Rayleigh Line-Broadening Studies of the Motions of Polystyrene in Dilute Solution

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ABSTRACT: A homodyning spectrometer has been used to determine the spectrum of the Rayleigh line in light scattered from 0.5 wt % solutions of polystyrene in cyclohexane. Measurements were made at 35.0° with solute molecular weights ranging from 179,000 to 4,500,000. At low molecular weights the spectra are Lorentzian in form with half-widths $\Gamma_{1/2}$ proportional to the square of the scattering vector κ^2. With increasing molecular weight deviations from a Lorentzian form and from proportionality of $\Gamma_{1/2}$ to κ^2 are observed. Possible causes of these deviations are discussed.

In a series of recent papers[2-8] Pecora has pointed out that measurement of the spectral distribution of the Rayleigh line in light scattered from dilute solutions of macromolecules should be an important addition to present methods of investigating macromolecular motion. According to theory, the Rayleigh line in the light scattered from a dilute solution of identical chain macromolecules should consist of a continuous Lorentzian distribution arising from translational diffusion of the molecules.[4] If the domain of the molecule is an appreciable fraction of the wavelength of the incident light, then additional Lorentzian components are present which are related to the relaxation times of long-range intramolecular configurational changes.[4] Accordingly, Rayleigh line-broadening spectroscopy should serve for small macromolecules as a relatively quick and convenient tool for determination of translational diffusion constants, while for large molecules there is in addition the possibility of studying intramolecular motions in the absence of a strong external field or shear gradient.

We report here the application of Rayleigh line width spectroscopy to study of the motions of polystyrene in cyclohexane at the Θ temperature. The measurements were done over a range of molecular weights in order to determine if the onset of deviations from theory for translation alone could be detected at high molecular weights.

Experimental Section

The homodyning spectrometer, for which a block diagram is shown in Figure 1, is similar to those which have been described at length in the recent literature.[9] The beam from the laser source passes through the sample cell containing the scattering solution, which is located in the center of a cylindrical Pyrex temperature control cell. Beam intensity is controlled by means of the polarization rotator mounted on the laser; only the vertically polarized component of the beam is admitted by the polarizer placed adjacent to the temperature-control cell. Constant temperature is achieved by pumping liquid from a large reservoir through coils surrounding the temperature-control cell. The temperature inside this cell remains constant within a few millidegrees when controlled near room temperature and within a few hundreths of a degree at higher controlled temperatures.

Scattered light is collected by a telescope which may be rotated through an angle θ from 20 to 135° from the incident beam. Light first passes through a slit placed at the focal length of the cylindrical lens formed by the temperature control cell. This light is collected by a lens and focused on a pinhole near the surface of an RCA-7326 photomultiplier tube. This collecting arrangement allows variation of the angular acceptance through variation of the slit width. For measurements reported here, a slit was used which gave an angular acceptance of ±0.15°. The field of view can be selected by choosing the pinhole size; a field approximately 3 mm wide when viewed at right angles to the incident beam is ordinarily chosen.

Building vibrations were found to interfere seriously with measurement unless special precautions were taken. Accordingly the laser source, temperature-control cell and collecting optics were all mounted on an 1800-lb concrete slab which was suspended by heavy coil springs. This spring–mass system is resonant at about 1 Hz and provides very effective isolation from vibrations at frequencies above 10 Hz.

Signals from the photomultiplier pass to a Hewlett-Packard 2470A preamplifier, where they are amplified by a factor of 100. The output of this preamplifier may be read on a slow-response dc voltmeter, which is used to read the direct current in the phototube anode resistor. For given experimental conditions the power of the incident beam is attentuated so that the phototube current is 10 μA or less, well within the range giving linear response. After adjustment of beam power to give the proper dc photocurrent, the signal from the preamplifier is switched to a Singer-Metrics LP-laz spectrum analyzer with RC-3b recorder for analysis of the fluctuating component of the phototube current.

The frequency and amplitude responses of the entire electrical system were calibrated over the range 10–21,000 Hz by injecting a sinusoidal signal of known frequency and amplitude at the photomultiplier load resistor and measuring the response at the recorder. This calibration was necessary to remove appreciable nonlinearity in the amplitude response of the spectrum analyzer as well as to correct for the frequency response of the preamplifier. After application of

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(1) Author to whom correspondence should be addressed.
(2) R. Pecora, *J. Chem. Phys.*, **43**, 1562 (1965).
(3) R. Pecora, *ibid.*, **48**, 4126 (1968).
(4) R. Pecora, *ibid.*, **49**, 1032 (1968).
(5) R. Pecora, *ibid.*, **49**, 1036 (1968).
(6) R. Pecora, *Macromolecules*, **2**, 31 (1969).
(7) Y. Tagami and R. Pecora, *J. Chem. Phys.*, **51**, 3293 (1969).
(8) R. Pecora and Y. Tagami, *ibid.*, **51**, 3298 (1969).
(9) See, for example N. C. Ford and G. B. Benedek, *Phys. Rev. Lett.*, **15**, 649 (1965). Recent general discussions have been given by H. Z. Cummins and H. L. Swinney [*Progr. Opt.*, in press]; see also M. J. French, J. C. Angus, and A. G. Walton, *Science*, **163**, 345 (1969). Details of the instrument used in the present work are given by T. F. Reed, Ph.D. Thesis, The University of Akron, 1970.

