Effect of Molecular Weight on the Rayleigh Line Spectrum of Polystyrene in 2-Butanone

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ABSTRACT: The spectrum of the Rayleigh line in the light scattered from dilute solutions of polystyrene in 2-butanone at 25° has been measured for four samples ranging in molecular weight from about 8.7×10^5 to 5×10^7. All spectra were fit fairly well by single least-squares Lorentzians, although small deviations from the least-squares Lorentzians were noticeable at high molecular weights. The spectral breadth increased more rapidly than in proportion to the square of the scattering vector κ^2 for the high molecular weight samples. This result is attributed to simultaneous effects of polydispersity and intramolecular motion. Calculations based on theory by Pecora and Tagami for the effect of intramolecular motion show that only small deviations of the spectral shape from a single Lorentzian are to be expected, although significant increases in the spectral breadth beyond that predicted from proportionality to κ^2 may be observed. The data are in accord with these predictions. The calculations and experimental results given establish guidelines for predicting when effects of polydispersity and intramolecular motion can influence measurement of translational diffusion coefficients for high molecular weight random-coil polymers, and they also allow specification of the restricted conditions where semiquantitative information concerning intramolecular motion may be obtained from Rayleigh line spectroscopy.

According to theory,[1-3] the Rayleigh line in the spectrum of light scattered from a dilute solution of a random-coil polymer contains information about both translational diffusion and intramolecular motions of the solute macromolecules. Several recent publications[4-6] have dealt with the application of line-width spectroscopy to experimental determination of translational diffusion coefficients, but comparatively little work has been reported which deals explicitly with the contributions of intramolecular motions to the spectrum. This latter aspect deserves further attention, however, since intramolecular motions in random-coil polymers are themselves the subject of extensive study, and the potential of an additional method for their investigation should be established. Also, the conditions under which intramolecular motions significantly influence the spectrum must be known in order that errors in the determination of translational diffusion coefficients may be avoided.

Effects of intramolecular motions on the Rayleigh line spectrum of macromolecules in solution are predicted to be observable only when the scattering species has an average dimension which is an appreciable fraction of the wavelength of the incident light.[1-3] This condition is satisfied for random-coil polymers only at high molecular weights. Unfortunately, the minimum degree of polydispersity attainable in synthetic random-coil polymers increases with molecular weight, and additional effects of polydispersity, when present, are likely to occur simultaneously with the effects of intramolecular motion.

In order to establish guidelines for when molecular weight dependent effects are important, Rayleigh line spectra have been obtained for dilute solutions in 2-butanone of several polystyrenes covering a wide range of molecular weight. Samples having molecular weight distributions as narrow as are commonly available have been used. The solvent chosen, 2-butanone, is one for which the specific refractive index increment dn/dc for polystyrene is high, making measurements possible at relatively low concentrations and thereby minimizing concentration effects.

Experimental Section

Details of the spectrometer and its operation have been reported previously.[7] Spectral data given here were obtained using the same methods described before. As will be shown, it was appropriate to fit all the spectra obtained to a single Lorentzian functional form. Such fits were performed using a computer least-squares program which weights the spectral amplitude at each frequency in inverse proportion to its variance, as described elsewhere.[6,7] This procedure achieves a two-parameter fit, one of these being the least-squares half-width and the other being the zero-frequency amplitude. For graphical presentation all spectral amplitudes have been divided by the least-squares zero-frequency amplitude.

Solutions of four polystyrene samples were prepared by weight. In order to eliminate possible significant effects of dust[6] on the spectra, all solutions were filtered through 450-nm Flotronics filters and centrifuged in a two-compartment cell for 2 hr at 1000 g immediately before spectral measurements were made.

Characterization data for the samples used and the concentrations at which measurements were made for each sample are given in Table I. Samples W 25167 and W 61970 were obtained from Waters Associates, who supplied the characterization data given. Samples LJF-9 and LJF-13-1 were made by anionic polymerization by Dr. L. J. Fetters and characterized by Mr. E. F. Slagowski. Approximately 0.1 wt % solutions were prepared for samples W 25167, W 61970, and LJF-9. This is near the lowest concentration at which solute scattering is high enough to allow reasonably precise spectral determinations over a range of angles for these samples. The angular dependence of the spectrum for the high molecular weight sample LJF-13-1 was readily observable using a 0.02 wt % solution.

Results

It is well established that for solutions of polymers having low or medium molecular weight the spectrum of the Rayleigh line is Lorentzian with half-width proportional to the square of the scattering vector κ^2. The scattering vector is given by $\kappa = (4\pi n/\lambda_0) \sin(\theta/2)$, where λ_0 is the wavelength of the incident light, n is the refractive index of the solution, and

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(1) R. Pecora, *J. Chem. Phys.*, **49**, 1032 (1968).
(2) Y. Tagami and R. Pecora, *ibid.*, **51**, 3293 (1969).
(3) R. Pecora and Y. Tagami, *ibid.*, **51**, 3298 (1969).
(4) N. C. Ford, Jr., F. Karasz, and J. E. Owen, *Discuss. Faraday Soc.*, **No. 49**, 228 (1970).
(5) J. E. Frederick, T. F. Reed, and O. Kramer, *Macromolecules*, **4**, 242 (1971).
(6) O. Kramer and J. E. Frederick, *ibid.*, **4**, 613 (1971).
(7) T. F. Reed and J. E. Frederick, *ibid.*, **4**, 72 (1971).

