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Brillouin Scattering and Segmental Motion in Polystyrene–Cyclohexane Solutions

Walter Lempert and C. H. Wang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.
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ABSTRACT: Brillouin spectra of bulk M_w = 390 000 polystyrene and its cyclohexane solutions have been studied as a function of temperature and scattering angle. Comparison with earlier studies on M_w = 20 000 polystyrene indicate that the Brillouin line width is molecular weight independent, both in the bulk polymer and in solution. The angular-dependent experiment shows that in the high-temperature (hydrodynamic) regime, the Brillouin line width is approximately $\sin^2(\theta/2)$ dependent but in the low-temperature regime is approximately independent of angle. The theory of Lin and Wang is used to extract the structural relaxation time, τ_s, as a function of temperature and scattering angle, as well as the adiabatic sound frequency, ω_s, and the relaxation strength. Good agreement between theory and experiment is obtained.

Introduction

Light scattering has emerged as a powerful tool for studying structural relaxation dynamics in viscoelastic systems.[1] Such phenomena occur over a wide range of frequencies and as such have been investigated with both the autocorrelation[2] and Brillouin[3] light scattering techniques. In the case of polymer fluids, initial Brillouin scattering work in this laboratory has demonstrated in the hypersonic frequency range the existence of a maximum in the line width, as well as considerable dispersion in the frequency shift, of the Brillouin component as a function of temperature.[4] These results could not be explained with a classical hydrodynamic theory of the liquid state and required a theory that took into account the viscoelastic behavior of the polymer fluid. Early theoretical work by Isakovich and Chaban[5] provided a phenomenological model that could be used to qualitatively describe the observed Brillouin spectra, but this theory lacked a strong statistical mechanics foundation.

Later experimental work with poly(propylene glycol) and poly(ethylene glycol) demonstrated that the hypersonic velocity and attenuation as probed by Brillouin scattering rapidly become independent of molecular weight[6,7] as the length of the polymer chain is increased beyond a single monomer unit. This result strongly implies that the dynamics of sound propagation and attenuation are determined by motions of the polymer involving very few segments, as opposed to motion of the entire polymer backbone. This idea became the motivating factor behind a theory developed by Lin and Wang,[8,9] in which statistical mechanics was used to incorporate the effects of segmental rearrangement on the observed features of the Brillouin spectrum of polymer fluids. This theory was subsequently used to interpret the earlier data and, recently, has been used to interpret the Brillouin spectra of bulk poly(phenylmethylsiloxane) and poly(dimethylphenylmethylsiloxane)[10] polymers as well as bulk M_w = 20 000 polystyrene and its cyclohexane solutions.[11]

In this work we continue our ongoing investigation of structural relaxation in polymer fluids and report the results of our Brillouin scattering study of M_w = 390 000 polystyrene and its cyclohexane solutions. The dynamics of the central Rayleigh component is currently being investigated by photon correlation spectroscopy and the results will be reported elsewhere.[12] The significance of the present work is to carry out a systematic study of the evolution of the structural component that dominates the Brillouin spectral features of the concentrated solution and the bulk sample. By comparison with the work of ref 11 we show that the Brillouin line width is independent of molecular weight for all concentrations and for the bulk polymer. We also show that for the solutions, the Brillouin frequency shift is also independent of molecular weight.

Experimental Section

Weighed amounts of styrene monomer (inhibitor removed) were Millipore-filtered into 13-mm Pyrex cells with two attached constrictions. After the cells were degassed, the upper constrictions were vacuum sealed and the samples were thermally polymerized by immersing them in an oil bath with its temperature controlled at 102 ± 0.5 K for approximately 4 days. This yields polystyrene of $M_w \simeq 390 000$.[13] All but one of the cells were then opened, and weighed amounts of filtered cyclohexane were added. The second constriction was then sealed and solutions were produced by rotating the cells in the hot oil bath. In this way, dust-free samples of bulk polymer, as well as solutions of up to 80% by weight, were produced. These samples were suitable for recording homodyne autocorrelation as well as Brillouin spectra. It should be noted that the solution process for the 80% sample took approximately 4 weeks, with homogeneity being ensured by recording experimental spectra as a function of height inside the cell.