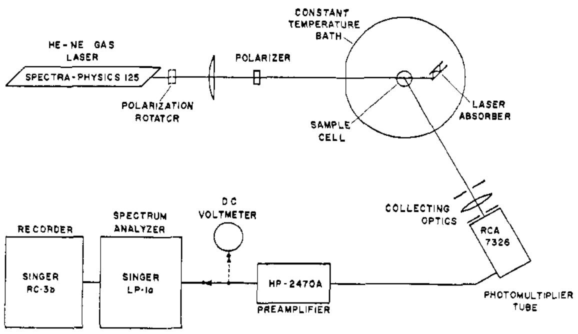

Figure 1. Block diagram of the homodyning spectrometer.

corrections for these known systematic errors, corrected data from a discrete-frequency source are believed to be linear within ±2% of full scale. Tests with a white noise source showed a reproducible small remaining variation in response at frequencies above 5 KHz, and a further correction was applied to subsequent noise measurements at these frequencies.

Additional possible systematic errors arising from variations in laser power and instability in electronic components were minimized by restricting run times for a complete spectrum to 30 min or less. Measurement of a spectrum consisted of determining the amplitude of the output from the phototube at a number of chosen frequencies, rather than scanning an entire range of frequencies. This procedure was believed to make more efficient use of the period during which the system was stable and to reduce bias in reading the average amplitude of the fluctuating output on the recorder.

After corrections for the frequency response and amplitude nonlinearity were applied, averaged amplitudes read from the recorder were squared to give the power spectral density of the photomultiplier current. This power spectrum includes a constant contribution from shot noise which was subtracted before further analysis of data. The amplitude of the shot noise contribution was determined during the run by either of two methods. The first consisted of measuring a component of the spectrum at frequency high enough so that only shot noise contributed to the spectrum. In the second method the phototube was exposed to white light of sufficient amplitude to give the same dc photocurrent as was observed for the scattered light during the spectral measurement. The spectrum from the white light then consists only of shot noise of the same magnitude as in the spectral determination. In the frequent cases where both methods could be used, close agreement was observed.

After subtraction of the shot noise component, the reciprocal of the remaining power spectral density (in arbitrary units) was plotted against the square of frequency. Such a plot is linear when the self-beating spectrum is Lorentzian, and the slope and intercept can be used to calculate the amplitude at zero frequency and half-width of the Lorentzian which fits the data. Reduced spectra (that is, spectra having an amplitude of unity at zero frequency) were then plotted against frequency along with the calculated Lorentzian for comparison.

Even after all corrections for systematic errors have been applied, measurements of noise signals such as power spectral density measurements have an inherent lack of precision because of their random nature. In order to estimate the precision of measurement twelve replicate determinations were made of one component of the output from a white noise generator at each of six amplitudes ranging from nearly full scale to less than 10% of full scale. These measurements were made using a 10-Hz band width usually used for spectral determinations. At every amplitude the level of the recorder output was estimated using a transparent straight edge in the same way later used for spectral determinations. The replicate points were all corrected for the systematic errors described above, and an average output and standard deviation were calculated at each amplitude. It was found that the standard deviation varied from 1.2 to 2.0% of the mean amplitude except at the lowest amplitude, where the standard deviation was about 2.6% of the mean. The absolute magnitude of the random error of measurement is thus nearly proportional to the amplitude, and to an adequate approximation the percentage error is constant at 1.5% at all but the lowest amplitudes measured, where it is somewhat greater. The percentage error would be somewhat greater if a smaller band width had been used and somewhat less with a larger band width.

As explained above, the corrected amplitude of the recorder output is squared before analysis. It is therefore the error in the squared amplitude which is significant. The distribution of deviations of replicate determinations about the mean of unsquared data arises both from the random nature of the signal and from random error in estimating the signal level. This distribution may be assumed to be Gaussian. If deviations in the unsquared data are small, then it can be shown that corresponding deviations of the squared data about the mean square are nearly Gaussian. Furthermore, the ratio R of the standard deviation of squared data to the mean square is then nearly equal to $2r$, where r is the ratio of the standard deviation of unsquared data to the mean. Since r has been determined to be approximately 0.015 and independent of amplitude, R is then approximately 0.03 and is also independent of amplitude.

The amplitude A_L of the portion of the squared signal due to self-beating of spectrally distributed light is obtained by subtracting the shot noise A_S from the total squared signal A_T

$$A_L = A_T - A_S \tag{1}$$

where A_S is the squared amplitude due to shot noise. The most probable error P_L in A_L may be determined from the standard formula

$$P_L = \pm\sqrt{\left(\frac{\partial A_L}{\partial A_T}\right)^2 P_T^2 + \left(\frac{\partial A_L}{\partial A_S}\right)^2 P_S^2} \tag{2}$$

Here P_T and P_S are the most probable errors in A_T and A_S, respectively, given by

$$P = \pm 0.6745\sigma \tag{3}$$

where σ is the standard deviation of the quantity considered. As already stated

$$\sigma = RA \tag{4}$$

and combination of eq 2, 3, and 4 yields

$$P_L = \pm 0.6745R(A_T^2 + A_S^2)^{1/2} \tag{5}$$

This expression has been used to calculate the error bars shown with experimental points on the spectra presented below.

Results

Initial tests of the apparatus were conducted using a standard latex obtained from the Bioproducts Department of the Dow Chemical Co. A suspension of particles having average diameter 109.0 nm was prepared at a concentration of 0.011 wt % solids by diluting the latex as received with filtered distilled water. The sample was then filtered again into a cleaned scattering cell using a hypodermic syringe with an attachment fitted with a Millipore filter having 450 nm pore size.

