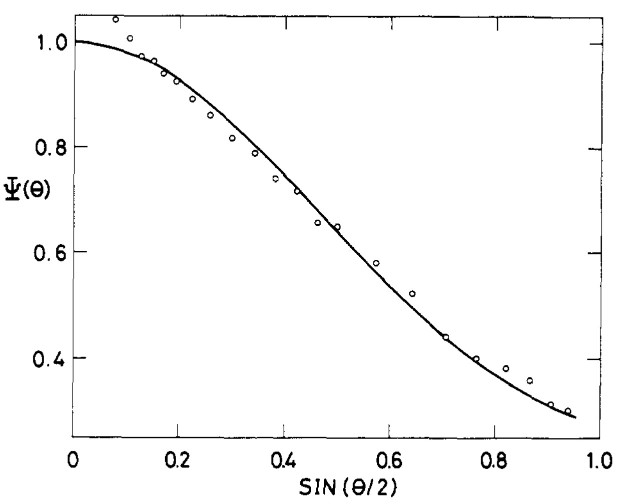

Figure 12. Comparison of theory (eq 13, full curve) and experimental results (open circles) of BMM-313 in toluene at 30° with the incident light of 4358 Å. The parameter values used in the calculation are taken from Table III.

The function $\Psi(\theta)$ is theoretically given by eq 8 as $(1 - \alpha)\Phi(X_a) + \alpha\Phi(X_b)$ with $\alpha = Ab^3/[(1 - A)a^3 + Ab^3]$. The extrapolation of $\psi(\theta)$ to infinite dilution is shown in Figure 10 for some selected angles on the experimental data shown in Figure 2. The plotted points fall on a straight line at each scattering angle, its slope being proportional to the apparent third virial coefficient. The values of $\psi_0(\theta)$ so obtained are plotted in Figure 11 *vs.* $\sin^2 (\theta/2)$ to estimate the value extrapolated at $\theta = 0$. This plot permits the more linear extrapolation than that *vs.* $\sin (\theta/2)$ as verified theoretically by the inset in Figure 7. Although $\Psi(\theta)$ contains three adjustable parameters, *e.g.*, *a*, *b*, and *A*, it can be shown that the parameter values can be estimated without introducing serious arbitrariness, and the results obtained are summarized in Table III. The theoretical values of $\Psi(\theta)$ calculated by using these values stand in satisfactory agreement with experimental data as shown in Figure 12 for toluene solutions as an illustration.

Comparison of the parameter values so obtained for toluene and benzene solutions is certainly instructive in view of the fact that for poly(methyl methacrylate) benzene is better solvent than toluene, while the two solvents are similar for polystyrene in the goodness as solvent. The *a* value is almost the same for the two solvents, but both *b* and ϵ/kT are significantly larger in benzene than in toluene in agreement with our expectation. If, on the contrary, *b* and ϵ/kT values are smaller under the circumstances that either the molecular weight of the poly(methyl methacrylate) subchain is small or the solvent is poor for it the anomaly may look less distinct. The former perhaps explains why this type of aberrant light-scattering behavior has long been left unfound.

Thus, we have given a reasonable explanation to the aberrant light-scattering results, *e.g.*, the upsweep of the reciprocal scattering function at small scattering angles at finite solute concentrations and the negative third virial coefficient, obtained on the two-block copolymer when the isorefractive solvents were used. We have also shown that the radius of gyration of the unmasked subchain can be precisely determined provided that the measurements be made to sufficiently low concentrations. The gyration radius of the polystyrene subchain could not be determined with precision when benzene was used as solvent, because the requirement was not fulfilled. However, the measurements were carried out with success by using toluene as solvent, and the gyration radius obtained is significantly larger than that of homopolystyrene RS-13 of equal molecular weight, indicating the effect of the heterocontact repulsion. Therefore, the present investigation supports the model that the domains of dissimilar segments overlap to a great extent in the two-block copolymer. It is indeed difficult to assume the presence of such a strong force as to induce segments to take the "segregated structure." The magnitude of the binary cluster integral of the heterocontact interaction relative to that of the homocontact one could be estimated on the basis of the random-coil statistics, which will be described in a separate report.