Brillouin spectra were recorded as a function of temperature and scattering angle using a Burleigh five-pass piezoelectrically scanned Fabry-Perot interferometer, with 4880-Å radiation from a single-mode argon ion laser as the source. The finess of the entire system was approximately 60 and the free spectral range employed varied from 15.00 to approximately 23.00 GHz. The experimental line shape was determined by recording the spectrum of a piece of ground glass.

Experimental spectra were photon counted, recorded with a PDP 11/10 minicomputer, and sent to a larger 11/34 computer for curve fitting. Autocorrelation spectra were also recorded and will be discussed in a subsequent publication.[12]

Theory and Curve-Fitting Procedure

Brillouin scattering occurs because as sound propagates in a viscous medium, the compression and rarefaction from the traveling longitudinal wave cause periodic fluctuations in the local density and, as such, in the local dielectric constant. These fluctuations give rise to a symmetric doublet whose position corresponds to the sonic frequency and whose width corresponds to the attenuation coefficient, which in a purely viscous medium is proportional to the fluid viscosity. In the simplest model of a viscoelastic system, the attenuation depends on the relationship between the period of the wave and the time it takes for the medium to relax to a new equilibrium structure, i.e., the time for the induced stress (both longitudinal and shear stress) to relax away. We expect the attenuation to be maximum when these times are approximately equal, i.e., when $\omega\tau_s \cong 1$, where ω is the sonic frequency and τ_s is the structural relaxation time.

The theory of Lin and Wang[9] assumes that the density fluctuation is due to the segmental rearrangement of

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polymer chains in the direction parallel to the direction of **q** (the scattering vector). Their calculation shows that for structural relaxation in a polymer fluid, the segmental rearrangement involves only a few monomer units. They treated the dynamics of segmental motion using the generalized equations of Mori and Zwanzig[14,15] with the result for the Rayleigh–Brillouin spectrum, $I(\mathbf{q},\omega)$, given by the rather involved expression

$$I(\mathbf{q},\omega) = \frac{N_1D_1 + N_2D_2}{D_1^2 + D_2^2} \tag{1}$$

where

$$N_1 = -\left(1 + \frac{\alpha_2''(\omega)}{\omega}\right)\left(1 + \frac{\alpha_3''(\omega)}{\omega}\right)\omega^2 + \alpha_2'(\omega)\alpha_3'(\omega) + (1 - 1/\gamma)\omega_s^2$$

$$N_2 = \omega\left[\alpha_2'(\omega) + \alpha_3'(\omega) + \frac{\alpha_2''(\omega)}{\omega}\alpha_3'(\omega) + \frac{\alpha_3''(\omega)}{\omega}\alpha_2'(\omega)\right]$$

$$D_1 = -\omega^2\left[\alpha_2'(\omega) + \alpha_3'(\omega) + \frac{\alpha_2''(\omega)}{\omega}\alpha_3'(\omega) + \frac{\alpha_3''(\omega)}{\omega}\alpha_2'(\omega)\right] + \left(\frac{\alpha_3'(\omega)}{\gamma}\right)\omega_s^2$$

$$D_2 = \omega\left[-\omega^2\left(1 + \frac{\alpha_2''(\omega)}{\omega}\right) \times \left(1 + \frac{\alpha_3''(\omega)}{\omega}\right) + \omega_s^2\left(1 + \frac{\alpha_3''(\omega)}{\omega\gamma}\right) + \alpha_2'(\omega)\alpha_3'(\omega)\right]$$

where $\alpha_i'(\omega)$ and $\alpha_i''(\omega)$ correspond to the real and imaginary parts of the structural relaxation spectrum. They are given by