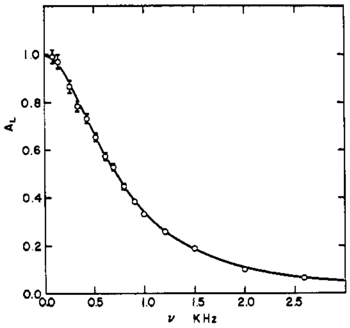

Figure 1. Photocurrent spectrum due to light scattered from 0.11 wt % W 25167 polystyrene in 2-butanone at $\theta = 40°$: O, experimental; ——, least-squares Lorentzian with half-width = 710 Hz. Data were taken at 25.0°.

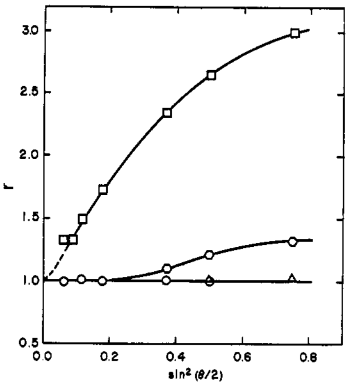

Figure 2. Relative spectral broadening r for four polystyrenes in 2-butanone at 25.0°: O, W 25167; Δ, W 61970; O, LJF-9; □, LJF-13-1.

Table I
Sample Characteristics and Diffusion Coefficients for Polystyrene Dissolved in 2-butanone

Polymer identification	M_w	M_w/M_n	Wt % polymer[c]	D, cm² sec⁻¹
W 25167	867,000	1.12	0.11	2.55×10^{-7}
W 61970	2,145,000	1.21	0.15	1.72×10^{-7}
LJF-9	4,500,000[a]	[b]	0.093	1.03×10^{7}
LJF-13-1	50,000,000[a]		0.02	

[a] From light scattering. [b] M_z, obtained from ultracentrifuge measurements, is about 5.6×10^6. [c] Multiplication of these values by the solvent density, 0.80 g cm⁻³, gives the solution concentration in grams of solute per milliliter of solution.

θ is the scattering angle. The results for sample W 25167 (M_w = 867,000) typify this behavior. Excellent Lorentzian spectra like that shown in Figure 1 were obtained over the range of angles 30–90°, and the photocurrent spectral half-width $\Gamma_{1/2}$ was proportional to $\sin^2(\theta/2)$. A plot of $\Gamma_{1/2}/\sin^2(\theta/2)$ is accordingly flat. The average over five angles from 30 to 90° of $\Gamma_{1/2}/\sin^2(\theta/2)$ was used to calculate the diffusion coefficient D by substitution in the relation

$$D = \Gamma_{1/2}(\lambda_0/n)^2/16\pi \sin^2(\theta/2) \qquad (1)$$

As for all solutions, n was taken as equal to 1.374, characteristic of the solvent, and λ_0 was taken as 632.8 nm. The value of D obtained is given in Table I.

An alternative means of illustrating the proportionality of the half-width to κ^2 is based on eq 1, which may be written in the form $\pi\Gamma_{1/2} = \kappa^2 D$. The average over angle of $\Gamma_{1/2}/\sin^2(\theta/2)$ may be used to calculate D, and the ratio $r \equiv (\pi\Gamma_{1/2}/\kappa^2 D)$ may then be plotted as a function of angle. When only translational diffusion contributes to the spectral broadening, this ratio should have a constant value of unity regardless of angle. This type of plot is given in Figure 2, where the data for W 25167 are plotted as circles; the ratio r is within experimental error equal to unity at all angles for this polymer.

Theory predicts that for random-coil polymers of high molecular weight the spectrum should consist of the Lorentzian form characteristic of translational diffusion plus other Lorentizian contributions arising from intramolecular motion.[1–3] The breadths of the contributions from intramolecular motions do not vary in proportion to κ^2, and the relative intensities of these contributions increase monotonically from a value of zero in the limit of zero scattering angle. It would be expected that for high molecular weight solutes the spectra may be Lorentzian with half-width proportional to κ^2 only at small scattering angles. At high scattering angles where intramolecular motions contribute significantly, the spectra may become non-Lorentzian, and the breadth may no longer be proportional to κ^2. The previously reported angular dependence of the spectra for polystyrenes W 61970 and LJF-9 in cyclohexane[7] indicated that both of these theoretically predicted effects were observable. However, the procedure used for analyzing these spectral data involved fitting the high-frequency tails of the spectra with a single Lorentzian. This procedure caused large apparent deviations from a Lorentzian form at low frequencies and tended to magnify the non-Lorentzian character of the spectra in a somewhat arbitrary way.