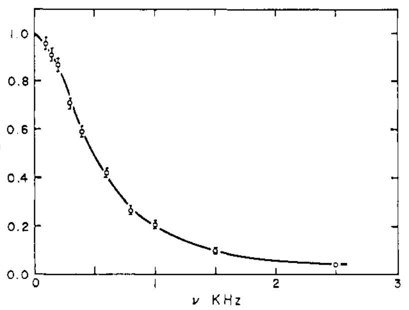

Figure 2. Spectrum of photocurrent due to light scattered from 1090 Å latex at a scattering angle of 90°: points, experimental; solid line, Lorentzian of half-width 496 Hz. Data were taken at 25.0°.

The spectrum of the Rayleigh line of light scattered from a monodisperse suspension of spherical particles consists of a single Lorentzian centered at ν_0, the frequency of the light source.[10–12] This Lorentzian has full width at half-maximum amplitude $\Delta\nu$ which is proportional to the translational diffusion constant D of the particles. When the spectrum of scattered light is Lorentzian, the power spectrum of the low-frequency portion of fluctuating component of the phototube current is also Lorentzian with half-width at half-maximum amplitude $\Gamma_{1/2}$ numerically equal to $\Delta\nu$[11]. In the case of the latex suspension, the photomultiplier spectra were Lorentzian at all angles at which data were taken. A typical spectrum obtained at a scattering angle $\theta = 90°$ is shown in Figure 2. The photocurrent spectral widths $\Gamma_{1/2}$ observed are reported as a function of angle in Table I. All data reported were obtained at 25.0°.

According to theory for spectral broadening due to translation of a monodisperse species, the spectrum of the scattered light is given by[8]

$$S_{0\infty}(\kappa,\omega) \propto (\kappa^2 D)/[\omega^2 + (\kappa^2 D)^2] \qquad (6)$$

Here $\omega = 2\pi(\nu - \nu_0)$ and κ is the magnitude of the scattering vector given by

$$\kappa = (4\pi n/\lambda_0)\sin(\theta/2) \qquad (7)$$

Table I

Experimental Half-Widths for 109.0-nm Latex Suspension

θ, deg	$\Gamma_{1/2}$ (=Δν), Hz	D,[a] cm² sec⁻¹	$[(D - D_{SE})/D_{SE}]100$,[b] %
30	60	4.02×10^{-8}	−10.3
45	152	4.69×10^{-8}	4.7
60	243	4.38×10^{-8}	−2.2
75	360	4.39×10^{-8}	−2.1
90	496	4.48×10^{-8}	0.0
119	715	4.35×10^{-8}	−2.9
	Av	4.39×10^{-8}	−2.1

[a] Calculated from eq 8. [b] D_{SE} calculated from eq 9 equals 4.48×10^{-8} cm² sec⁻¹.

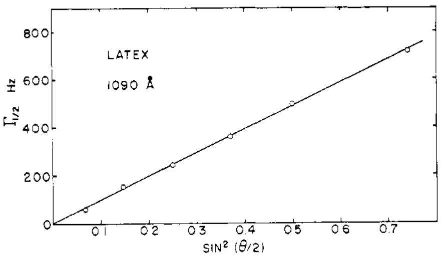

Figure 3. Plot of photocurrent spectral half-width against $\sin^2(\theta/2)$ for 1090 Å latex. Data were taken at 25.0°.

where λ_0 is the wavelength under vacuum of the incident light and n is the refractive index of the scattering solution. The half-width of the Lorentzian given in eq 6 is proportional to $\kappa^2 D$ and accordingly the spectral half-width should be proportional to $\sin^2(\theta/2)$. As shown in Figure 3, a plot of $\Gamma_{1/2}$ against $\sin^2(\theta/2)$ is indeed linear for the latex suspension.

An additional check of these experimental results is given by comparison of the experimentally determined diffusion constants with the value predicted for spheres by the Stokes–Einstein relation. The diffusion coefficient obtained experimentally from the spectral width is calculated from the relation

$$D = \frac{\Delta\nu(\lambda_0/n)^2}{16\pi\sin^2(\theta/2)} \qquad (8)$$

where experimental values of $\Gamma_{1/2}$ may be substituted for $\Delta\nu$ since the spectra are Lorentzian. According to the Stokes–Einstein relation

$$D_{SE} = kT/6\pi\eta_s r \qquad (9)$$

where k is the Boltzman constant, T is the absolute temperature, η_s is the solvent viscosity, and r is the radius of the sphere. As shown in Table I, the average of data obtained at all scattering angles yields an experimental diffusion coefficient of 4.39×10^{-8} cm² sec⁻¹, which compares very favorably with the value of 4.48×10^{-8} cm² sec⁻¹ calculated from eq 9.

After completion of tests with the latex, measurements of spectra were made on a series of solutions of polystyrene in spectral grade cyclohexane at 35.0°. The solutions were prepared by weight in small weighing bottles at a temperature above 35.0°, then transferred to a warmed syringe having a filter attachment. The warm solutions were filtered through Millipore filters having 450 nm pore size into carefully cleaned scattering cells which were then capped or sealed. Each sample was made up in approximately 0.5 wt % concentration, and the spectra were determined at a number of angles ranging from 30 to 90° for each solution.