$$\alpha_i'(\omega) = k_{ii}(0)\tau_i/(1 + \omega^2\tau_i^2) \tag{2}$$

$$\alpha_i''(\omega) = k_{ii}(0)\tau_i^2\omega/(1 + \omega^2\tau_i^2) \tag{3}$$

Here $k_{ii}(0)$ is the relaxation strength, corresponding to the ith diagonal component of the memory function matrix[9] at $t = 0$, with $i = 2$ or 3. τ_i is the associated relaxation time for the relaxation strength, γ is C_p/C_v, and ω_s is the adiabatic sound frequency. For small q, $K_{ii}(0)$ is proportional to q^2 and ω_s is linear in q. The relaxation time τ_i is q independent for small q. These results are tested in this work.

Physically, the $i = 2$ component corresponds to relaxation due to segmental rearrangement, and the $i = 3$ term corresponds to the entropy relaxation. In the interferometric region, the dispersion of the central component is extremely small and therefore we set $\omega\tau_3 \cong 0$, obtaining

$$\alpha_2'(\omega) = k_{22}(0)\tau_s/(1 + \omega^2\tau_s^2) \tag{4}$$

$$\alpha_2''(\omega) = k_{22}(0)\tau_s^2\omega/(1 + \omega^2\tau_s^2) \tag{5}$$

$$\alpha_3'(\omega) = \gamma D_T q^2 \cong 10\ \text{MHz} \tag{6}$$

$$\alpha_3''(\omega) \cong 0 \tag{7}$$

where D_T is the thermal diffusion coefficient.

In order to test the experimental result, we have recorded Rayleigh–Brillouin spectra as a function of temperature and scattering angle and least-squares fit them to eq 1, utilizing eq 4–7. Hence the parameters required are ω_s, $k_{22}(0)$, τ_s, γ, and α_3'. In addition, we add parameters corresponding to the interferometer free spectral range, spectral origin, and normalization constant. It should be noted that because of the high contrast of the five-pass instrument, the base line could be determined quite well, and as such the base line was entered as a known constant and was not a parameter. The instrumental response function was determined by recording the spectrum of a piece of ground glass and was accounted for via a convolute and compare algorithm. The uncertainties in the individual parameters were estimated by their reproducibility from mulitple runs under the same experimental conditions.

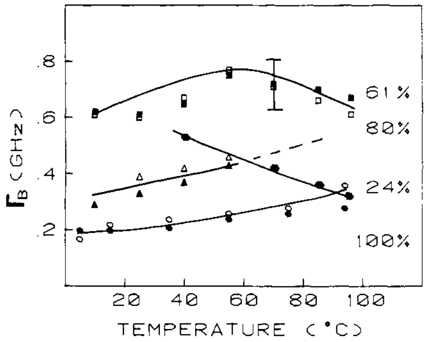

Figure 1. Experimental Γ_B as a function of temperature: (●) 24%, M_w = 390 000; (■) 61%, M_w = 390 000; (□) 61%, M_w = 20 000; (▲) 80%, M_w = 390 000; (△) 80%, M_w = 20 000; (●) 100%, M_w = 390 000; (○) 100%, M_w = 20 000. The solid curves are meant to clarify the figure and have no theoretical significance. The uncertainties are estimated at ±10%.

Results and Discussion

A. Line Width and Frequency Shift. Before performing a detailed spectral fit using eq 1, we have measured the Brillouin spectral half-line-width and the apparent frequency for all samples. Figure 1 shows the Brillouin half-widths at half-maximum, Γ_B, as a function of temperature for the bulk polymer, as well as for the solutions studied. The solid figures correspond to the M_w = 390 000 sample used in this investigation, whereas the open figures correspond to the data collected from the M_w = 20 000 sample in the earlier work for reference.[11]. The curves are meant only to clarify the drawing and have no theoretical significance. It should be noted that the values of Γ_B were extracted by hand from the experimental data, with the effect of convolution estimated by subtracting the width of the central component. This is a crude procedure, with uncertainties estimated as ±10%, but serves to demonstrate a number of important features.

