activation entropies. This indicates that the activated complex is more ordered than the reactants. In contrast with this, viscoelastic relaxations tend to have positive activation entropies which are frequently very large. In these cases, the activated state must be more disordered than the ground state, and the relaxations are believed to involve complex cooperative interactions among neighboring groups.

An activation entropy close to zero is a limiting value, and relaxations in this class generally involve relatively simple motions of small molecular subgroups.

There is evidence that some complex relaxations may consist of a spectrum of simple relaxations involving different amounts of material and having different activation energies. As the frequency is increased, the absorption of energy is dominated by components having progressively smaller activation energies. This results in an apparent activation energy which is larger than that of the simple, component relaxations and a large, positive apparent activation entropy.

The glass transition has been treated by many different approaches. For example, Williams[24] has compared the Arrhenius model, transition state theory, free volume theories, and dipole diffusion. The free volume approach has been especially effective in treating the curvature of Arrhenius plots.[25,26] Of special relevance to the present discussion are the relationships among the enthalpy, entropy, and volume of activation.[27,28]

Many phenomena have been treated in terms of a distribution of relaxation times from which may be inferred a distribution of activation energies, activation entropies, or both. This possibility complicates the application of eq 2 to the analysis of experimental data. If a relaxation is governed by a nonexponential decay function,[29-31] the necessity to invoke a distribution of relaxation times may be avoided. However, these functions may have the effect of stretching the frequency scale, thereby increasing the apparent activation energy and entropy.[32]

The examples given here suggest that in at least some cases, the glass transition may be treated in terms of a special kind of distribution of relaxation times characterized by activation entropies close to zero and small-to-moderate activation energies.

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Brillouin Scattering from Polyepoxide Solutions and Gels

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ABSTRACT: The Brillouin splitting and line width are measured for the system consisting of the solvent Cellosolve Acetate and a polyepoxide formed from glycerol and bisphenol-A with epoxide end groups. Gels were formed by end-linking the chains in solution with a low molecular weight poly(propylene glycol) with amine end groups. Addition of polymer does lead to increased hypersonic attenuation and a greater Brillouin splitting, but cross-linking the chains has no measurable effect at constant concentration.

Introduction and Theory

Brillouin scattering probes the high-frequency mechanical properties of fluids.[1] The velocity and attenuation of hypersonic waves can be determined from the Brillouin frequency shift and line width. The longitudinal Brillouin splitting is given by

$$\pm\Delta\omega_l = qV_l(q) \tag{1}$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector for light of vacuum wavelength λ traveling in a medium of refractive index n which is scattered

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through an angle θ in the scattering plane and $V_l(q)$ is the longitudinal sound velocity for waves of wavevector magnitude q. The Brillouin line width Γ_l is related to the attenuation α by

$$\Gamma_l = \alpha V_l / 2\pi \qquad (2)$$

for Γ_l measured in GHz.

During the propagation of longitudinal sound waves, the local density, shear, and temperature are changed. Any process which can respond to the change and relax the local gradient will lead to attenuation of the waves. There are two main sources of hypersonic attenuation in polymer fluids:[2] (1) structural relaxation and (2) vibrational specific heat relaxation. The Brillouin line width can be expressed formally as[1]

$$\Gamma_l \approx \frac{q^2}{2\rho}[\eta_V(\Delta\omega_l) + {}^4\!/_3\eta_S(\Delta\omega_l)] \qquad (3)$$

where η_V and η_S are the hypersonic volume and shear viscosities. Structural relaxation of the fluid contributes to both the volume and the shear viscosity. Vibrational specific heat relaxation contributes to η_V. The small loss due to direct conduction of heat has been neglected.

The shear viscosity is a function of frequency for a viscoelastic medium.[3] It can be expressed as

$$\eta_S(\omega) = \sum_{i=1}^{N} \frac{G_i\tau_i}{1 + (\omega\tau_i)^2} \qquad (4)$$

where the G_i are the relaxation strengths for the processes which couple to shear and the τ_i are the corresponding relaxation times. A similar expression applies to the volume viscosity. For polymer fluids, the total shear viscosity is very large. For gels the zero shear viscosity is infinite. Typical Brillouin frequencies are in the range 3–10 GHz, so the viscosities that must be used in eq 3 may differ greatly from the zero shear viscosity. At high frequency, only those modes of relaxation with short relaxation times will contribute to the hypersonic viscosities. In this work we examine Brillouin scattering from polymer solutions and their corresponding gels formed by cross-linking at the same concentration. The effect of permanent cross-links on the high-frequency structural relaxation is determined.