The characteristics of the polystyrene solutions used are given in Table II. For each molecular weight an effort was made to find samples as monodisperse and as well-characterized as possible. Sample NBS-705 was obtained from the National Bureau of Standards. The weight-average molecular weight M_w determined by light scattering and the ratio of the weight-average to number-average molecular weights M_w/M_n determined by fractionation were provided with the sample and are given in Table II. Samples W-25167 and W-61970 were obtained from Waters Associates, who also sup-

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(10) H. Z. Cummins, N. Knable, and Y. Yeh, *Phys. Rev. Lett.*, **12**, 150 (1964).

(11) S. B. Dubin, J. H. Lunacek, and G. Benedek, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1164 (1967).

(12) F. T. Arecchi, M. Giglio, and U. Tartari, *Phys. Rev.*, **163**, 186 (1967).

TABLE II
SAMPLE CHARACTERISTICS AND DIFFUSION CONSTANTS FOR POLYSTYRENE DISSOLVED IN CYCLOHEXANE

Polymer identification	M_w	M_w/M_n	Concn, wt % polymer	D, cm² sec⁻¹
NBS-705	179,300	1.07	0.54	2.62×10^{-7}
W-25167	867,000	1.12	0.50	1.20×10^{-7}
W-61970	2,145,000	1.21	0.50	0.80×10^{-7}
LJF-9	4,500,000		0.51	0.34×10^{-7}

plied values of M_n and M_w. Sample LJF-9 was prepared by Dr. L. J. Fetters by anionic polymerization. The value of M_w listed for this sample in Table II was obtained by equilibrium ultracentrifugation. The *z*-average molecular weight M_z, also obtained from the ultracentrifuge measurement,[13] was found to be about 5.6×10^6. This sample accordingly has a somewhat broader molecular weight distribution than the samples of lower molecular weight.

A typical result of a spectral measurement with a Lorentzian fit of the data is shown in Figure 4 for the low-molecular-weight NBS-705 polystyrene at $\theta = 30°$. Data at 45, 60, 75, and 90° are similarly well fit by a Lorentizan distribution, although the precision of data points is slightly lower at higher scattering angles because of the higher relative contribution of shot noise to the spectrum. In addition, the angular dependence of the half-width was in good agreement with the proportionality to $\sin^2(\theta/2)$ predicted by theory for spectral broadening due to translational diffusion. The dependence of $\Gamma_{1/2}$ on $\sin^2(\theta/2)$ is shown in Figure 5. The half-widths obtained were 460 Hz at $\theta = 30°$, 905 Hz at 45°, 1720 Hz at 60°, 2460 Hz at 75°, and 3450 Hz at 90°. Taken together, the measurements made at various angles on this sample give an average value of $\Gamma_{1/2}/\sin^2(\theta/2)$ from which the diffusion coefficient may be calculated by use of eq 8. The value of D calculated in this way is given in Table II.

With increasing solute molecular weight, evidence appears of deviations from behavior predicted for simple translational diffusion. Data at low frequencies are more scattered than was the case for any of the spectra obtained for NBS-705, with the scatter being high compared to the precision of measurement. More importantly, at higher angles deviations from a Lorentzian line shape occur, particularly for the two samples of highest molecular weight.

These deviations are first evident in the data for sample W-25167. The spectrum at $\theta = 30°$ shows only small deviations from a Lorentzian of half-width $\Gamma_{1/2}$ equal to 207 Hz and is very similar to that shown in Figure 4 for the NBS-705. In the spectrum at $\theta = 45°$, for which $\Gamma_{1/2}$ is about 445 Hz, the points at frequencies below 100 Hz have considerably more scatter than corresponding points in the spectrum obtained at $\theta = 30°$. At $\theta = 60$ and 75° the data below about 300 Hz show similar scatter. The half-widths at these angles are roughly 750 and 1150 Hz, respectively. The spectrum at $\theta = 90°$, given in Figure 6, typifies the increased scatter and degree of fit to a Lorentzian shown by all the spectra at angles above 30°; the half-width of this spectrum is about 1600 Hz. The average value of $\Gamma_{1/2}/\sin^2(\theta/2)$ over all angles was used to calculate the value of the diffusion coefficient given in Table II. If the low-frequency points in the spectra obtained at angles above 30° are disregarded then an excellent Lorentzian fit may be made to the high-frequency points in every case. A graph of these half-widths of these Lorentzians plotted against $\sin^2(\theta/2)$ is curved slightly upward. However, in the absence of a known reason for ignoring the low-frequency points we feel that such a procedure is misleading and that it is preferable to weight all points equally in the analysis. If this

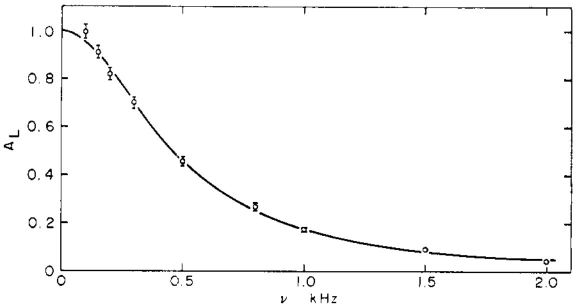

Figure 4. Spectrum of photocurrent due to light scattered from 0.54% NBS-705 polystyrene in cyclohexane at $\theta = 30°$: points, experimental; solid line, Lorentzian of half-width 460 Hz. Data were taken at 35.0°.