Acknowledgments. The authors are indebted to Professor M. Kurata for advice in preparing the manuscript and to Dr. Y. Tsunashima for his help in experiments.

Determination of Intramolecular Motion in a Random-Coil Polymer by Means of Quasielastic Light Scattering

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ABSTRACT: Quasielastic light-scattering measurements have been made which determine both the translational diffusion coefficient D and the longest internal relaxation time τ_1 for a polystyrene having weight-average molecular weight 27.3×10^6 in dilute solutions in cyclohexane at 35.4° and in 2-butanone at 25.0°. Solute concentrations ranged from 0.04×10^{-3} to 0.16×10^{-3} g-cm^{-3} in cyclohexane and from 0.07×10^{-3} to 0.37×10^{-3} g-cm^{-3} in 2-butanone. The values of τ_1 obtained are in essential agreement with values calculated from normal-coordinate theories. A discussion is given of corrections required when the self-beating spectrometer signal is processed by an analog-to-digital converter and an autocorrelator.

Since the appearance of methods for accurately determining the breadth and shape of the Rayleigh line in the spectrum of scattered light, there has been considerable interest in applying these methods to the determination of intramolecular motion in macromolecules having internal degrees of freedom. One system in which internal motion is of particular interest is the random-coil molecule in dilute solution. The theoretical basis for interpreting quasielastic scattering in this system was given by Pecora,[1-5] who showed that the spectrum of the Rayleigh line should consist of a Lorentzian component due to the

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translational motion of the entire molecule plus additional Lorentzian components due to changes in the normal coordinates which describe internal motions of the molecule.

Whether the internal modes of motion contribute significantly to the spectrum is predicted to depend on the value of the parameter $x = q^2\langle s^2\rangle$, where q is the scattering vector and $\langle s^2\rangle$ is the mean-square radius of gyration of the molecule. For $x \ll 1$, only the translational mode contributes significantly to the spectrum, which is then Lorentzian with half-width equal to q^2D, where D is the translational diffusion coefficient. For $x \gg 1$, the spectrum is a weighted sum of many Lorentzians arising from both translational and internal motions. Because it is not practical to decompose such a multi-Lorentzian spectrum into its Lorentzian components and calculate a series of relaxation times from the half-widths of these components, this type of spectrum is presently best treated by other methods.[6-8]

However, theory predicts an intermediate range of x where almost all of the observed intensity is distributed between only two Lorentzian components. The first component is due to translation and has half-width q^2D; the second broader component has half-width $(q^2D + 2/\tau_1)$, where τ_1 is the relaxation time of the first normal mode of motion. For carefully chosen conditions, it is feasible to analyze spectra taken in this intermediate range of x into two components and to obtain a value of τ_1 from the half-width of the second component.

Several series of experiments have been carried out in this laboratory[8-10] which help to define the range of x for which a two-Lorentzian analysis of spectra may be successfully carried out. These studies have established that for polystyrene in either cyclohexane or 2-butanone solution, spectra are dominated by translational motion for values of x less than about 1. Under this condition spectra are Lorentzian within experimental error, and the diffusion coefficient may be determined without significant interference from spectral components due to intramolecular motions. For $1 \leq x \leq 6$, there is increasing deviation of the half-width from proportionality to q^2, and deviations from a Lorentzian form may be detectable in high-precision spectra. It is in this range of x that spectra should consist essentially of two Lorentzians, and an analysis to determine τ_1 may be performed. At much higher values of x, the overall half-width of the spectrum is proportional to a power of q which is greater than two,[8] and deviations from a Lorentzian form may be detectable.

The experimental results presented below were taken in the intermediate range of x where a two-Lorentzian analysis of the spectrum is justified. Because for $x \sim 1$ the contribution from internal motion is very small, this is the effective lower limit for a valid two-Lorentzian analysis. The upper limit of validity is set by the condition that contributions from internal modes of motion other than the first mode should be small. This limit has not been established experimentally. Using the calculations of Pecora[2,4] as a guide, we have somewhat arbitrarily chosen for this work a value of $x = 6$ as an upper limit beyond which two-Lorentzian analyses should not be performed.

