical spectrum of light scattered from the cyclohexane solution at 35.0° is shown in Figure 4 for data taken at a scattering angle

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(5) A. H. Stroud and D. Secrest, "Gaussian Quadrature Formulas," Prentice-Hall, Englewood Cliffs, N. J., 1966.

(6) J. Mazur and F. L. McCracken, *J. Chem. Phys.*, **49**, 648 (1968).

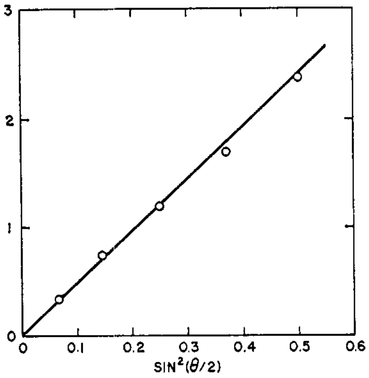

Figure 5. Plot of photocurrent spectral half-width against $\sin^2(\theta/2)$ for 0.54% NBS-706 in cyclohexane. Data were taken at 35.0°.

$\theta$ of 90°. Error bars representing most probable errors were calculated as determined previously.[2] This spectrum is very well fit by a Lorentzian, as are the spectra at angles of 30, 45, 60, and 75°. The angular dependence of the half-width is given in Figure 5 and it is clear that within experimental error the half-width is proportional to $\sin^2(\theta/2)$. The half-widths observed were 335 Hz at 30°, 745 Hz at 45°, 1190 Hz at 60°, 1690 Hz at 75°, and 2380 Hz at 90°.

A solution of 0.59 wt % of the same polymer was prepared in 2-butanone. The solvent, Fisher Scientific reagent grade, was filtered through a Flotronic metal filter with 450-nm pore size and used without further purification. The polymer solution was gravity filtered before use through a Flotronic metal filter having 200-nm pore size.

Results obtained with the 2-butanone solution, for which data were taken at scattering angles of 30, 45, 60, 75, and 90° were very similar to those obtained with the cyclohexane solution. A representative spectrum for $\theta = 45°$ is shown in Figure 6. Data at this angle are more precise than data at higher angles, where the breadth of the spectrum is so large that shot noise makes a large contribution to the spectrum. The angular dependence of the half-width is given in Figure 7 for the 2-butanone solution. The spectrum at each angle is Lorentzian within experimental error, and the half-width is proportional to $\sin^2(\theta/2)$. The observed half-widths were 645 Hz at 30°, 1355 Hz at 45°, 2410 Hz at 60°, 3380 Hz at 75°, and 4640 Hz at 90°.

## Discussion

The Lorentzian line shape and proportionality of the line width to $\kappa^2$ observed for NBS-706 in cyclohexane and in 2-butanone is in complete accord with theory. For this polymer the mean-square radius of gyration of the species with weight-average molecular weight in cyclohexane at 35.0° may be calculated from the relation given by Berry[7]

$$\langle s^2 \rangle = (7.6 \times 10^{-18} M)$$

The value of $\kappa$, the magnitude of the scattering vector, is given by

$$\kappa = (4\pi n/\lambda_0)\sin^2(\theta/2) \qquad (10)$$

Use of either the sedimentation or light scattering value of the weight-average molecular weight with the expressions above and eq 3 shows that the maximum value of $x$ attained at $\theta = 90°$ is about 0.09 for either the cyclohexane or 2-butanone solution. As is evident from Table I, the ratio $D_c/D_w$ is nearly constant for values at $x$ in this range, and accordingly near-proportionality between the half-width and $\sin^2(\theta/2)$ should be observed.

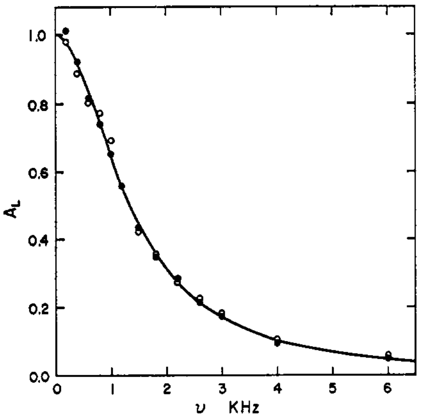

Figure 6. Spectrum of photocurrent due to light scattered from 0.59% NBS-706 polystyrene in 2-butanone at $\theta = 45°$: ○, ●, experimental; —, Lorentzian of half-width 1355 Hz. Data were taken at 25.0°.

For polystyrene in cyclohexane at 35.0° the value of $\alpha$ has been reported[8] as 0.49, close to the value of 0.5 for which calculations have been made in Table I. In the case of the 2-butanone solution at 25.0°, $\alpha$ has been reported[9] as 0.53, again close to the value of 0.5 for which calculations have been made. Both systems may then be represented by values of the parameters $z = 1.0$ and $\alpha = 0.5$, with $x$ being below 0.09. As shown by numerical calculation, curves calculated with these values of parameters are very nearly Lorentzian in form and have half-widths nearly proportional to $\sin^2(\theta/2)$. This case corresponds to the calculated curve shown in Figure 1.