First, while we have no M_w = 20 000 data for the 24% by weight solution, we see that to within the 10% estimated uncertainty, the Brillouin line widths for the bulk sample, as well as for the 80% and 61% solutions, are independent of molecular weight. We note that closer examination reveals that the M_w = 20 000 data points generally lie somewhat above those of the M_w = 390 000 data points, but this effect is less than the quoted 10% uncertainty. A more accurate determination of the line width would be required to ascertain whether or not this is a real effect. This result is similar to that found in bulk PPG[4] and supports the concept of segmental motion being responsible for the attenuation of sound in polymer fluids. In addition, this result extends the range of the earlier work in two directions. First, the molecular weight range employed is 2 orders of magnitude greater than that employed in ref 6, and second, in addition to the bulk material, the molecular weight independence is confirmed for the solution phase as well.

Figure 2 shows the Brillouin frequency shifts, f_B, for the 61%, 80%, and bulk samples, along with the results from the M_w = 20 000 data. In this case, we see that for the

Table I
Brillouin Line Width (Γ_B) as a Function of Angles

concentration	Γ_B, GHz 38°	60°	90°	120°	150°
bulk	0.11 (1.04)[a]	0.15 (0.60)	0.18 (0.36)	0.15 (0.20)	0.21 (0.23)
80%	0.10 (0.94)	0.16 (0.64)	0.22 (0.44)	0.35 (0.47)	0.40 (0.43)
61%	0.24 (2.26)	0.50 (2.00)	0.71 (1.42)		1.18 (1.26)
24%	0.10 (0.94)	0.17 (0.68)	0.34 (0.68)	0.60 (0.80)	0.67 (0.72)

[a] The quantity within parentheses is $\Gamma_B/\sin^2(\theta/2)$.

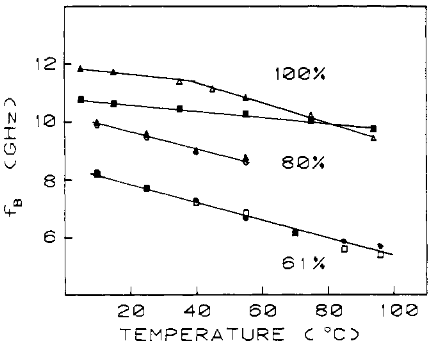

Figure 2. Experimental frequency shift as a function of temperature: (■) 100%, M_w = 390000; (△) 100%, M_w = 20000; (▲) 80%, M_w = 390000; (○) 80%, M_w = 20000; (●) 61%, M_w = 390000; (□) 61%, M_w = 20000. The solid curves are meant to clarify the figure and have no theoretical significance.

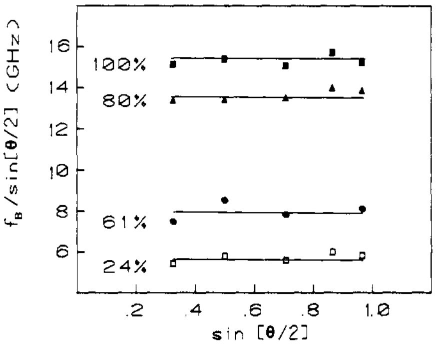

Figure 3. Experimental $f_B/\sin(\theta/2)$ as a function of $\sin(\theta/2)$: (■) 100%; (▲) 80%; (●) 60%; (□) 24%. The solid curves are meant to clarify the figure and have no theoretical significance.

solutions, the frequency shift is molecular weight independent. For the bulk polymer, T_g for the M_w = 20 000 and M_w = 390 000 samples is different. One thus expects to observe a different frequency shift for two bulk samples, in agreement with the experimental results. The result for bulk polymers is very similar to that reported by Brody et al., who have shown that the Brillouin shift is related to T_g and that in polystyrene T_g moves to lower temperature for the lower molecular weight sample.[16] The molecular weight independence indicates that in the presence of solvent the elastic modulus does not depend on molecular weight. This makes sense since intuitively, one would expect that the small solvent molecules would penetrate the polymer coils forming a network glass whose rigidity depends only upon the relative concentration of monomer units and solvent particles. On the other hand, in the bulk sample, the packing of the individual polymer chains is dependent on the polymer size.