Choice of Experimental Conditions

In order to obtain spectra suitable for two-Lorentzian analysis, experimental conditions must be chosen carefully. The accessible range of x should include values somewhat less than 1, so that single Lorentzian analyses can be performed to determine D. It must also be possible to attain values of x from 1 to 6 where two-Lorentzian analyses may be performed to determine τ_1. The scattering vector q is given by $q = (4\pi n/\lambda_0) \sin (\theta/2)$, where n is the refractive index of the solution, λ_0 is the wavelength of the incident light in vacuum, and θ is the scattering angle. Because the accessible values of q are determined primarily by the values of θ over which spectra may be obtained, the values of x which may be investigated depend on $\langle s^2\rangle$ and hence the molecular weight of the sample. For our experimental conditions, attainment of the proper values of x necessitated use of a sample of very high molecular weight. The sample for which data are reported is optimal for our apparatus and was chosen after preliminary experiments on samples of higher and lower molecular weight. For a higher molecular weight sample, it was not possible to obtain a low enough value of x for determining the purely translational contribution, while for available samples of lower molecular weight it was not possible to obtain high enough values of x for accurate two-Lorentzian fits. These problems can be partially overcome with improved apparatus.

Attention must also be given to the solute molecular weight distribution, solute concentration, and solvent used. The solute should have a very narrow distribution of molecular weight if comparisons with theories for monodisperse systems are to be made. Solute concentrations should be as low as is consistent with obtaining suitable spectra, so that results may be compared with infinite dilution theories; no methods for extrapolation of quasielastic scattering measurements of internal motion to infinite dilution have yet been devised. Scattering from solution should be large to maximize the signal-to-noise ratio. This can be achieved by use of solvent–solute systems for which the specific refractive incrment $\partial n/\partial c$ is high.

In addition, consideration must be given to correction of systematic errors introduced by the signal processing equipment used. Although these corrections can be very significant, they have usually been ignored in the literature. The corrections applicable to our particular instrumentation are discussed below.

Apparatus and Corrections

A self-beating spectrometer described previously[9] was used for all measurements, except that the photocurrent was processed by an autocorrelator instead of a spectrum analyzer. The signal from the load resistor of the phototube was first amplified using a Kiethley Model 103A amplifier. This amplifier has both high-pass and low-pass filters, which modify the spectrum of the input signal. The filtered signal was then processed by a Nicolet Instruments Model 1070 signal averaging computer equipped with an SW-77 time base and an SD-75A correlator unit. The signal was further filtered by a low-pass filter at the input of the correlator, then sampled at 30-μsec intervals by an analog-to-digital converter. In typical runs, 8192 samples of the signal were autocorrelated and the smooth averaged autocorrelation function $C_u(t)$ was obtained and displayed on an oscilloscope.

When the sampling rate used is not high compared to the highest frequencies in the spectrum of the signal, it is necessary to filter the high frequencies from the input signal to prevent aliasing error. The sampling theorem[11] (Nyquist theorem) states that sampling must occur at least

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twice during one cycle of the highest frequency present if this error is not to occur. Because it is not usually practical to correct for aliasing error once it is present, a low-pass filter must be used which effectively eliminates all frequencies greater than one-half the sampling frequency.

However, this necessary filtering distorts the spectrum of the input signal. As a result, the observed autocorrelation function $C_u(t)$, which is the Fourier transform of the power spectrum, is also distorted. The time constant of the input filter used must be only large anough to prevent aliasing error so as not to introduce too much distortion in $C_u(t)$. For our experimental conditions, a low-pass filter at the autocorrelator input having a time constant of 100 μsec was sufficient to practically eliminate aliasing error; however some signal distortion resulted. Signal distortion from the low-pass filter of the amplifier was negligible, but a small amount of additional distortion was introduced by the high-pass filter of this amplifier.