An alternative procedure which is subject to less bias in giving an estimate of deviations from a Lorentzian form is to fit spectra to single Lorentzian forms by least squares. When the present data for solutions of polystyrenes W 25176, W 61970, LJF-9, and LJF-13-1 in 2-butanone were analyzed in this way, in no case did any spectrum obtained differ very markedly from the least-squares single Lorentzian with which it was fit. There was, however, a slight deviation observed for samples of LJF-9 and LJF-13-1, examples of which are given in Figures 3 and 4. The experimental points fall slightly below the least-squares curve at frequencies just below the half-width, and high-frequency points lie somewhat above the least-squares curve. These effects, although small, were observed consistently in high-angle spectra of LJF-9 and for spectra at all angles in the range 30–120° for sample LJF-13-1. Because the deviations were in no case large and all spectra could be fit fairly well with single Lorentzians, the half-width $\Gamma_{1/2}$ of the least-squares Lorentzian was used as a convenient and unbiased indicator of the spectral breadth.

Although large deviations from a Lorentzian form were not seen even for spectra of the samples of highest molecular weight studied, the deviation of the spectral breadth from proportionality to κ^2 was readily observable with increasing molecular weight. For sample W 61970, the spectra were all Lorentzian within experimental error and similar to those obtained for W 25167. The least-squares spectral half-width was proportional to κ^2 over the range of angles 30–90°. At $\theta = 120°$ there was a slight increase in the ratio $\Gamma_{1/2}/\sin(\theta/2)$. The average value of this ratio over the range 30–90° was used in eq 1 to calculate the value of D given in Table I. This value of D was then used to plot the data in the form given in Figure 2. Only two points corresponding to data at $\theta = 90$ and 120° have been plotted; low-angle points scatter about a value of unity, like the points for W 25167.

In the case of samples LJF-9 and LJF-13-1, there was a significant rise in the ratio $\Gamma_{1/2}/\sin^2(\theta/2)$ over the experimentally accessible range of angles. For LJF-9 this ratio was practically the same for $\theta = 30$ and 40°; the average value over these two angles was used to calculate the value of D given in Table I and to plot the results in Figure 2. It is apparent from Figure 2 that the half-width at high angles for LJF-9 is about 30% higher than it would be if $\Gamma_{1/2}$ were proportional to κ^2. For sample LJF-13-1, the ratio $\Gamma_{1/2}/\sin^2(\theta/2)$ was not constant even in the lowest range of angles experimentally accessible (30–40°), and a value of D was not obtainable from line-width measurements. No literature data are available which allow estimation of the diffusion coefficient for this very high molecular weight polymer, even in the limit of zero concentration, and very little is known of the concentration dependence of D at this molecular weight. In order that the data for LJF-13-1 could be compared with the results in Figure 2 for the other samples, a rough estimate of D was made by extrapolating $\Gamma_{1/2}/\sin^2(\theta/2)$ to zero angle and using the extrapolated value in eq 1. The resulting value of D, 3.5×10^{-8} cm² sec⁻¹, may easily be considerably in error. The uncertainty in D means that the vertical positions of the points for LJF-13-1 in Figure 2 may be incorrect. However, this does not obscure the important result that spectral half-widths at high angles are about three times as broad as would be predicted from proportionality of $\Gamma_{1/2}$ to κ^2.

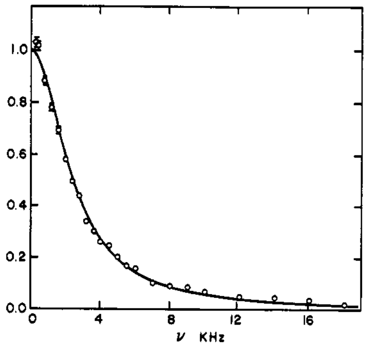

Figure 3. Photocurrent spectrum due to light scattered from 0.093 wt % LJF-9 polystyrene in 2-butanone at $\theta = 120°$: O, experimental; ——, least-squares Lorentzian with half-width = 2431 Hz. Data were taken at 25.0°.

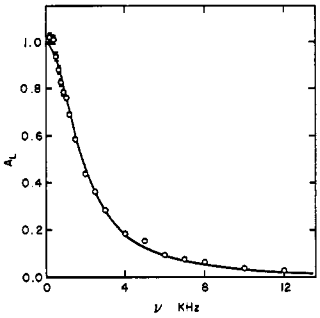

Figure 4. Photocurrent spectrum due to light scattered from 0.02 wt % LJF-13-1 polystyrene in 2-butanone at $\theta = 120°$: O, experimental; ——, least-squares Lorentzian with half-width = 1876 Hz. Data were taken at 25.0°.

Effect of Polydispersity at High Molecular Weight. The increase of the spectral breadth more rapidly than in porportion to κ^2 is the most noteworthy feature of the results for high molecular weight solutes. It was pointed out previously[7] that this effect is not likely to be due to finite concentration or to critical scattering. The most likely remaining possibilities are that the excess broadening is due to the influence of polydispersity on the translational spectrum at high molecular weight or that intramolecular motion is influencing the spectrum.

