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Rayleigh–Brillouin Spectroscopy and Molecular Motion in Toluene Solutions of Polystyrene

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ABSTRACT: The Rayleigh–Brillouin spectra of toluene and solutions of 110 000 molecular weight polystyrene are studied. The reorientation relaxation time of the toluene is relatively unaffected by the presence of the polystyrene even up to concentrations of 150 mg/mL of polymer. Also, the hypersonic loss determined by Brillouin scattering is unaffected within experimental error. Thus, the local viscosity as probed by Rayleigh–Brillouin spectroscopy remains similar to the solvent viscosity even though the macroscopic viscosity increased by almost two orders of magnitude.

The presence of a small fraction of high molecular weight polymer in a solvent can have dramatic effects on the macroscopic properties of the solution.[1] However, the effects of polymer on the microscopic dynamics of the solvent may be quite different. In order to study such effects we have measured the Rayleigh–Brillouin spectra of toluene and its solutions with 110 000 molecular weight polystyrene.

Theory

The depolarized (I_{VH}) Rayleigh spectra of liquids such as toluene have been extensively studied.[2-6] The spectrum consists of a Lorentzian line centered at the incident frequency with width $\Gamma_{VH} = (2\pi\tau_{ls})^{-1}$ where τ_{ls} is the collective reorientation relaxation time for the liquid. It has been observed that [2,6]

$$\tau_{ls} = \frac{g_2}{J_2}\left[\frac{C'\eta_s}{T} + \tau_0\right] \qquad (1)$$

where g_2 is a static pair orientation correlation parameter, J_2 is a dynamic pair orientation correlation parameter, C' depends only on the size and shape of the molecule, η_s is the shear viscosity, T is the temperature, and τ_0 is the inertial limit for the single molecule reorientation correlation time. If polystyrene is added to toluene, the macroscopic shear viscosity will be greatly increased. The present study examines the effect of added polystyrene on the molecular reorientation time determined for the toluene. The polymer itself will give rise to a very narrow depolarized Rayleigh peak[7] compared to the toluene and the spectrum can be fit to a sum of two peaks.

The Brillouin spectrum of liquids consists of two shifted peaks with splitting given by

$$\pm\frac{\Delta\omega_l}{\omega_0} = \frac{2nV_l}{C}\sin\frac{\theta}{2} \qquad (2)$$

where ω_0 is the incident frequency, V_l is the longitudinal hypersonic velocity, C is the speed of light in a vacuum, n is the refractive index, and θ is the scattering angle in the scattering plane. The line width is

$$\Gamma_l = \frac{q^2}{2\rho}\left[\eta_v + \frac{4}{3}\eta_s\right] + \frac{\kappa q^2}{2\rho C_p}(\gamma - 1) \qquad (3)$$

where $q = (4\pi n/\lambda)\sin\theta/2$ is the magnitude of the scattering vector and λ is the wavelength of the incident light in a vacuum, ρ is the density, η_v is the volume viscosity, κ is the thermal conductivity, C_p is the specific heat at constant pressure, and γ is the ratio of specific heats C_p/C_v. For most organic liquids κ is very small and the contribution to Γ_l due to thermal conductivity can be ignored. The volume and shear viscosities that are appropriate in eq 3 must be evaluated at the frequency of the hypersonic phonons and hence may differ appreciably from the zero frequency macroscopic viscosity. The phonon velocity is given by

$$V_l = \left(\gamma\frac{M'}{\rho}\right)^{1/2} \qquad (4)$$

where M' is the real part of the longitudinal modulus $M = K + {}^4/_3G$ where K is the modulus of compression and G is the shear modulus. Again, M' must be evaluated at the frequency of the hypersonic waves.