Both of the filters which appreciably affected the signal were simple R-C networks for which the power transfer functions can readily be calculated. The overall power transfer function $T(\omega)$ of the two filters combined can be shown to be given to a high degree of approximation by

$$T(\omega) = L_b(\omega) - L_c(\omega) \quad (1)$$

Here $L_b(\omega)$ and $L_c(\omega)$ are normalized Lorentzian functions of the angular frequency ω with half-widths b and c, respectively; the parameters b and c are the reciprocals of the time constants of the low-pass and high-pass filters, respectively. Values for b and c were determined experimentally, and the two-Lorentzian form of $T(\omega)$ was verified.

If the spectrum of scattered light arises from translational diffusion, the photocurrent spectrum $P(\omega)$ will be of the form

$$P(\omega) = L_a(\omega) + \gamma + (\mathrm{dc}) \quad (2)$$

(A constant of proportionality which is of no consequence for further calculations has been ignored in this expression.) The first Lorentzian term of half-width a is the only one containing molecular information. The second constant term γ corresponds to shot noise. The third term corresponds to the direct current part of the signal; this is blocked experimentally and will be ignored in subsequent calculations.

The signal reaching the analog-to-digital converter of the autocorrelator has a power spectrum which is the product of $P(\omega)$ and $T(\omega)$. The Fourier transform of this product is the observed autocorrelation function $C_u(t)$. Using standard transform techniques,[11] we obtain

$$\begin{aligned} C_u(t) = {} & [(1/2)(b^2 - a^2)(a^2 - c^2)]\{a^3(b^2 - c^2)\exp(-at) + \\ & b(a^2 - c^2)[\gamma(b^2 - a^2) - a^2]\exp(-bt) - \\ & c(b^2 - a^2)[a^2 + \gamma(a^2 - c^2)]\exp(-ct)\} \quad (3) \end{aligned}$$

The uncorrected function $C_u(t)$ contains three exponential terms. The first of these is dominant and contains the molecular information sought. The second and third terms are spurious exponentials caused by filtering.

In order to obtain a, it is necessary to correct $C_u(t)$ by removing the spurious exponentials. Doing so, however, requires the unknown value of a for calculation of amplitudes of the spurious terms, and the value of the shot noise γ is also needed. Because the first term in eq 3 is dominant, a rough value of a can be obtained by fitting $C_u(t)$ to a single exponential, the decay rate of which will be approximately equal to a. The value of the shot noise γ can be obtained from the results of previous runs using power spectral density analysis of the signal; details of the procedure used here will be given by Huang.[12]

From the known values of b, c, and γ, and the approximate value of a, it is possible to calculate the spurious terms in eq 3 and remove them from $C_u(t)$ to obtain a corrected autocorrelation function $C(t)$. It is possible in principle to iterate the correction procedure by using a corrected value of a obtained from $C(t)$ to make more accurate corrections, but in practice this is not necessary. If corrections are so large as to require iteration, the resulting corrected function is unlikely to have acceptable accuracy.

It should be noted that the assumption in eq 2 and 3 of a Lorentzian power spectrum for purposes of making electrical corrections is nearly always valid, although further analysis of the corrected autocorrelation function $C(t)$ can proceed either on a single- or multiexponential basis, whichever is appropriate.

The autocorrelation apparatus and the validity of the corrections just described were checked by comparison between runs made on the same solutions over a range of angles using both power spectral analysis and autocorrelation. Diffusion coefficients measured by the two methods agreed within the usual estimated experimental error of a few per cent. Use of the uncorrected correlation function $C_u(t)$ was found to lead to errors in D of 15% or more under unfavorable conditions. The autocorrelation data reported here were obtained under nearly optimum conditions where relatively small corrections were required. The effect of these corrections on calculations of internal relaxation times remains significant, however.