B. Structural Relaxation and Angular Dependence. In order to investigate the effect of structural relaxation and test the applicability of the theory of ref 9, we have investigated the angular dependence of the Brillouin spectrum of each sample at a selected temperature. The temperature is chosen so as to change the relaxation regime in which the angular dependence is performed. Specifically, we studied the bulk and 80% solution at room temperature, the 61% solution at 75 °C, and the 24% solution at 95 °C. Referring to Figure 1, we see that at room temperature the bulk sample and the 80% solution are in the "low-temperature" regime (i.e., $\omega_s\tau_s \gg 1$) of the attenuation curve; i.e., decreasing the temperature causes the attenuation (line width) to decrease. Conversely, at 95° °C, the 24% solution is in the "high-temperature" regime ($\omega_s\tau_s \ll 1$), where the fluid resembles a classical hydrodynamic liquid closely, and at 75 °C, the 61% solution corresponds to $\omega_s\tau_s \simeq 1$ and the line width in this case is approximately at the maximum.

Figure 3 shows a plot of $f_B/\sin(\theta/2)$ against $\sin(\theta/2)$ for each of the solutions studied. While there is some scatter in the data, due to a combination of angular uncertainty and frequency shift uncertainty, the data clearly display the expected linear dependence of f_B with $\sin(\theta/2)$. This basically serves to demonstrate that our technique is suitable. One notes that a data point for the 61% solution is missing. This is because the interferometer free spectral range was such that at this angle, the point could not be determined. Although we could have changed the plate separation to obtain the frequency at this concentration, we felt it was not necessary.

Table I shows Γ_B as a function of angle for each of the solutions. One can see that for the bulk sample, the line width is only slightly dependent on **q** (or scattering angle), and one could argue that to within experiment uncertainty, the data appear to be independent of angle. This result deviates significantly from classical hydrodynamic theory, in which a q^2 dependence is predicted for Γ_B. Whether Γ_B in the bulk sample is independent of angle or slightly dependent on angle is not the most important point. Our main concern is to investigate the change in the **q** dependence as the temperature regime probed is changed from "low" to "high". One notes that the **q** dependence in Γ_B is significant as the polymer concentration and temperature of the sample are changed. Although the bulk sample shows very little angular dependence, the 24% sample at 95 °C increases by a factor of almost 7 (as the scattering angle is increased). The other samples show increases but lie somewhere in between.

As mentioned above, in the hydrodynamic limit, Γ_B should be proportional to $\sin^2(\theta/2)$,[17] whereas in the slow relaxation limit, Γ_B is approximately angular independent, as shown by Lin and Wang.[9] This behavior is illustrated more clearly by the data in parantheses in Table I, which give $\Gamma_B/\sin^2(\theta/2)$ as a function of angle. For the 24% sample, Γ_B follows approximately $\sin^2(\theta/2)$ dependence, although the uncertainty in the data makes precise determination of the angular dependence impossible. At any rate, as the concentration is increased, the samples show increased deviation from $\sin^2(\theta/2)$ dependence, as one would expect as deviations from the classical hydrodynamic behavior increase.