The collective reorientation relaxation time τ_{ls} given in eq 1 is proportional to the shear viscosity η_s. However, the reorientational motions of small molecules are sensitive only to the local environment composed of the first and at most second nearest neighbor shells of molecules. The shear strain created by the rotation is thus very short ranged and the appropriate viscosity would be a more general q-dependent shear viscosity $\eta_s(q)$, where the value of q is determined by the size and shape of the reorienting unit. The shear strain associated with the longitudinal acoustic waves probed by Brillouin scattering is much longer ranged ($q \approx 0.002$ Å^{-1}), but it has a definite frequency given by $\Delta\omega_l$. Thus, the appropriate shear viscosity to use in eq 3 is

$$\eta_s(q,\omega) = \sum_j \frac{G_j(q)\tau_i}{1 + (\omega\tau_j)^2} \qquad (5)$$

where the $\{G_j(q)\}$ are q-dependent relaxation strengths and the $\{\tau_j\}$ are the corresponding relaxation times for the modes of motion which determine η_s. The value of $\eta_s(q,\omega)$

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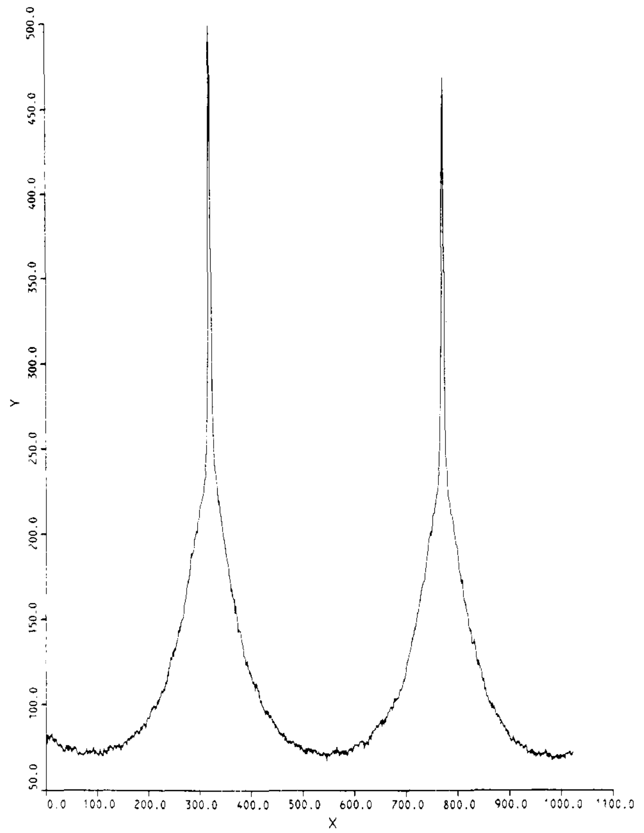

Figure 1. Depolarized (I_{VH}) Rayleigh spectrum of the 37.1 mg/mL polystyrene solution showing two Fabry-Perot orders.

may be reduced either because the range of strain is small (high q), or because the frequency of the strain is high.

Depolarized Rayleigh scattering leads to a peak centered at the incident frequency, so that the appropriate frequency to use in determining η_s is $\omega = 0$. However, the short range of interaction means that only the very local motions of polymer molecules will affect the reorientational relaxation time. Because the frequency associated with Brillouin scattering is so high ($\omega \approx 10^{10}$ Hz), only the fastest motions of the polymer molecules will affect the hypersonic viscosities and hence Γ_l. In discussing the viscosity of polymer solutions it is important to consider both the effects of scale and frequency.

Experimental Section

Rayleigh–Brillouin spectra were obtained as described previously.[3,8] The incident light was at 5145 Å and the scattering was observed at 90°. The free spectral range for the I_{HV} spectra was 233 GHz and for the Brillouin spectra 15.1 GHz. The Fabry-Perot plates used in this study yielded finesses in excess of 90 for all spectra.

All liquids and solutions were filtered through 0.2 μm membrane filters directly into 1-cm square quartz fluorimeter cells. The temperature was controlled at 25.0 °C with a circulating water bath.

The toluene was chromatoquality solvent. The polystyrene of 110 000 molecular weight was obtained from the Pressure Chemical Co. and had a M_w/M_n ratio of less than 1.10.

The spectra were recorded digitally with a 1024 point multichannel analyzer. Two Fabry-Perot orders were observed. The spectra were fit with a non-linear least-squares program.