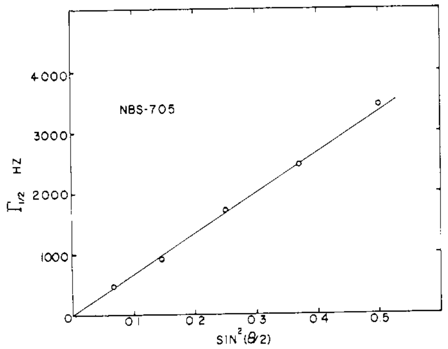

Figure 5. Plot of photocurrent spectral half-width against $\sin^2(\theta/2)$ for 0.54% NBS-705 in cyclohexane. Data were taken at 35.0°.

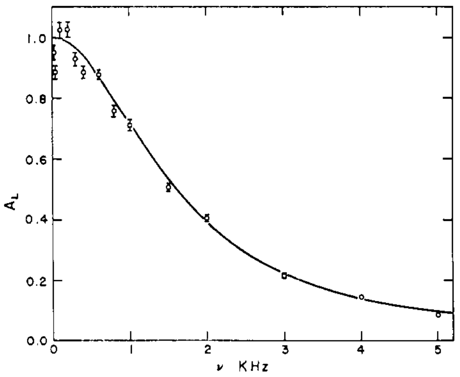

Figure 6. Spectrum of photocurrent due to light scattered from 0.50% W-25167 polystyrene in cyclohexane at $\theta = 90°$: points, experimental; solid line, Lorentzian of half-width 1600 Hz. Data were taken at 35.0°.

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[13] We are indebted to Mr. E. F. Slagowski for the ultracentrifuge characterization data.

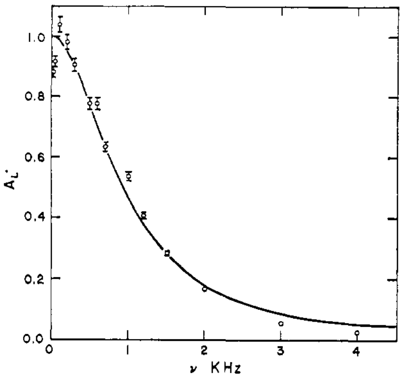

Figure 7. Spectrum of photocurrent due to light scattered from 0.50% W-61970 polystyrene in cyclohexane at $\theta = 90°$: points, experimental; solid line, Lorentzian of half-width 930 Hz. Data were taken at 35.0°.

is done, spectra for W-25167 are Lorentzian within a higher-than-normal experimental error, and a plot of the half-widths of these Lorentzians against $\sin^2(\theta/2)$ is linear within experimental error.

Results for the solution of W-61970 are similar to those for W-25167, although low-frequency scatter is more pronounced, and definite evidence of a non-Lorentzian spectrum appears at $\theta = 90°$. As was the case for W-25167 the spectrum at $\theta = 30°$ can be precisely fit by a Lorentzian, while there is increasing scatter in the low-frequency points at $\theta = 45°$ and $\theta = 60°$. Scatter in low-frequency data at $\theta = 75°$ is very high. At $\theta = 90°$ scatter is moderate, but it is not possible to achieve an acceptable fit with a Lorentzian of any half-width. This spectrum is shown in Figure 7, along with a calculated Lorentzian which fits the low-frequency data. High-frequency points are not fit by the calculated curve, and a Lorentzian curve fit to high-frequency points will not fit the data at low frequencies. A plot of the half-widths of the spectra obtained at θ = 30, 45, 60, and 75° against $\sin^2(\theta/2)$ is linear within experimental error. A half-width may be obtained for the non-Lorentzian spectrum obtained at $\theta = 90°$ by drawing a curve directly through the data points. The estimated values of $\Gamma_{1/2}$ are 130 Hz at $\theta = 30°$, 300 Hz at $\theta = 45°$, 550 Hz at $\theta = 60°$, 750 Hz at $\theta = 75°$, and 930 Hz at $\theta = 90°$. The average value of $\Gamma_{1/2}/\sin^2(\theta/2)$ from the first four scattering angles was used to calculate the value of D given for W-69170 in Table II.

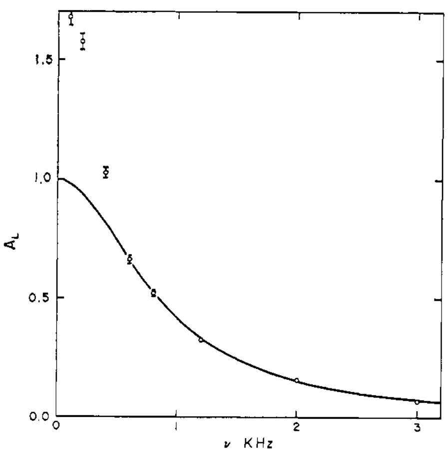

Figure 8. Spectrum of photocurrent due to light scattered from 0.51% LJF-9 polystyrene in cyclohexane at $\theta = 90°$ points experimental; sold line, Lorentzian of half-width 850 Hz. Data were taken at 35.0°.

For the sample of highest molecular weight, LJF-9, a good fit to a Lorentzian could be made for the spectra obtained at θ = 30 and 45°. However, a pronounced and uniform type of deviation from a Lorentzian was observed at higher angles. The spectrum of the photocurrent at $\theta = 90°$ shown in Figure 8 illustrates this deviation; similar deviations were seen in the spectra at θ = 60 and 75°. It is possible in each case to fit the high-frequency tail to a Lorentzian, but deviations from a Lorentzian at low frequencies are pronounced and well outside the experimental precision of measurement. The half-widths of the Lorentzian spectra obtained at $\theta = 30°$ and $\theta = 45°$ were 57 and 133 Hz, respectively. These values were used to calculate the diffusion constant given in Table II. Half-widths may be obtained for the non-Lorentzian spectra obtained at higher angles by drawing a curve directly through the data points and estimating the frequency at which the amplitude has fallen to one-half its zero-frequency value. The half-widths obtained in this manner were 230 Hz at $\theta = 60°$, 350 Hz at 75°, and 500 Hz at 90°. These values are very approximate, since no effort was made at the time data were taken to obtain highly reliable values of the amplitude of the spectrum at low frequency.