An indication of the amount of excess broadening to be expected because of polydispersity is readily obtained from theory.[2,3] The quantity which determines the range over which excess broadening would be predicted is the parameter x, defined as $\kappa^2\langle s^2\rangle_w$, where $\langle s^2\rangle_w$ is the mean-square radius of gyration of the species having molecular weight equal to the weight-average molecular weight. For x ranging up to a few tenths, a difference of only a few per cent is predicted between the calculated dependence of the half-width and proportionality to κ^2. This prediction has been confirmed[5,6] using a polystyrene of relatively low weight-average molecular weight having the fairly broad most probable molecular weight distribution. For the experimental conditions under which the data reported here were obtained, the value of x becomes much higher than a few tenths, however: up to about 1.9 for LJF-9 at $\theta = 120°$ and up to about 21 for LJF-13-1 at $\theta = 120°$. Calculations of the variation of the half-width with x must accordingly be extended to higher values in order to estimate the excess broadening due to polydispersity.

The variation of the half-width with x depends on two system parameters for which values must be chosen. One of these is the exponent α in the relationship between the diffusion constant and the molecular weight

$$D_0 = CM^{-\alpha}$$

where C and α are constants characteristic of the polymer and solvent at a given temperature. The second parameter is z, which specifies the breadth of the Schulz distribution of molecular weights $f(M)$ assumed in theoretical calculations

$$f(M) = (1/z)y^{z+1}M^z \exp(-yM)$$

where $Y = (z + 1)/M_w$. Rayleigh line-width studies of the diffusion of polystyrene in 2-butanone show than α is not far from 0.5 for this system.[4,6] The value of z is readily calculated from the weight- and z-average molecular weights, since for the Schulz distribution $M_z/M_w = (z + 2)/(z + 1)$. The value of z is thus about 3.5 for sample LJF-9, and preliminary characterization data[8] for LJF-13-1 indicate that z is between 3 and 5.

Calculations of spectra for polydisperse samples were performed as described previously[5] with $\alpha = 0.5$ for values of z of 3 and 5; these values of z bracket the distributions of LJF-9 and LJF-13-1. Additional calculations were performed with $\alpha = 0.5$ and $z = 10$ in order to estimate the effect of polydispersity in the case of a vary narrow distribution. The results are plotted in Figure 5 as D_c/D_w against x, where D_c is the apparent diffusion coefficient of the polydisperse sample and D_w is the diffusion coefficient of the species having the weight-average molecular weight. (This figure is an extension of the data of Table I of ref 5.) It is apparent that in contrast to the situation where x varies over only a small range, there can be significant excess broadening when a large range of x is covered. The calculated excess is about 6% when x

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(8) D. McIntyre and E. F. Slagowski, private communication.

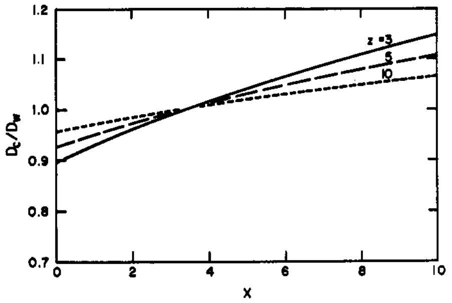

Figure 5. Variation of D_c/D_w with x for three values of the parameter z: ——, $z = 3$; – – –, $z = 5$; ------, $z = 10$.

ranges from 0 to 2 with $z = 3$, and it is about 28% when x ranges from 0 to 10 for $z = 3$. Although these results are for the light spectrum, it would be expected that the variation of the width of the homodyning photocurrent spectrum would be of similar magnitude.

While not negligible, the calculated excess broadening due to the effect of polydispersity on the translational portion of the spectrum is still in the case of both LJF-9 and LJF-13-1 only a fraction of that observed. Most of the excess must be due to some other cause. It is reasonable to attribute this to intramolecular motion, and it is in fact possible to show that the results are in qualitative agreement with the theory for this effect. In order to do so, we give a simplified analysis based on theory for intramolecular motion given by Pecora and Tagami.[2,3]

Analysis of Spectra Influenced by Intramolecular Motion. The simultaneous excess broadening due to polydispersity and contributions of intramolecular motion to the spectrum seem to preclude analysis of the present data to obtain quantitative information about intramolecular motion. It is still useful, however, to attempt a qualitative comparison with theory. In addition to showing that the observed effects are consistent with theoretical predictions, such a comparison points out the conditions under which quantitative analysis may be made and outlines the method by which data may be analyzed. The calculations below are based on the assumption of a monodisperse sample, since it appears from the calculations above that quantitative analysis of the effects of intramolecular motion will not be possible for samples which are appreciably polydisperse, because the effects of intramolecular motion and polydispersity enter in the same way.