The viscosities of the solutions were measured with Cannon-Ubbelodhe viscometers in a constant temperature bath.

Results and Discussion

The depolarized Rayleigh spectrum of the 37.1 mg/mL solution is shown in Figure 1. The two contributions are clearly separated. The line widths Γ_{VH} determined for the toluene are given in Table I. The result for pure toluene is within experimental error of previously published results.[2] The viscosities of toluene and the solutions are also given in Table I. Although the macroscopic shear viscosity increases by almost two orders of magnitude there is only a small decrease in Γ_{VH} for the highest concentrations. This suggests that the polymer has only a small effect on the local rotational motions of the solvent when the polymer is the minor constituent.

Table I
Depolarized Rayleigh Line Widths and Viscosities for Toluene and Polystyrene Solutions

	Γ_{VH}, GHz	η, cP
toluene	30 ± 1	0.55 ± 0.01
37.1 mg/mL	30 ± 1	2.40 ± 0.03
73.6 mg/mL	28 ± 1	6.5 ± 0.1
150.0 mg/mL	27 ± 1	30 ± 1

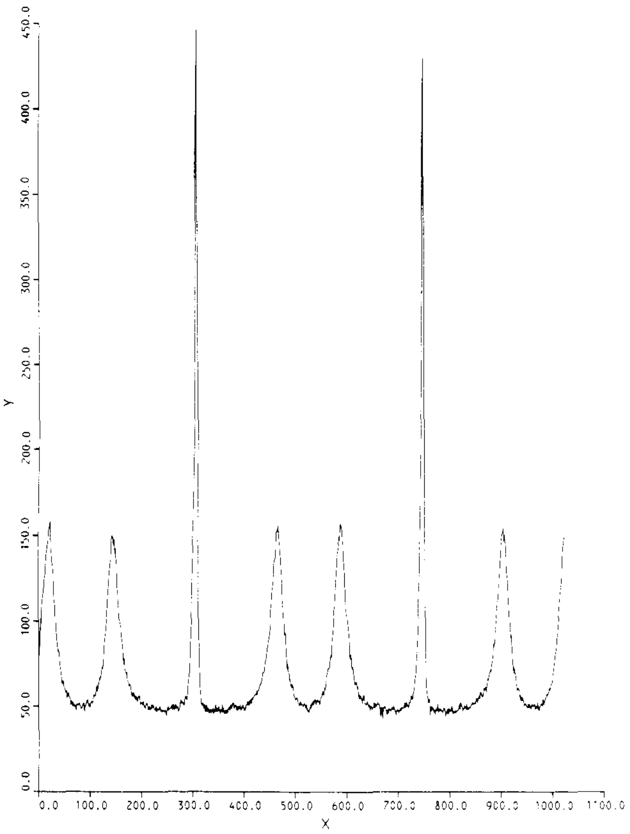

Figure 2. Rayleigh–Brillouin spectrum of toluene at 25 °C.

The Brillouin spectrum of toluene is shown in Figure 2. The Brillouin splitting is 5.44 ± 0.04 GHz. This corresponds to $V_l = 1.32$ Km/s which compares well with the literature values for toluene.[9] The observed line width is $\Gamma_l = 0.38 \pm 0.04$ GHz. The Brillouin splitting increases linearly up to 5.68 ± 0.04 GHz for the 150 mg/mL solution, but there is no detectable change in Γ_l within experimental error. For the pure toluene there is essentially no contribution of G' to M' and the phonon velocity is determined primarily by the modulus of compression. For the solutions it is reasonable to assume that at 5 GHz G' will contribute to M' and the phonon velocity will rise. The observation that Γ_l remains unchanged means that the hypersonic viscosities remain the same for the polymer solutions. The polymer motions with long relaxation times make a negligible contribution to $\eta_s(q,\Delta\omega_l)$ and the higher frequency motions are similar enough to those of the solvent that the total hypersonic viscosities of the solution remain close to those of the solvent. Thus, within our experimental error the limiting high-frequency intrinsic viscosity of polystyrene is zero. It should be noted that our limits of error are large (±10%) and that a more sensitive technique might be able to detect the small residual contribution of the polymer to $\eta_s(\omega)$ at 5 GHz. However, it appears that Brillouin scattering will not be useful in determining the high-frequency limiting viscosity in polysytrene. A more flexible chain would be required to shorten the intramolecular relaxation times. However, it is unlikely that relaxation times as short as 10^{-10} s will be observed for conformation changes in most polymers. Brillouin scattering has found great utility in the study of the glass–rubber relaxation in bulk amorphous polymers,[10] but the frequencies are too high to effectively probe the dynamics of intramolecular conformation changes for polymers in solution.