Discussion

Rayleigh line broadening is a convenient tool for measurement of translational diffusion coefficients of macromolecules in dilute solution, and its use for this purpose has been reported several times in the recent literature.[11,14,15] The results given here for the NBS-705 polystyrene represent a straightforward application of the technique to determination of a diffusion constant. Also of importance, however, is the possibility of investigating other relaxation processes in solution, particularly intramolecular motion and rotary diffusion. These processes give rise to additional spectral contributions which should be observed as deviations from the behavior characteristic of translational diffusion alone. The measurements reported here were made for the purpose of seeing if additional spectral contributions could be detected for random-coil polymers of high molecular weight. Deviations were indeed found for solutes of moderate molecular weight at high scattering angles, and these deviations become more apparent and detectable at lower scattering angles as the molecular weight was increased. However, such behavior can result from several unrelated causes, among which are contributions to the spectrum from sample polydispersity, critical scattering, intermolecular interactions, and intramolecular motions. Each of these will be considered in detail.

The primary effect of polydispersity on the spectrum is to give Lorentzian contributions from translational

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(14) T. H. Herbert, F. D. Carlson, and H. Z. Cummins, *Biophys. J.*, 8, A-95 (1968) (abstract).

(15) N. C. Ford, W. Lee, and F. E. Karasz, *J. Chem. Phys.*, 50, 3098 (1969).

motion of each species present; these contributions combine to form a composite spectrum which is non-Lorentzian.[7,8] This effect is minimized in a Θ solvent, where the dependence of the diffusion coefficient on molecular weight is smallest. Numerical calculations show[16] that in order for the effect to be appreciable in a poor solvent the distribution of molecular weights must be much broader than that of any of the samples for which spectra are reported here. Unless the distribution is very broad, composite spectra resulting from polydispersity will appear to be Lorentzian with half-widths that are very nearly proportional to κ^2. These theoretical predictions of the effect of polydispersity have been experimentally confirmed for a low molecular weight polystyrene having a most probable distribution.[16] The spectra from 0.5 wt % solutions of this polymer are precisely fit over a range of angles by Lorentzian curves, and the half-widths are proportional to κ^2 even for this relatively broad distribution. There is no reason to expect different results for a polydisperse sample of higher molecular weight, and accordingly it seems unlikely that the deviations seen in the spectra of W-61970 and LJF-9 arise because of sample polydispersity.

There was believed to be a small possibility in the case of the solution of LJF-9 that the deviations observed were a manifestation of critical scattering. The 0.5 wt % concentration may not be far from the critical solution concentration for this polymer, and if this were the case the temperature of measurement would be only a few degrees above the critical consolute temperature. Effects of critical scattering in polymer solutions persist further above the critical consolute temperature than in binary mixtures,[17] and the possible influence of critical scattering on the spectrum must be considered. In order to see if this were the case the same solution of LJF-9 used for the measurements at 35.0° reported above was used for spectral determinations at 39.9° at scattering angles 30, 45, 60, 75, 90, 105, and 135°. The same qualitative type of distortion of the spectrum was observed at this temperature as at 35.0°. The spectrum at $\theta = 30°$ could be precisely fit by a Lorentzian, while at higher angles deviations like those seen previously were observed. A typical example of high-angle spectrum at 39.9° is shown in Figure 9; spectra at other angles above 30° were similar. It is very unlikely that critical scattering persists at this temperature, and the deviations must therefore be attributed to some other cause.

The nature of possible spectral contributions from intermolecular interactions is unknown. An experimental study was made of the influence of concentration on the spectral shape and on the dependence of the half-width on scattering angle. The spectra of solutions of NBS-705 polystyrene in cyclohexane at 35.0° were determined as a function of angle for concentrations up to nearly 30%. At concentrations below about 18% no significant deviations from a Lorentzian spectral shape were found, and proportionality of the half-width to $\sin^2(\theta/2)$ was observed. Small deviations were observed at the highest concentrations, although it is not certain that these were outside the limit of error. These measurements indicate that intermolecular interactions in concentrated solution are not manifest as deviations like those reported above, at least at low molecular weights. In order to explain the deviations at high molecular weights on the basis of intermolecular interactions it would be necessary to postulate a slow relaxation mechanism in dilute solution which is not evident even at high concentrations at low molecular weights. This does not seem justified on the basis of presently available data.

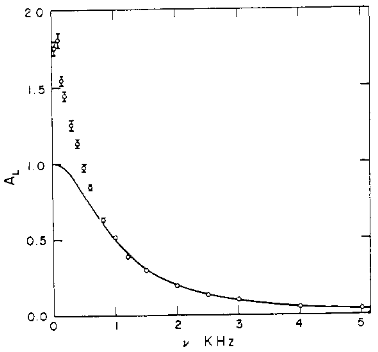

Figure 9. Spectrum of photocurrent due to light scattered from 0.57% LJF-9 polystyrene in cyclohexane at $\theta = 90°$: points, experimental; solid line, Lorentzian of half-width 985 Hz. Data taken at 39.9°.