Experimental Section

The polymer used in this work is a polyepoxide of bisphenol-A and glycerol with glycidyl epoxide end groups of molecular weight 6500. The solvent is ethylene glycol monoethyl ether acetate (Cellosolve Acetate). The cross-linking agent is a poly(propylene glycol) of molecular weight 400 with amine end groups. Gels were formed by reacting stoichiometric amounts of diepoxide polymer and diamine at 80 °C for 5 days. The polymer solutions and gel precursor solutions were filtered through 0.2-μm membrane filters to remove particulates. This procedure produced solutions and gels of high optical quality.

A single-frequency mode of an Ar ion laser operated at 5145 Å was used as the incident light. Incident intensities in the range 100–500 mW were employed. The scattered light was observed at 90°. The incident light was polarized vertically with respect to the scattering plane and no analyzer was used with the scattered light. Because the scattering due to concentration fluctuations in the polymer solutions and gels is very intense, the Rayleigh–Brillouin spectrum was obtained with a triple-pass Fabry-Perot interferometer. The high contrast allowed the weak, shifted Brillouin peaks to be observed in the presence of the strong central Rayleigh peak. The triple-pass arrangement was also required for the pure polymer, which was studied without filtration. The free spectral ranges used in this work were 14.8 GHz for the solvent and the 40% solution and gel and 26.0 GHz for the 65% gel and pure polymer. The finesse of the system was typically 60. The scattered light was detected with a photomultiplier and photon counter and the spectra were recorded digitally with a multichannel analyzer. Brillouin splittings were determined directly from the observed peak shifts, and the line widths were corrected for instrumental broadening by subtracting the instrumental half-width from the observed half-width at half-height.

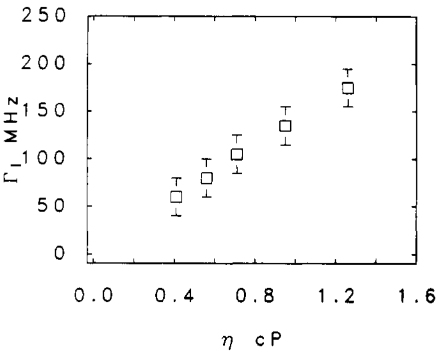

Figure 1. Brillouin line width Γ_l plotted against the shear viscosity η for the solvent Cellosolve Acetate.

The samples were held in a thermostatically controlled aluminum block regulated to ±0.5 °C. The temperature was measured with a platinum resistance thermometer. Solvent viscosities were determined with a Cannon-Ubbelohde viscometer in a constant-temperature bath.

Results and Discussion

In order to understand more fully the Brillouin scattering from the solutions and gels, the pure solvent and pure polymer were examined. For a typical low molecular weight liquid far above its glass transition temperature, the Brillouin line width follows the shear viscosity. A plot of Γ_l vs. η for the Cellosolve Acetate is shown in Figure 1. The Brillouin line width extrapolates to near zero at vanishing shear viscosity. Since vibrational specific heat relaxation is not a strong function of temperature in most liquids,[4] the lack of a low-viscosity residual line width indicates that vibrational specific heat relaxation does not make a significant contribution to the Brillouin line width in this liquid. Another factor which supports this contention is that the volume viscosity calculated from the observed Brillouin line width under the assumption that the hypersonic shear viscosity is equal to its zero-frequency value is comparable in magnitude to η_S. Since the structural part of the volume viscosity is approximately equal to the shear viscosity in small-molecule liquids, the magnitude of the contribution of vibrational specific heat relaxation to η_V must be small. Cellosolve Acetate is an ideal solvent for studying the effects of added polymer.