According to the theory of Pecora and Tagami,[1-3] the spectrum $S(\kappa, \omega)$ of the Rayleigh line in light scattered by a dilute solution of monodisperse random-coil macromolecules is given by

$$S(\kappa, \omega) = \frac{1}{\pi}\left\{P_0(x)\frac{\kappa^2 D}{(\omega - \omega_0)^2 + (\kappa^2 D)^2} + \sum_{\substack{k=2\\(k\ \text{even})}}^{\infty} P_1(x, k)\frac{\kappa^2 D + (1/\tau_k)}{(\omega - \omega_0)^2 + [\kappa^2 D + (1/\tau_k)]^2} + \sum_{k=1}^{\infty} P_2(x, k, k')\frac{\kappa^2 D + (2/\tau_k)}{(\omega - \omega_0)^2 + [\kappa^2 D + (2/\tau_k)]^2} + \ldots\right\} \quad (2)$$

Here ω_0 is the frequency of the incident light, ω is the frequency of the scattered light, the τ_k's are relaxation times of the normal modes[9,10] and the factors P_0, P_1, and P_2 are the intensities of scattering corresponding to the Lorentzian terms which they multiply. The spectrum is seen to consist of a sum of many Lorentizans centered about the frequency of the incident light.

Each of the intensity factors P_i are functions of the parameter $x = \kappa^2\langle s^2\rangle$. Tagami and Pecora[2] have calculated the relative values of the P_i which contribute most strongly to the spectrum as a function of x. The result is that for low values of x ($x \lesssim 1$), P_0 is much larger than the sum of all other P_i's, and only the single Lorentzian corresponding to translational diffusion contributes appreciably to the spectrum. This is the basis of single-Lorentzian analysis of spectra to determine translational diffusion constants, as was done above for the solution of W 25167 and for the solutions of W 61970 and LJF-9 at low angles.

As x becomes large, the other P_i's become a significant fraction of P_0, and the spectrum consists of the Lorentzian due to translation plus other Lorentzians due to intramolecular motion. A general analysis of experimental spectra under these conditions appears impossible, since a multi-Lorentzian fit with several unknown parameters would be required. Accurate determination of more than one or two unknown parameters by curve fitting is not possible given the present accuracy of a few per cent in the amplitude of Rayleigh line spectra at a given frequency.

Fortunately, for a limited range of x ($1 \leq x \leq 3$), the theoretical calculation[2] of the intensities of the various terms in eq 2 shows that only one additional term contributes strongly, that corresponding to P_2 ($k = k' = 1$). Where only this single additional term contributes, the light spectrum is given by

$$S(\kappa, \omega) \propto A\frac{\kappa^2 D}{(\omega - \omega_0)^2 + (\kappa^2 D)^2} + B\frac{(\kappa^2 D + 2/\tau_1)}{(\omega - \omega_0)^2 + (\kappa^2 D + 2/\tau_1)^2} \quad (3)$$

where $A \equiv P_0$ corresponds to the intensity of the translational Lorentzian and $B \equiv P_2$ ($k = k' = 1$) is the intensity of the predominant Lorentizian due to intramolecular motion. This relation, although only approximately valid over a limited range of x, appears to be the most complex with which spectral analysis can presently be attempted. Experimental determination of the spectrum according to eq 3 involves finding three quantities. The first of these is the half-width $\kappa^2 D$ of the Lorentzian due to translation, which may be determined by making measurements at low enough values of x (low angles) so that the second term in eq 3 does not contribute. The second experimental quantity is the half-width of the Lorentzian due to intramolecular motion ($\kappa^2 D + 2/\tau_1$), and the third is the intensity ratio of the two contributions A/B.

Ideally, the latter two quantities could be determined by least-squares fitting of non-Lorentzian spectra, but determination of even two independent parameters in this way is not practical given the present accuracy of our Rayleigh spectra. The analysis is further complicated by the fact that the experimentally observed quantity is the photocurrent power spectral density, which is proportional to the convolution of the light spectrum. Additional information about one of the two remaining parameters must therefore be sought independently of the experiment. One approach is to use theoretical values of the ratio A/B and regard the half-width of the intramolecular Lorentzian as the remaining free parameter. Tagami and Pecora[2] have calculated the relative intensities of the various contributions, thus making available the ratio A/B as a func-

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(9) P. E. Rouse, Jr., *J. Chem. Phys.*, 21, 1272 (1953).
(10) B. H. Zimm, *ibid.*, 24, 269 (1956).

tion of x. They cautioned that their results are based on the bead–spring model of the polymer chain and are not likely to be quantitatively accurate. However, this is the most explicit estimate available of the relative importance of the translational and intramolecular contributions, and we accordingly use it here in order to proceed with an analysis.

Given the translational half-width $\kappa^2 D$ from experiment and estimate of A/B from theory, the half-width of the dominant intramolecular Lorentzian remains as a fitting parameter. It is in principle possible to determine this half-width by restricted least-squares fitting of a spectrum and then to calculate τ_1, the longest intramolecular relaxation time. This has been attempted with high-angle spectra of the solution of LJF-9, with unsatisfactory results. The values of τ_1 obtained are usually in agreement, within a factor of 2, with the value of τ_1 calculated from the low-shear steady-flow viscosity,[11] but this is believed to be fortuitous. Such an analysis of the present data is questionable because of the effects of polydispersity on the breadth and perhaps the shape of the spectrum.