Experimental Section

The preparation and characterization of the sample used in this work have been reported elsewhere.[13-14] From sedimentation equilibrium, the weight-average molecular weight was found to be 26.8 (±0.2) × 10^6, and the z-average molecular weight was 31.8 (±2.6) × 10^6. The weight-average molecular weight determined from light scattering was 27.8 (±1.2) × 10^6. The cyclohexane used for making solutions was Spectroquality manufactured by Matheson, Coleman & Bell; the 2-butanone, manufactured by Matheson, Coleman & Bell, was reagent grade. Both solvents were used as received, without further purification. Solutions in 2-butanone were prepared at room temperature by placing a weighed amount of solute in a weighed quantity of solvent and allowing the mixture to stand with occasional gentle swirling. The sample dissolved in about 2 days. A similar procedure was used for making cyclohexane solutions, except that the mixture was maintained at about 36-40° for 2-4 days. All solutions were prepared just before use and were centrifuged for 2 hr at about 1000g as described previously[15] before spectral measurements were made. Centrifugation was performed in the same specially constructed cells used for scattering measurements.

For each solvent, several solutions were prepared which ranged upward in concentration from the lowest concentration giving adequate scattering. Runs were made on each solution at angles from 25 to 70°. Several hundred points of the autocorrelation function $C_u(t)$ were determined at each angle. The correlator base line was removed by subtracting from $C_u(t)$ the average value of the flat tail observed at very long times. The remaining data set for each run was then subjected to a least-squares two-parameter fit to a single exponential for the purpose of making the electrical corrections above described.

For autocorrelation measurements, the correlation function determined is the Fourier transform of the power spectrum. The Lorentzian power spectrum characteristic of diffusion corresponds to

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Table I
Intramolecular Relaxation Times τ_1 and Relative Intensities $B/(A + B)$ for Polystyrene (M_w = 27.3 × 10^6) in Cyclohexane at 35.4°

Concn × 10^3 (g-cm^{-3})	$D \times 10^7$ (cm^2-sec^{-1})	Angle θ (deg)	$x = q^2 \langle s^2 \rangle$	$\tau_1 \times 10^3$ (sec)		$B/(A + B)$ (%)
0.04	0.27 (30°)	40	2.3	1.3		4
		50	3.6	2.3	av 2.1	17
		55	4.3	2.8		26
0.05	0.26 (25, 30°)	35	1.8	1.6		4
		40	2.3	2.3		6
		50	3.6	2.2	av 2.1	17
		60	5.0	2.5		33
		65	5.8	1.9		33
0.09	0.27 (30°)	35	1.8	2.3		4
		40	2.3	1.3		6
		50	3.6	2.1	av 2.0	17
		55	4.3	2.3		22
0.16	0.25 (30, 35°)	40	2.3	1.8		6
		50	3.6	1.4	av 1.7	12
		60	5.0	2.0		25

Table II
Intramolecular Relaxation Times τ_1 and Relative Intensities $B/(A + B)$ for Polystyrene (M_w = 27.3 × 10^6) in 2-Butanone at 25.0°

Concn × 10^3 (g-cm^{-3})	$D \times 10^7$ (cm^2-sec^{-1})	Angle θ (deg)	$x = q^2 \langle s^2 \rangle$	$\tau_1 \times 10^3$ (sec)		$B/(A + B)$ (%)
0.07	0.40 (25°)	45	4.1	1.8		28
		50	5.0	1.7	av 1.8	37
		55	6.0	1.9		50
		60	7.0	1.4		44
		70	9.3	1.4		71
0.13	0.45 (25°)	35	2.5	1.1		9
		40	3.3	1.3		11
		45	4.1	1.8	av 1.5	19
		50	5.0	1.7		27
		55	6.0	1.7		34
0.22	0.48 (25°)	40	3.3	1.4	av 1.2	10
		50	5.0	1.0		19
		60	7.0	1.3		36
		70	9.3	1.2		47
0.30	0.47 (25°)	40	3.3	1.3		11
		45	4.1	1.3	av 1.4	15
		50	5.0	1.7		25
		55	6.0	1.3		26
		60	7.0	1.1		30
0.37	0.40 (25°)	40	3.3	1.7		19
		45	4.1	1.7	av 1.7	25
		50	5.0	1.8		40
		55	6.0	1.6		44
		60	7.0	1.6		53

an exponential autocorrelation function with decay constant τ_c equal to the reciprocal of the spectral half-width. At low values of x, where only translational motion contributes to the spectrum

$$\tau_c = 1/2q^2D \qquad (4)$$

As for spectral analysis, a factor of two arises because of convolution of the Lorentzian light spectrum in the self-beating spectrometer.