In order to quantify the above results, as well as to demonstrate the suitability of the approach utilized by Lin

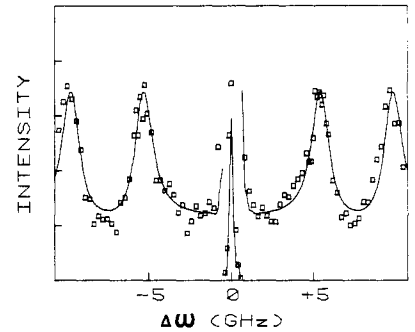

Figure 4. Experimental spectrum (□) along with least-squares fit (——) to eq 1. The central component has been scaled down by a factor of 150 and the points have been edited so that only one point in eight is displayed.

and Wang, we have fit several of the experimental spectra to eq 1, using eq 4–6. Since the cost of computing the spectra is rather high (≃\$20.00 each), we have not performed the curve fitting on every spectrum but rather chose to fit two representative sets of data that we fell illustrate the essential points. Specifically, we fit the 90° spectra for each concentration studied, and we also fit the 61% concentration at each angle studied.

Figure 4 shows the results of the fit for a typical spectrum (61% at 90° scattering angle). One notes that while the fit to the Brillouin component is quite good, the fit to the Rayleigh component is a little off. This is due to several factors. First, it is impossible to exactly reproduce the experimental instrumental response function, and since the width of the Rayleigh component is about 10 MHz, which is essentially a δ function convolved with the instrument function, it is not possible to exactly reproduce the Rayleigh component. Second, the Rayleigh component is more susceptible to parasite scattering from the cell wall and while great care has been given to eliminate the parasitic intensity contribution, we are not certain that it has been completely eliminated. Last, the anisotropic scattering will also contribute to the Rayleigh component, and this is not accounted for in the model. However, the I_{VH} intensity in solution is low ($\rho_{\mathrm{v}} \cong 0.033$ for the 61% solution at room temperature) and since the width of the I_{VH} spectrum is also much less than the instrumental resolution, the effect of the I_{VH} signal is simple to add to the intensity of the Rayleigh component, with no effect on the line shape. For these reasons, we make no attempt in this paper in the discussion that follows to comment on the Rayleigh component and restrict our attention to the parameters that determine the Brillouin side bands.

The least-squares values of the parameters obtained are given in Table II. The values α_3' are not included in Table II because in all cases they are very small (1–10 MHz), corresponding to the width of the central component, and cannot be determined with any certainty with the Fabry-Perot interferometer.

There are, however, several important trends that one sees in the remaining parameters listed in Table II. First, the structural relaxation time, τ_s, is seen to increase significantly as the concentration is increased, consistent with the results reported in ref 11. This result indicates clearly that segmental rearrangement is slowing down as the concentration is increased. In addition, ω_s, the adiabatic frequency, increases as the concentrtion is raised, indicating that the effective elastic modulus of the solution is increasing. Both of these trends are what one would expect as the elastic character of the viscoelastic system increases.

Table II

Results from Fitting Data to Eq 1, 90° Spectra

concentration	τ_s, ns	ω_s, GHz	$k_{22}(0)$, GHz	γ	$\omega_s\tau_s$, rad
bulk	0.320	9.85	19.65	1.99	19.8
80%	0.250	8.75	20.74	1.68	13.7
61%	0.071	5.16	16.87	1.28	2.3
24%	0.046	3.62	21.67	1.14	1.0

Parameters for 61% Solution as a Function of Angle

θ, deg	τ_s, ns	ω_s, GHz	$k_{22}(0)$, GHz^2	γ
38	0.070	2.40 (7.37)[a]	8.24	1.21
60	0.075	4.11 (8.22)	13.81	1.27
90	0.071	5.16 (7.30)	16.87	1.28
150	0.073	7.56 (7.83)	29.46	1.16

[a] The quantity in parentheses is $\omega_s/\sin(\theta/2)$.

Of greater significance is the produce $\omega_s\tau_s$, which is given (in units of radians) in the right-hand column of Table II. One can see that $\omega_s\tau_s$ increases by about a factor of 20 as the concentration increases from 24% to bulk polymer.