Whether the quantitative relationship given in Table I between the diffusion constant calculated from the apparent Lorentzian spectra observed for polydisperse samples and the diffusion constant of the species of weight-average molecular weight is correct cannot be verified precisely using presently available experimental results. Accurate relationships between $D$ and $M$ for the systems under consideration are necessary. These relationships must be established in the limit of zero concentration using accurately characterized samples with very sharp molecular weight distributions. The establishment of correct zero-concentration limiting values of $D$ is difficult because of the decreased precision of experiments at low concentrations and the rapid changes in the diffusion constant with concentration at very low concentrations.[10]

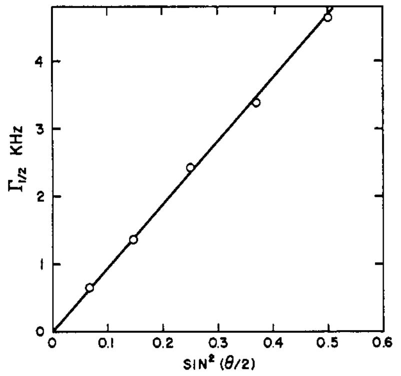

Figure 7. Plot of photocurrent spectral half-width against $\sin^2(\theta/2)$ for 0.59% NBS-706 in 2-butanone. Data were taken at 25.0°.

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[7] G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).

[8] H. J. Cantow, *Makromol. Chem.*, **30**, 169 (1959).

[9] N. C. Ford, W. Lee, J. E. M. Owen, and F. E. Karasz, *Bull. Amer. Phys. Soc.*, **14** (II), 362 (1969) (abstract).

[10] V. N. Tsvetkov and S. I. Klenin, *J. Polym. Sci.*, **30**, 187 (1958).

In addition, the required data should be obtained by means of Rayleigh line-broadening measurements, since it is not yet clearly established that diffusion constants obtained by other methods are identical with results from line broadening. (For polystyrene in cyclohexane at 35.0° at concentrations under 2%, values of the diffusion constants obtained in this laboratory[2,11] are 15–25% lower than those obtained by Cantow[8] from ultracentrifuge experiments on the same system.)

Analysis of the data for NBS-706 polystyrene in cyclohexane reported above yield a single diffusion constant of $1.89 \times 10^{-7}$ $cm^2\ sec^{-1}$ at a concentration of 0.54% polymer by weight. A plot of log $D$ against log $M$ using data obtained previously for the polystyrene–cyclohexane system[2] at about the same polymer concentration can be used to determine an estimated value of the diffusion constant of the species having the weight-average molecular weight. For $M$ equal to 257,800 ($M_w$ from light-scattering), the value of $D$ estimated in this fashion is approximately $2.16 \times 10^{-7}$ $cm^2\ sec^{-1}$; for $M$ equal to 288,100 ($M_w$ from sedimentation equilibrium) the estimated value of $D$ is $2.07 \times 10^{-6}$ $cm^2\ sec^{-1}$. The experimentally determined ratio $D_c/D_w$ is thus 0.87 or 0.91, depending on whether the value of $M_w$ from sedimentation or light scattering, respectively, is used. These values compare very favorably with the computed value of 0.82 given in Table I for $x = 0.1$, $\alpha = 0.5$, $z = 1$. The agreement can probably be considered excellent when it is taken into account that all the data used in calculating the experimental value of $D_c/D_w$ were obtained at a fairly high concentration.

## Summary

The experimental results reported here confirm two predictions of theory for the spectrum of light scattered from polydisperse samples of random-coil polymers of relatively low molecular weight. The spectrum from samples with fairly broad distributions of molecular weight will be close to a single Lorentzian, and discrepancies from the Lorentzian form will be detectable only by measurements of very high precision. Second, the angular dependence of the spectral half-width for such samples will be very nearly proportional to $\kappa^2$. These results point out the relative insensitivity of line-width studies to sample polydispersity; this should be taken into account in interpretation of diffusion studies by this technique. On the other hand, this insensitivity may be beneficial in studies of other variables (*e.g.*, intramolecular motion) because of the lack of complication due to polydispersity.

Finally, additional experimental work will be necessary to allow quantitative comparison of theory for polydisperse materials with experimentally observed apparent diffusion constants. Particular emphasis should be placed on obtaining reliable extrapolated values at zero concentration and on firm establishment of the relationship between diffusion constants obtained by spectral determinations and those obtained by other methods.

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(11) T. F. Reed, Ph.D. Thesis, The University of Akron, 1970.

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# A Nuclear Magnetic Resonance Study of Poly(L-proline) in Aqueous and Aqueous Salt Solutions

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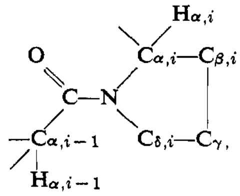
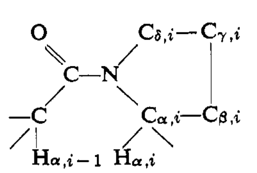
ABSTRACT: The isomerization of poly(L-proline) I has been followed in $D_2O$ using 220-MHz nmr. It was found that the reaction follows zero-order kinetics with an activation enthalpy of *ca.* 23 kcal/mol. It is suggested, on the basis of these results and the behavior during the reaction of the clearly observed α-trans and α-cis proton resonances, that in $D_2O$ isomerization begins at the carboxyl end of the polymer and proceeds in a stepwise fashion down the chain. The effects of concentrated solutions of KI, NaSCN, $CaCl_2$, and LiBr on the structure of poly(L-proline) I and II were also examined using 220-MHz nmr. Resonances corresponding to both α-trans and α-cis protons were found in all these solutions. It is therefore concluded that the disruption of the ordered poly(L-proline) structure in these solutions is primarily due to the presence of both trans and cis peptide bonds randomly distributed along the polymer chain.

The conformational isomerization of poly(L-proline) in water and organic solvents and the effects of high concentration of salts on the structure of poly(L-proline) have been the subject of many investigations employing optical and hydrodynamic techniques. A detailed discussion of this work will not be given since several recent reviews summarizing and evaluating these results are available.[1-3] One conclusion resulting from previous work is that when poly(L-proline) I, containing only cis peptide bonds, is dissolved in water, it undergoes an isomerization at the peptide bonds and is converted to the all-trans form II. The geometry of the peptide bond in the trans and cis conformations is shown. The *i*th



trans



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