The corrected correlation function $C(t)$ was for each solution fit to a single exponential at each angle of measurement to determine the range of angles for which $1/q^2\tau_c$ was constant. Data in this range of angles were averaged and used to calculate D according to eq 4. For the cyclohexane solutions, a nearly constant value of $1/q^2\tau_c$ was observed for angles 25 and 30°; corresponding values of x are 1.0 and 1.3, respectively. Because still lower values of x were not accessible, the values of D obtained may be slightly high because of spectral broadening due to intramolecular motion. The error should be only barely outside the experimental precision of a few per cent, however. For the 2-butanone solutions, it was not certain that constant values of $1/q^2\tau_c$ corresponding to translational motion only were obtained even at θ = 25°, where x is about 1.3. The 25° data were used to calculate D; accordingly, the values obtained may be as much as 10% high, although it is likely that the error is smaller.

At angles above 35°, the values of D obtained from low-angle data were used in fitting $C(t)$ to the following three-exponential form

$$C(t) = A^2 \exp[-2q^2Dt] + B^2 \exp[-2(q^2D + 2/\tau_1)t] + 2AB \exp[-(2q^2D + 2/\tau_1)t] \qquad (5)$$

Here A is the intensity of the translational contribution of half-width q^2D in the light spectrum, and B is the intensity of the intramolecular contribution having half-width $(q^2D + 2/\tau_1)$. The factors of two in the decay times and addition of a "cross term" in the photocurrent autocorrelation function are both due to convolution in the spectrometer. This function is the Fourier transform of the sum of Lorentzians expected for spectral analysis.[9,10]

This three-exponential analysis of the photocurrent autocorrelation function (corresponding to a two-exponential light spectrum) gives experimental values for τ_1 and for the fractional intensity of the scattering due to intramolecular motion. The fractional intensity $B/(A + B)$ is predicted theoretically to increase with x, and the results can be compared with theory. A value of τ_1 is obtained at each angle for which the fit is performed. This value should be constant with angle. A trend in the values of τ_1 with angle might indicate either that a systematic experimental error exists or that the premise that only two Lorentzian components contribute significantly to the light spectrum is not justified.

Results and Discussion

Tables I and II summarize the results for the cyclohexane and 2-butanone solutions, respectively. The parameter x is calculated in Table I using the value for $\langle s^2 \rangle = 2.48 \times 10^{-10}$ cm^2 given by Slagowski[13] for this sample in cyclohexane at 35.4°. For the 2-butanone data of Table II, no directly measured value of $\langle s^2 \rangle$ was available for calculating x. An approximate value of $\langle s^2 \rangle = 3.8 \times 10^{-10}$ cm^2 was used which was obtained by plotting the data of Oth and Desreux[16] as log $\langle s^2 \rangle_z$ *vs.* log M_w and extrapolating to the weight-average molecular weight of the present sample.

The values of D given in Tables I and II are calculated from eq 4 using the average value of $1/q^2\tau_c$ at the angle(s) given in parentheses. As stated, it is not certain, particularly for the 2-butanone solutions, that a low enough value of x was obtained to avoid errors in D because of spectral contributions from intramolecular motion. Because of this possible error, stated values of D may be as much as 5% high for the cyclohexane solutions and 5–10% high for the 2-butanone solutions. Because of possible errors and the limited range of concentration covered, a discussion of the concentration dependence of D is not warranted.

In order to evaluate the potential of quasielastic scattering for determining intramolecular motion, it is of considerable interest to estimate the magnitude of possible sources of error in the values of τ_1 reported. These errors include the use of an uncertain value of D in curve fitting to obtain τ_1, the error due to an incorrect correlator baseline, the error due to neglecting polydispersity, and the error due to neglect of all spectral contributions due to modes of motion higher than the first.

The influence of an error in D on the calculated τ_1 was examined by renalayzing several sets of data using values of D higher and lower than those reported. For variations up to 10–15%, a certain percentage change in D caused a roughly equal change in τ_1 in the opposite direction. Reported values of τ_1 may accordingly be in error by 5–10% because of error in D.