However, use of eq 3 with the assumption that the ratio A/B is known makes it possible to present the results of theory in a simple and concise way that is easily compared with experiment. Two predictions of theory are of particular interest: the shape of the spectrum at values of x where intramolecular motion contributes and the variation of the spectral breadth with scattering angle (or, equivalently, with x). The shape of the spectrum depends on only two quantities, the intensity ratio of the two contributing Lorentzians and the ratio of their half-widths. We may regard the relative intensities as given by theory[2] as a function only of x. It is easily shown that the relative half-widths are also a function of x and a single system parameter q. The ratio of the half-widths is

$$[\kappa^2 D + (2/\tau_1)]/\kappa^2 D = 1 + (2/\tau_1 \kappa^2 D) = 1 + (2\langle s^2\rangle/\tau_1 D x) = 1 + (2/qx)$$

where $q = (D\tau_1/\langle s^2\rangle)$. The half-width ratio thus depends only on x and the constant q, which is characteristic of the system studied. The shape of the spectrum is thus also a function of x alone, with q as a parameter.

The parameter q is dimensionless and in addition is conveniently independent of molecular weight in a Θ solvent. For a Θ solvent, $D \propto M^{-0.5}$ and $\langle s^2\rangle \propto M$. According to the Rouse theory[9]

$$\tau_1 = 6M\eta_s[\eta]/\pi^2 RT \qquad (4)$$

where η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, and RT is the usual product of the gas constant and the absolute temperature. The intrinsic viscosity is proportional to $M^{0.5}$ in a Θ solvent, and accordingly τ_1 is proportional to $M^{1.5}$ according to the Rouse theory. (The same molecular weight dependence is obtained for the Zimm theory,[10] but the proportionality constant is slightly different.) The constant q is thus independent of M in a Θ solvent. The power dependences of D, τ_1, and $\langle s^2\rangle$ on M do not change sharply in good solvents, and so q is not a strong function of M even for good solvents.

With the assumption that the ratio A/B is given by theory, the shape of the spectrum can be calculated at any value of x with q as a parameter. It is therefore important to obtain a numerical estimate of q for a representative system so that this calculation can be performed. A well-studied system for which this estimate can readily be obtained is polystyrene in cyclohexane at the Θ temperature of 35.0°. For this system the diffusion relation has been given by Cantow[12] as

$$D = 1.21 \times 10^{-4} M^{-0.49}$$

The variation of $\langle s^2\rangle$ with molecular weight according to Berry[13] is

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

and τ_1 may be estimated from eq 4 by taking $\eta_s = 0.0057$ P and[12] $[\eta] = 0.07 \times M^{0.50}$. Use of these values shows that q is approximately 0.1–0.2 for this system. A similar calculation for the system polystyrene in 2-butanone, for which less accurate information is available, shows that q should also be in the range 0.1–0.2.

The quantity observed in a homodyning experiment is the power spectral density of the photocurrent resulting when the spectrally distributed light impinges upon the photocathode; accordingly, it is the photocurrent spectrum which should be calculated for comparison with experiment. This photocurrent spectrum is proportional to the convolution[14] of the light spectrum. Convolution of eq 3 gives for the photocurrent spectrum $P(\nu)$

$$P(\nu) \propto A^2\left[\frac{\Gamma_{1/2}}{\nu^2 + \Gamma_{1/2}^2}\right] + 2AB\left[\frac{(\Gamma_{1/2} + 1/\pi\tau_1)}{\nu^2 + (\Gamma_{1/2} + 1/\pi\tau_1)^2}\right] + B^2\left[\frac{(\Gamma_{1/2} + 2/\pi\tau_1)}{\nu^2 + (\Gamma_{1/2} + 2/\pi\tau_1)^2}\right] \qquad (5)$$

where ν is the frequency in hertz of the photocurrent spectrum and $\Gamma_{1/2} = \kappa^2 D/\pi$ is the half-width at half-maximum intensity of the photocurrent spectrum in hertz. Calculations were performed according to eq 5 to determine the shape of the homodyning photocurrent spectrum at various values of x with $q = 0.2$. The ratio A/B for this calculation as well as for others given below was taken from the tabulated results of Tagami and Pecora[2] for a monodisperse sample ($z = \infty$) by assuming that all intensity not distributed in the translational term of eq 3 is distributed in the dominant intramolecular term, the second term of eq 3. This is approximately true only for $x \lesssim 3$, although the present calculations have sometimes been extended further. The results for $x = 2$, 4, and 6 are given in Figure 6. The computed results have been least squares fit to a single Lorentzian, and it is apparent that for this value of q the calculated homodyning spectra do not differ greatly from a least-squares Lorentzian for any value of x. Additional calculations have been performed using other values of q and the same values of the ratio A/B in order to determine at which values of q a large amount of distortion occurs, with the result that serious spectral distortion does not occur unless q is very small ($q \ll 0.1$) and the intensity of the intramolecular Lorentzian is large ($x > 3$).