In order to interpret properly non-Lorentzian spectra like those predicted to result from intramolecular motion, it must be recognized that for homodyning measurements the power spectral density of the photocurrent is proportional to the convolution of the spectrum of the light impinging upon the photocathode.[18] If this light spectrum consists of two Lorentzians with integrated intensities A and B, respectively, and half-widths $(X/2)$ and $(Y/2)$, respectively, then the power spectral density of the photocurrent $P(\nu)$ is given by

$$P(\nu) \propto A^2 \frac{X}{\nu^2 + X^2} + B^2 \frac{Y}{\nu^2 + Y^2} + 2AB \frac{[(X+Y)/2]}{\nu^2 + [(X+Y)/2)]^2} \qquad (10)$$

This spectrum consists of three Lorentzians, two with half-widths twice those of the Lorentzians in the light spectrum, plus a "cross-term" Lorentzian with half-width equal to the mean of the half-width of the other two Lorentzians in the photocurrent spectrum. The relative intensities of these components are in the ratio $A^2{:}B^2{:}2AB$, while the corresponding amplitudes at zero frequency are (A^2/X), (B^2/Y), and $2AB/[(X+Y)/2]$. These relations are the basis of interpretation of homodyning data arising from light spectra consisting of two Lorentzians.

According to theory,[4,7] the predominant effect of intramolecular motion on the spectrum of scattered light is to add a second Lorentzian component to the primary Lorentzian component due to translational diffusion. This second component is also centered

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at the frequency of the incident light beam and has full width at half-maximum amplitude given by

$$\Delta\nu_2 = (1/2\pi)[\kappa^2 D + (2/\tau_1)] \tag{11}$$

The width is seen to be equal to the sum of a term due to translational motion and a term due to motion in the first normal-mode coordinate. In the absence of direct measurements, the order of magnitude of τ_1 can be estimated from normal coordinate theory, which gives for the free-draining case at infinite dilution[19]

$$\tau_p = \frac{6M\eta_s[\eta]}{\pi^2 p^2 RT} = \frac{6M\eta_s}{\pi^2 p^2 RT}\left(\frac{\eta_{sp}}{c}\right)_{c\to 0} \tag{12}$$

where η is the solution viscosity, η_s is the solvent viscosity, M is the molecular weight, c is the concentration in grams per cubic centimeter, R is the gas constant, and T is the absolute temperature. Here η_{sp} is the specific viscosity, equal to $(\eta - \eta_s)/\eta_s$ If it is assumed for purposes of estimation that τ_p follows the same concentration dependence as (η_{sp}/c), then eq 12 may be used with experimental data obtained at finite concentration. The experimental value of (η_{sp}/c) for 0.51% LJF-9 in cyclohexane at 35.0° is about 350 $\text{cm}^{-3}\ \text{g}^{-1}$. Substitution of this value into eq 12 then shows τ_1 to be about 2.6×10^{-4} sec. The full width at half-maximum amplitude of the Lorentzian contribution to the light spectrum arising from intramolecular motion is then given by eq 11 as $[(\kappa^2 D/2\pi) + 1200]$ Hz. The composite spectrum of the photocurrent should then consist according to eq 10 of a Lorentzian due to translation with half-width at half-maximum amplitude $\kappa^2 D/2\pi$; a Lorentzian due to intramolecular motion with half-width at half-maximum amplitude $[(\kappa^2 D/2\pi) + 1200]$ Hz; and a cross term Lorentzian with half-width at half-maximum amplitude equal to the mean of the other two.

It should be noted that according to eq 11 the Lorentzian in the light spectrum due to intramolecular motion must always be broader than the Lorentzian due to translation. The corresponding Lorentzian in the photocurrent spectrum as well as the cross term Lorentzian will also be broader than the primary translational component. The composite photocurrent spectrum must therefore always have a larger half-width than would be computed for translation alone. Since intramolecular contributions are small at low angles and increase with angle, a plot of the half-widths of the composite photocurrent spectra against $\sin^2(\theta/2)$ should curve upward. It is difficult to generalize further, however. The amount of distortion from a Lorentzian and the additional broadening of composite curves with angle must be determined by use of eq 10 with the particular intensities and half-widths of the contributing Lorentzian components.

The relative intensity of the contributions to the light spectrum from intramolecular motion has been given by Pecora[4,7] as a function of x, where $x = \kappa^2 nb^2/6$. If we set the group of parameters $nb^2/6$ from Gaussian chain statistics equal to $\langle s^2 \rangle$, the experimental mean-square radius of gyration of the molecule, then for data reported here on sample LJF-9 the range of x is from 0.18 at $\theta = 30°$ to 1.4 at $\theta = 90°$. The relative intensity of contributions of all motions other than translation is predicted to be much less than 1% for $x = 0.18$ and about 8% for $x = 1.4$. These contributions are thus negligible at 30°.