Although correlator baseline was in every case removed experimentally, the adequacy of the procedure described was checked by reanalyzing several autocorrelation functions without removing the baseline. A change of less than 5% in τ_1 typically resulted. Because the baseline could be determined fairly precisely and removed, error from this source is probably completely negligible.

Although the theory used for data analysis applies to monodisperse systems, the sample used was not monodisperse. The effect of polydispersity is difficult to estimate, but it is believed to be small. Use of the weight-average and z-average molecular weights given and assumption of a Schulz distribution of molecular weights leads to a value of the heterogeneity parameter z equal to 4.5, indicating a narrow distribution. Previous calculations[10] indicate that for $2 \le x \le 6$ an increase in half-width of about 6% will occur in the translational contribution to the spectrum. The intensity of this contribution decreases with x, however. The effect of polydispersity on the intensity of the first intramolecular contribution is predicted to be small.[5] We estimate the total error in τ_1 due to neglect of polydispersity effects to be less than 10% for our sample.

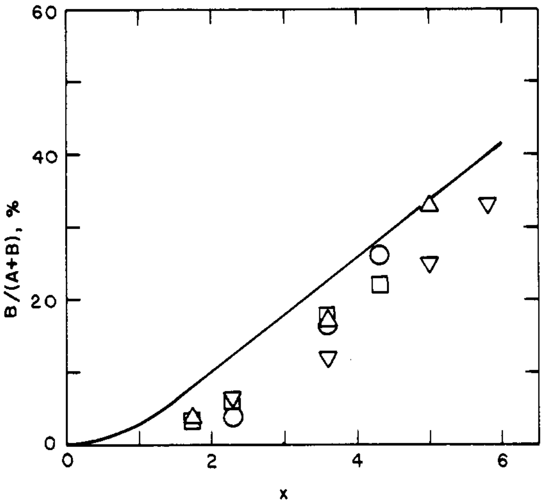

Figure 1. Variation with x of the relative intensity of scattering contributed by intramolecular motion for polystyrene having mol wt 27.3×10^6 in cyclohexane at 35.4°: (○) $c = 0.4 \times 10^{-4}$ g-cm^{-3}; (△) $c = 0.5 \times 10^{-4}$ g-cm^{-3}; (□) $c = 0.9 \times 10^{-4}$ g-cm^{-3}; (▽) $c = 1.6 \times 10^{-4}$ g-cm^{-3}.

The effect of ignoring spectral contributions from higher modes is also hard to estimate. For both the cyclohexane and 2-butanone solutions, the values of τ_1 are constant with changing x within experimental error; this random error is larger for the cyclohexane solutions, for which the scattering is less than that for the 2-butanone solutions. An upper limit of x beyond which two-Lorentzian analyses of spectra should not be undertaken can be determined experimentally by finding the value beyond which τ_1 shows a trend with x. Apparatus limitations prevented us from obtaining spectra of adequate accuracy over a broad enough range of x to establish this limit, however.

Having discussed some possible errors in the values of τ_1 given, we now compare these values with those calculated from infinite dilution theories. Recent advances in experimental technique for measuring viscoelastic properties of dilute polymer solutions[17,18] have shown that refined versions of these theories can quantitatively predict τ_1 within the error of such measurements, which is presently probably less than 15%. Confidence can accordingly be placed in calculated theoretical values. Errors in the present quasielastic scattering measurements are too large to allow distinctions to be made among subtle refinements of theory, and it is sufficient to compare the present results with the basic theoretical treatment of Rouse[19] for free-draining coils.