When the variation of the homodyning spectrum from a Lorentzian is small, the half-width $\Omega_{1/2}$ of the least-squares Lorentzian fit to the calculated spectrum can be taken as a measure of the spectral breadth, as was the case for the experimental data. A concise presentation of the predicted variation of the spectral breadth with x is then possible. The ratio of $\Omega_{1/2}$ to the half-width of the term due to translational

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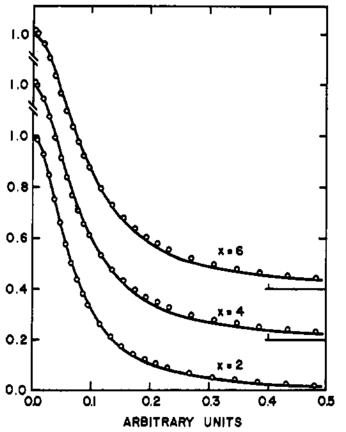

Figure 6. Calculated homodyning spectra for $q = 0.2$ and $x = 2$, 4, and 6, as indicated: ○, computed spectral amplitude; —, least-squares single Lorentzians.

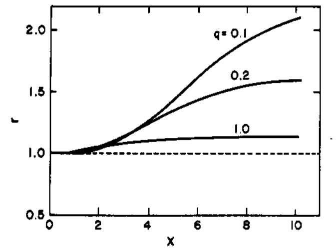

Figure 7. Calculated relative spectral broadening r due to intramolecular motion as a function of x for $q = 0.1$, 0.2, and 1.0.

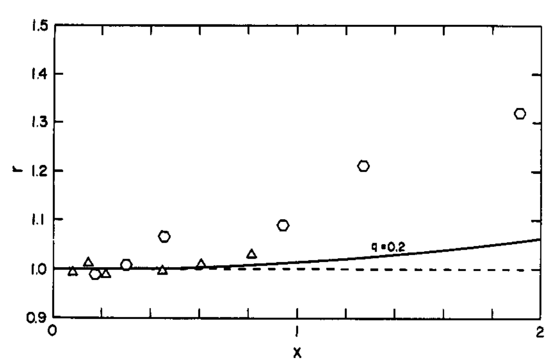

Figure 8. Experimental relative spectral broadening r for W 61970 and LJF-9 polystyrenes compared with the calculated curve for monodisperse polymer with $q = 0.2$: △, W 61970; ○, LJF-9.

diffusion alone can be calculated as a function of x for various values of q. This measure of the excess broadening is exactly comparable to the experimental ratio r plotted in Figure 2. The calculated ratio r is plotted against x in Figure 7 for q = 0.1, 0.2, and 1.0. The plot shows that there is significant excess broadening for $x \gtrsim 2$. Although values of the ratio have been plotted for values of x as high as 10, calculations are not even approximately valid for x higher than about 3 because of failure of the assumption that the spectrum is a sum of only two Lorentzians. Additional intramolecular contributions are very significant at values of x larger than 3.[2]

Comparison of Theory and Experiment. A quantitative comparison of the data for the 2-butanone system with theory is not possible because of the influence of polydispersity on the excess broadening. Several qualitative predictions of theory are confirmed, however. The first of these is that large deviations of homodyning spectra from a least-squares Lorentzian are not observed. The small deviations like those shown in Figures 3 and 4 are in fact similar to the deviations of calculated spectra from a least-squares Lorentzian shown in Figure 6.

A second important prediction of theory is that for scattering from a random-coil molecule in a Θ solvent, plots of relative broadening r *vs.* x should superpose for all molecular weights. The polystyrene–2-butanone system is not a Θ system, but as shown above only a weak dependence of r on M should be observed, since q is only weakly dependent on M in non-Θ solvents. Accordingly, the relative spectral broadening r for samples W 61970 and LJF-9 has been plotted against x in Figure 8, along with the theoretically predicted value for a monodisperse sample with $q = 0.2$. (Although they superpose well, the data for sample LJF-13-1 have been omitted because of the uncertainty in their vertical position.) For comparison, the theoretical prediction for a monodisperse sample with $q = 0.2$ has also been plotted. The degree to which the results for LJF-9 and W 61970 superpose is not well determined by the available data. It is apparent, however, that significant excess broadening is exhibited by this system when x is greater than about 0.8. Also, the observed excess broadening is considerably greater than predicted by theory for a monodisperse polymer. Theory does predict that the intensity of intramolecular contributions is somewhat larger for polydisperse samples,[2] but no quantitative calculations of relative broadening for polydisperse material have been made for comparison with present data because the experimental results are complicated somewhat by the effect of polydispersity on the translational contribution.

Conclusions

The simplified theoretical calculations and data for the polystyrene–2-butanone system given above lead to the following conclusions.