The local (high q) viscosity of polymer solutions has also been probed by several other techniques. Chapoy[11] has used fluorescence depolarization to measure the rotational relaxation time of probe molecules in concentrated polymer solutions. Boss, Stejskal, and Ferry[12] have studied self-diffusion of benzene in polyisobutylene solutions using NMR. Anderson and Liu[13] have measured spin–lattice relaxation times in benzene solutions of poly(methyl methacrylate). All the above studies demonstrated that the rate of the process being studied was determined by a local viscosity which changed only slightly upon addition of large amounts of polymers. Self-diffusion of benzene in PIB[12] correlated very well with the Fujita–Doolittle[14] theory of free volume. The importance of free volume in determining the local viscosity of polymer solutions should be a central concept in future theories of local viscosity. The local translational and orientational motions of the solvent are determined primarily by the available free space.

The concept of local viscosity is important for the understanding of bulk polymerization. While the macroscopic viscosity becomes large, the rate of polymerization will depend on the local mobility of the monomer. The local viscosity has now been studied as a function of conversion in the thermal polymerization of styrene using depolarized Rayleigh spectroscopy.[15] The collective orientational relaxation time increases only 50% after 80% of the reaction is complete. The technique of depolarized Rayleigh spectroscopy should prove to be very useful in the study of the local viscosity of polymer solutions.

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A ^{13}C Nuclear Magnetic Resonance Study of Gel-Forming (1→3)-β-D-Glucans: Molecular-Weight Dependence of Helical Conformation and of the Presence of Junction Zones for Association of Primary Molecules

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ABSTRACT: In order to gain better understanding of conformational behavior, aggregation of the helical segments, and its consequence to the gelation mechanism of gel-forming (1→3)-β-D-glucans, we have undertaken ^{13}C NMR studies of lower molecular-weight glucans of bacterial (1→3)-β-D-glucan (curdlan 13140) obtained from *Alcaligenes faecalis* var. *myxogenes* IFO 13140. It was found that, from the displacements of the ^{13}C chemical shifts of C-1 and C-3 with respect to those of glucans with $\overline{\mathrm{DP}}_n < 14$, helix conformation is adopted by the glucans with $\overline{\mathrm{DP}}_n \geq 49$. This is consistent with the ^{13}C NMR study of the mixed gel prepared by the mixture of curdlan 13140 and its lower molecular-weight glucans, in which $\overline{\mathrm{DP}}_n \leq 20$ gives sharp ^{13}C signals characteristic of the random-coil conformation, suggesting that they are just trapped in the interstices of the gel network. Examination of the variation of the peak intensity vs. $\overline{\mathrm{DP}}_n$ exhibits that the helical conformation is associated to form junction zones, presumably composed of the double- or triple-stranded helices. It was also shown that the line width of the glucan with $\overline{\mathrm{DP}}_n \geq 49$ is approximately proportional to $\overline{\mathrm{DP}}_n$. Thus, the broad linewidths observed in the physically cross-linked glucans and gels are ascribed to the entanglement of the polymers due to the presence of the cross-links. The evaluation of the correlation times of the local motions, on the basis of the approximation by the log χ^2 distribution, showed that there exists distinct difference between the glucans with finite network and the gels with the infinite network.

It is known that (1→3)-β-D-glucans function as structural components in the cell walls of many plants and microorganism and also act as reserve polysaccharides.[3] Thus, (1→3)-β-D-glucans isolated from various sources differ widely in their properties; laminaran is a water-soluble glucan, while pachyman is not; curdlan (from