According to the Rouse theory, at infinite dilution τ_1 may be calculated either by

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

or

$$\tau_1 = \langle r^2 \rangle / 3\pi^2 D_0 \qquad (7)$$

Here η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, R is the gas constant, $\langle r^2 \rangle$ is the mean-square end-to-end distance, and D_0 is the diffusion constant. For the cyclohexane solutions, use of the value of $[\eta]$ given by Sla-

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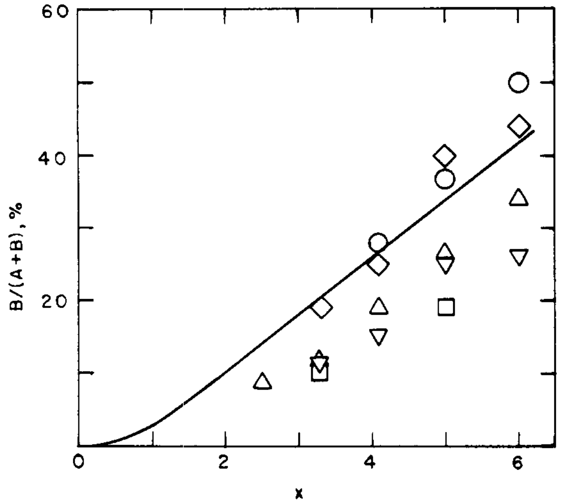

Figure 2. Variation with x of the relative intensity of scattering contributed by intramolecular motion for polystyrene having molecular weight 27.3×10^6 in 2-butanone at 25.0°: (○) $c = 0.7 \times 10^{-4}$ g-cm^{-3}; (△) $c = 1.3 \times 10^{-4}$ g-cm^{-3}; (□) $c = 2.2 \times 10^{-4}$ g-cm^{-3}; ▽, $c = 3.0 \times 10^{-4}$ g-cm^{-3}; (◇) $c = 3.7 \times 10^{-4}$ g-cm^{-3}.

gowski[13] for this sample yields from eq 6 that $\tau_1 = 1.6 \times 10^{-3}$ sec; substitution of $\langle r^2 \rangle = 6 \langle s^2 \rangle_z = 15 \times 10^{-10}$ cm^2 into eq 7 gives $\tau_1 = 1.9 \times 10^{-3}$ sec. The experimental values in Table I compare favorably with these theoretical values. For the 2-butanone solutions, use of eq 7 with $\langle s^2 \rangle_z = 3.8 \times 10^{-10}$ cm^2 gives $\tau_1 = 2.1 \times 10^{-3}$ sec; agreement with the experimental values in Table II is fair.

This approximate agreement of experiment with theory is at variance with the results of King, Knox, and McAdam,[20] who find experimental values of τ_1 which are about one-fourth of the theoretical values calculated from the Rouse theory. However, these authors do not report making any corrections to their autocorrelation functions, and this may account for their observed discrepancy. Reanalysis of our uncorrected autocorrelation functions for the 2-butanone solution having concentration 0.07×10^{-3} g-cm^{-3} yielded values of τ_1 which were nearly a factor of two lower than the corrected values reported in Table II for $\theta = 45°$; a strong upward trend with angle was also observed when the uncorrected data were analyzed.

Finally, Figures 1 and 2 show the percentage of scattering due to intramolecular motion in cyclohexane and 2-butanone solutions, respectively. The solid lines in these figures correspond to theoretical values given by Tagami and Pecora.[4] Agreement is better than would be expected, given the limitations of the model upon which the calculations are based.

Conclusions

The results reported here show that under optimum conditions and with the use of appropriate corrections, quasielastic scattering may be used to quantitatively determine the relaxation time of the first normal mode in high molecular weight random-coil polymers. The overall accuracy of scattering values of τ_1, although well within a factor of two, is not as high as for careful viscoelastic measurements, where the error may be 15% or less. However, advances in scattering techniques give reason to believe that the accuracy with which τ_1 can be determined may increase to a point where these techniques may be comparable in accuracy to viscoelastic measurements for the case of high molecular weight solutes. With such increased accuracy, quasielastic scattering will become a valuable tool for investigating the concentration dependence of τ_1 and the variation of τ_1 with solvent for a given solute.

Acknowledgments. We are grateful to Professor L. J. Fetters for providing samples of several very high molecular weight polystyrenes, and to Professor Donald McIntyre and Dr. E. L. Slagowski for their characterization data for these materials. We thank Professors John Schrag and A. L. Lodge for making available to us unpublished calculations concerning intramolecular relaxation in dilute solution. This work was supported through National Science Foundation Grant GP-8328.

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