This indicates that in the bulk polymer[16] the relaxation process is in the slow relaxation limit, corresponding to $\omega_s\tau_s \gg 1$, and as such the attenuation should be small. In addition, we note that $\omega_s\tau_s$ for the 61% solution is equal to 2.3 and is equal to 1 for 24%. This result suggests that the hydrodynamic region is approached as the polymer concentration decreases. It is, thus, very important that care be taken to use the ordinary hydrodynamic theory to interpret the data even at low polymer concentration. A new parameter τ_s to characterize the dynamics of structural relaxation is necessary.

We also note that the values of the parameter $k_{22}(0)$ are to within about a ±10% scatter, independent of concentration. This is an important result in that it gives further support to the idea that relaxation is due to movement involving only a small number of monomer units. The fact that Γ_B changes with concentration but $k_{22}(0)$ does not change with concentration indicates that relating $k_{22}(0)$ to the second moment of an intersegmental potential,[7] which dies rapidly with segment separation, is realistic.

The lower part of Table II gives the values of the parameters obtained for the 61% solution as a function of scattering angle. The most significant result is the angular independence of the parameter τ_s. Over the angular range probed, Table I shows that Γ_B changes by a factor of approximately 5, yet τ_s does not change. This gives further evidence that eq 1 together with eq 4–6 constitutes an essentially correct description of the Brillouin spectra. We also note that to within ±5%, the ω_s values are proportional to sin $(\theta/2)$. This is what we expect since ω_s corresponds to the adiabatic sound frequency.

The values of $k_{22}(0)$ increase with increasing sin $(\theta/2)$ as they should but the results do not increase as rapidly as the $\sin^2(\theta/2)$ dependence predicted by the theory.[9] While we do not have any definite explanation for this, the deviation can be accounted for by including the intramolecular thermal relaxation component in the spectral fit.

Summary and Conclusions

We find that the Brillouin line width for bulk polystyrene, as well as its cyclohexane solutions, is independent of molecular weight over the molecular weight range 20 000–390 000, indicating that the dynamics of structural relaxation are dependent upon a segmental rearrangement. In solution, the Brillouin frequency shift is molecular weight independent.

The significant result of this work concerns the angular dependence of the Brillouin line width over a wide range of relaxation regimes for different concentrations at different temperatures. We find that in the low-temperature, slow-relaxation ($\omega_s\tau_s \gg 1$) regime, Γ_B is approximately independent of angle. On the other hand, Γ_B is quite angularly dependent in the high-temperature regime.

We have computed the spectra according to the expression given by Lin and Wang and have compared them with the experimental spectra. In this effort we have extracted the values of various parameters present in the theory. We have found proper angular dependences for ω_s, τ_s, $k_{22}(0)$, and α_3' as a function of concentration. The values determined for these parameters are shown to behave in a physically meaningful way, indicating that the basic principles inherent in the generalized hydrodynamic theory are reasonable.

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References and Notes

(1) Montrose, C. J.; Litovitz, T. A. *J. Acoust. Soc. Am.* **1970** *42*, 1250.
(2) Demoulin, C.; Montrose, C. J.; Ostsowsky, N. *Phys. Rev. A* **1974**, *9*, 1740.
(3) Montrose, C. J.; Solovyev, V. A.; Litovitz, T. A. *J. Acoust. Soc. Am.* **1968**, *43*, 117.
(4) Huang, Y. Y.; Wang, C. H. *J. Chem. Phys.* **1974**, *61*, 1868.
(5) Isakovich, M. A.; Chaban, I. A. *Sov. Phys. JETP* **1965**, *23*, 893.
(6) Wang, C. H.; Huang, Y. Y. *J. Chem. Phys.* **1976**, *64*, 4847.
(7) Wang, C. H.; Lin, Y.-H.; Jones, D. R. *Mol. Phys.* **1979**, *37*, 287.
(8) Lin, Y.-H.; Wang, C. H. *J. Chem. Phys.* **1978**, *69*, 1101.
(9) Lin, Y.-H.; Wang, C. H. *J. Chem. Phys.* **1979**, *70*, 681.
(10) Fytas, G.; Lin, Y.-H.; Chu, B. *J. Chem. Phys.* **1981**, *74*, 3131.
(11) Lempert, Walter; Wang, C. H. *J. Chem. Phys.* **1980**, *72*, 2570.
(12) Lempert, Walter; Wang, C. H., to be published.
(13) Boundy, R. H., Ed. "Styrene, Its Polymers, Copolymers, and Derivatives", Reinhold: New York, 1952.
(14) Mori, H. *Prog. Theor. Phys.* (*Kyoto*) **1964**, *33*, 1123.
(15) Mori, H. *Prog. Theor. Phys.* (*Kyoto*) **1965**, *34*, 399.
(16) Brody, E. M.; Lubell, C. J.; Beatty, C. L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 295.
(17) Berne, B. J.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976; Chapter 10.