At $\theta = 90°$ a composite spectrum for the solution of LJF-9 may be calculated in the following manner. The experimental half-width at $\theta = 30°$, which is Lorentzian, may be assumed to arise from translation alone. The value of the half-width expected for the translational component at $\theta = 90°$ can then be calculated from the proportionality of this component to $\sin^2(\theta/2)$; this is about 450 Hz. The half-width of the Lorentzian component due to intramolecular motion is then calculated using eq 11 and the estimated value of τ_1 given above to be 1650 Hz. Substitution of the relative intensities given above into eq 10 shows that only the translational and cross-term components contribute significantly. The resultant calculated composite spectrum is qualitatively similar to the experimental spectrum shown in Figure 8. It appears to be a Lorentzian spectrum except that the low-frequency portion lies above a Lorentzian curve fit to the high-frequency portion. The apparent low-frequency deviation is not so pronounced as that observed experimentally, but the experimental deviations appear to be qualitatively consistent with the theoretically predicted effects due to contributions from intramolecular motion.

Apparent agreement obtained in this manner can be misleading, however. Whether experimental deviations from a Lorentzian are said to occur at low frequencies or at high frequencies depends on which portion of the non-Lorentzian data are fit. If high-frequency points are fit, the deviation appears to occur at low frequencies, and *vice versa*. Given a single experimental spectrum it is only possible to say whether or not it is distorted from a Lorentzian form. Distortion could arise either from addition of components of greater breadth or of lesser breadth than the primary translational component. When low-angle spectra are Lorentzian and believed to be due to translation alone, it is possible to predict the half-width at higher angles from proportionality of the half-width to κ^2. The variation of the experimental half-widths with angle at higher angles then shows whether the distorting component is broader or narrower than the primary component. This is difficult to do accurately, since the true half-width depends upon a reliable experimental value of the amplitude at frequencies low compared to the half-width, and this is not easy to obtain. Rough estimates have been given above for the experimental half-widths of the spectra of LJF-9 at 35.0° at each angle. Although no special care was taken to obtain accurate low-frequency amplitudes, it is readily seen that the spectrum broadens with angle more than is predicted from κ^2 dependence, in accordance with the predicted effect of intramolecular motion.

In the case of the same solution of LJF-9 at 39.9°, significant broadening of the spectrum with angle beyond that predicted from κ^2 dependence of the half-width is not observed, although the spectra at all angles above 30° are non-Lorentzian. This different result does not preclude interpretation of the distortion as being due to intramolecular motion, since the variation of the half-width of the composite spectrum with

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angle must be calculated from eq 10, and this variation may be small even though considerable distortion occurs. Insufficient data are available to perform this calculation with sufficient accuracy; in particular, directly measured values of τ_1 would be helpful.

In summary, the observed deviations are qualitatively consistent with the predictions of theory for the effect of intramolecular motion on the spectrum, although the data are not yet accurate enough nor extensive enough to establish definitely this as the cause. It seems unlikely, however, that these deviations are due to polydispersity, critical scattering phenomena, or concentration effects. Whatever their origin, the appearance of non-Lorentzian spectra at moderate molecular weights points out the need for caution in routine application of Rayleigh line-broadening measurements to the determination of translational diffusion constants, particularly if data are of limited accuracy. It is desirable to determine the spectrum for a given sample as a function of angle, since deviations which seriously affect the results may not be apparent in results obtained at a single angle.

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Infrared Spectroscopic Approaches to the Polymer Transitions. I. The Multiple Transitions in Poly(acrylonitrile) (PAN)

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ABSTRACT: The multiple transitions in poly(acrylonitrile) (PAN) were investigated by means of infrared absorption spectrophotometry in the range from 80 to 145°. The temperature behavior of peak absorbance and infrared dichroism and the time–temperature dependence of peak absorbance at various temperatures were examined. From these data, four transition points (90, 110, 120, and 140°) were detected and the results suggest that the band for the CN group is the most sensitive one for the thermal transition in PAN. The nature of the temperature dependence of peak absorbance in the infrared spectrum of the polymer was also discussed.

Many authors have reported thermal transitions in polymers; however, their natures have not been clear. If it is considered that a polymer transition is associated with a change in the state of molecular motion in a polymer molecule (or a change of conformation), the behavior of the infrared spectrum in the transition regions may provide certain clues for understanding the nature of polymer transitions more clearly. In a polymer solution, such an attempt was first carried out by Takeda, Iimura, and Ochiai.[1]

In the solid state, recently, several authors[2–8] have demonstrated that infrared absorption spectrophotometry may be used to detect thermal transitions in polymers. Table I summarizes the thermal transition temperatures which were detected by infrared.

In the present paper, the multiple thermal transitions in poly(acrylonitrile) (PAN) in the range from 80 to 145° are reported using measurements of the temperature dependences of infrared absorbance and infrared dichroism, and time–temperature dependence of infrared absorbance at various temperatures.

Experimental Section

(1) Polymer. PAN was prepared according to the redox recipe of Beaman,[9] details of which are given in Table II.

(2) Molecular Weight. Intrinsic viscosities were measured in dimethylformamide (DMF) solution at 25° and molecular weight (M_n = 689,000) calculated from the relation of Onyon[10] ($[\eta] = 1.97 \times 10^{-3} M_n^{0.625}$).

(3) Preparation of Sample. The PAN homopolymer films used in this work were cast from 2% solutions of the polymer in DMF. The residual DMF in the films was extracted with methanol and they were then dried under vacuum at low temperature. The well-dried films (50–60 μ) were stretched 300% at room temperature. None of the films used in this work was annealed.

(4) Infrared Measurements. A Nihon Bunko DS-402G type of infrared spectrophotometer and heated cell apparatus were used. This instrument has a frequency accuracy of ±2 cm^{-1} and a transmission accuracy of ±0.5% under the conditions used. The temperature was raised at a rate of about 0.3°/min. The temperature of the sample was controlled with a thermoregulator and temperatures were

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