Even for large x, corresponding to high scattering angles or high molecular weight, large deviations of homodyning spectra from a least-squares-fit single Lorentzian are not likely to be observed. This implies that fitting of spectra to more than one Lorentzian to determine the half-width of the component due to intramolecular motion will be imprecise unless spectra of very high accuracy are available. The amount of distortion to be expected for a given system depends on the parameter q, which is characteristic of a system, and on the relative intensities of the contributing Lorentzians.

If the half-width of the least-squares single Lorentzian is taken as the measure of spectral breadth, then for spectra of samples having fairly narrow molecular weight distributions the breadth will begin to increase more rapidly than in proportion to κ^2 for $x \gtrsim$ 0.8–1.0 if we assume that the results given above for the polystyrene–2-butanone system are typical. Experimental evidence for this effect in the polystyrene-2-butanone system is summarized in Figure 8. Because the spectral shape is not expected to deviate greatly from a single Lorentzian for most systems, excess broadening may go undetected and cause errors in routine measurements of translational diffusion coefficients where $x \gtrsim 0.8$. Accordingly, the angular dependence of the half-width should be determined in careful diffusion coefficient measurements of high molecular weight samples, as this is a more sensitive indicator of perturbing effects than the spectral shape.

The conditions under which analysis of spectra is possible to quantitatively determine intramolecular motion are fairly restricted. The molecular weight must be such that at the lowest angles of measurement x is small (less than about 0.5, judging from Figure 8), so that only the translational motion contributes to the spectrum and a value of D may be obtained. At the highest scattering angles x must be about 2–3 so that the maximum possible contribution from the dominant intramolecular term will be observed while contributions from other intramolecular motions remain negligible.

Finally, the fact that even a small amount of polydispersity is predicted to cause some excess broadening and some spectral distortion at high values of x because of its influence on the spectrum due to translation alone implies that samples having very narrow molecular weight distributions must be used if effects of polydispersity are not to interfere with quantitative determination of intramolecular motion.

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Solution Properties of Novel Polyelectrolytes[1]

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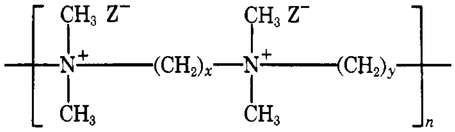
ABSTRACT: A series of polyelectrolytes, of different molecular weights, with the unit segment structure



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_x-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_y-\right]_n$$

were synthesized through the Menschutkin reaction and are referred to as ionene polymers. The solution properties of a high charge density ionene polymer (3,4 Br, $x = 3$, $y = 4$, Z = Br) were compared with those of an ionene polymer in which the positive charges are separated by six CH_2 groups (6,6 Br, $x = 6$, $y = 6$, Z = Br). These polyelectrolytes, when dissolved in aqueous 0.4 M KBr, were found to approximate the behavior of conventional polymers. The intrinsic viscosity–molecular weight relationship in aqueous 0.4 M KBr was determined for 3,4 Br and 6,6 Br by means of the light-scattering technique and can be expressed by $[\eta]_{3,4\mathrm{Br}} = (2.94 \times 10^{-4})M^{0.61}$ and $[\eta]_{6,6\mathrm{Br}} = (6.22 \times 10^{-4})M^{0.58}$. A viscosity study as a function of concentration of a number of potassium salts in water revealed that the reduced viscosity of a 6,6 Br increases as the anions change in the following order: $CNS^- < I^- < NO_3^- < Br^- < Cl^- < F^-$. This trend is attributed to a parallel decrease of counterion site binding. In the absence of added salts, the viscosity behavior is adequately represented by the Fuoss equation.

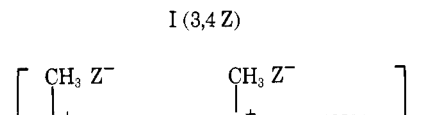
The solution properties of polyelectrolytes are currently of considerable interest. Although a substantial amount of work has been carried out using polyanions, only a limited number of investigations have been performed to elucidate the properties of polycations.

One class of polycations, quaternary ammonium polymers which are readily prepared by means of the Menschutkin reaction,[2] has so far received very little attention. The structure of these cationic polyelectrolytes, termed ionenes, has recently been established,[3] and for several reasons ionenes are ideally suited for a study of polycation behavior. First, their synthesis is simple and straightforward; second, the chains are not branched; third, their molecular weights are in a low range where the viscosity behavior is not complicated by a velocity gradient dependence; and fourth, the charge density in the polymer backbone can be varied readily.

This paper describes part of a study into the solution properties of ionene polymers, covering light-scattering and viscosity measurements.

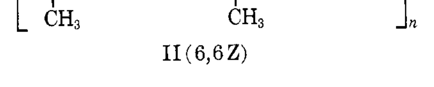
Experimental Section

The 3,4 and 6,6 ionene polymers, having the unit segment structures I and II, respectively, where Z = Br or Cl and n = degree of



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_3-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_4-\right]_n$$

I (3,4 Z)



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_6-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_6-\right]_n$$

II (6,6 Z)

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

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