Light Scattering and Spectroscopic Studies of Polymerization Processes. 2. Thermal Polymerization of Styrene

Benjamin Thomas Peng-Nien Chu* and Georg Fytas

Chemistry Department, State University of New York at Stony Brook, Long Island, New York 11794. *Received September 9, 1981*

ABSTRACT: By using the thermal polymerization of styrene as an illustration, we propose a scheme which utilizes Raman spectroscopy and light scattering as probes for concentration, molecular weight, and size determinations in specific polymerization processes. Raman-active lines for polymer and monomer can be used to monitor the respective concentrations while the osmotic compressibility, $(\partial\pi/\partial C)_{T,P}$, and the Rayleigh ratio, $R_{vv}(K)$, can be related to the molecular weight of the polymer empirically even at very high polymer solution concentrations. In addition, we have studied static and dynamic properties of polystyrene in cumene and in styrene in dilute solutions in order to ascertain the general behavior of polystyrene dissolved in its own monomer, styrene.

I. Introduction

Studies of polymerization processes have been difficult because we lack a convenient probe which can measure *on line* the concentrations of the monomer(s) and of the polymer in a polymerization reaction. Spectroscopic techniques such as NMR, IR, Raman, and fluorescence spectroscopy and other physical methods such as density and surface tension measurements offer reasonable and possible alternatives which permit us to monitor the appropriate concentration changes in chemical reactions. However, in a polymerization process, we really want to know not only the concentrations of the monomer (C_m) and/or of the polymer (C_p) but also the molecular weight (M) of the polymer during the reaction. In the present article, we demonstrate that it is feasible to devise a scheme which can accomplish the above goals, i.e., the determination of C_p and/or C_m and M as a function of time for specific polymerization processes. In particular, we plan to devote our attention to studies of the thermal polymerization of styrene, including light scattering measurements of polystyrene in cumene and in its own monomer, styrene.

Light scattering intensity measurements can be used to determine the molecular weight, the second virial coefficient (A_2), and the radius of gyration (r_g) in very dilute solutions. At higher polymer concentrations we propose to take advantage of our understanding of the scaling concept[1] which will permit us to establish an empirical relationship between light scattering intensities and the molecular weight as well as the correlation length ξ as a function of M and C_p. In a later article, we shall also examine the molecular weight distribution[2] (MWD) and pseudogel formation using Rayleigh line width measurements and correlation function profile analysis.[3]

It should be emphasized that we are interested mainly in the application of light scattering intensity and spectroscopic techniques to study polymerization reactions and in the development of a practical *concentration* and *molecular weight* probe for polymerization process control. We are concerned with utilizing our knowledge of light scattering in the semidilute regime and of Raman spectroscopy as probes which will permit us to examine polymerization kinetics *on line*, based on sound fundamental principles. An outline of this work was presented as an invited lecture at the Symposium on Applications of Spectroscopy to Problems in Polymer Engineering and Science in the 1981 Spring National Meeting of the American Institute of Chemical Engineers, Houston, Texas.

II. Theoretical Rationale

1. Raman Spectroscopy. Raman spectroscopy has been a useful tool to elucidate the structure of polymers. On occasion, it has been used to determine concentrations

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