The Brillouin frequency is also typical[5] of a liquid far above its glass transition temperature. In the thermodynamic limit

$$\pm\Delta\omega_l = q(\gamma/\rho\kappa_T)^{1/2} \qquad (5)$$

where κ_T is the isothermal compressibility and $\gamma = C_p/C_v$ is the ratio of specific heats at constant pressure and volume. The hypersonic sound velocity in Cellosolve Acetate decreases from a value near 1200 m/s at room temperature to less than 1000 m/s at 110 °C.

The pure polymer had a glass transition temperature of 85 °C as determined by differential scanning calorimetry. The Brillouin line width at 100 °C was approximately 500 MHz. Since the structural relaxation time of the fluid near T_g is very long, the hypersonic shear viscosity and the structural part of the volume viscosity should be very small. Although there are still some unanswered questions[2] about sources of line broadening near the glass transition,

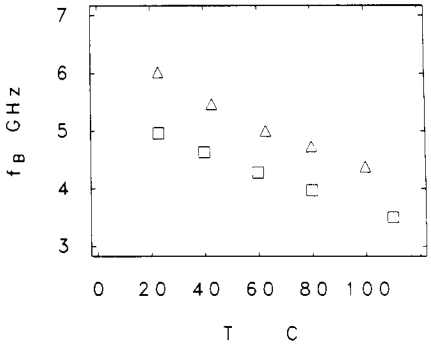

Figure 2. Brillouin frequencies f_B plotted against temperature for the 40% solution (△) and the pure solvent (□).

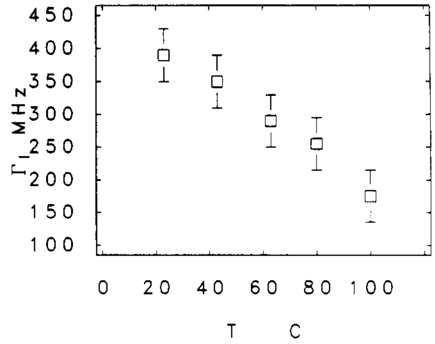

Figure 3. Brillouin line widths Γ_l plotted vs. temperature for the 40% solution.

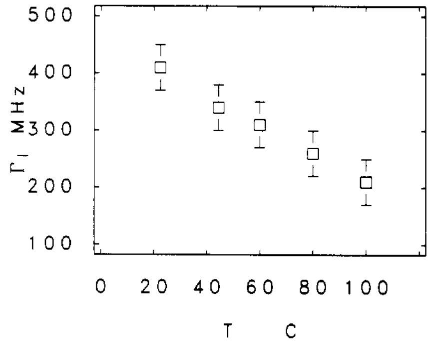

Figure 4. Brillouin line widths Γ_l plotted vs. temperature for the 40% gel.

we attribute most of the hypersonic attenuation in this polymer near T_g to vibrational specific heat relaxation. This is consistent with the presence of the bisphenol-A groups in the polymer. In a typical[6] polymer fluid, Γ_l increases as the material is heated above T_g and eventually goes through a maximum when the structural relaxation time is comparable to $(\Delta\omega_l)^{-1}$. The line width did increase as the polyepoxide polymer was heated above T_g, but the sample degraded before a clear maximum was established.

The Brillouin splitting near T_g is determined by the limiting high-frequency longitudinal modulus, $M_\infty = K_\infty + {}^4/_3G_\infty$, where K_∞ is the adiabatic modulus of compression and G_∞ is the shear modulus:[7]

$$\pm\omega_l = q(M_\infty/\rho)^{1/2} \qquad (6)$$

In the region of the Brillouin line width maximum, typical[2] Brillouin frequencies for polymers are in the range 4–6 GHz. The Brillouin splitting for the pure polymer was entering the above range at 240 °C when thermal degradation became severe. This is far enough above T_g to suggest that the maximum would be in this range of temperature.

Adding polymer to the pure solvent will affect the Brillouin scattering in several ways. Most polymer solutions have a lower free volume than the pure solvent. This will lead to a greater modulus of compression and a greater local viscosity, which in turn will give a larger sound velocity and an increase in the Brillouin line width. Because the polymer dynamics associated with conformation changes are slow relative to $(\Delta\omega_l)^{-1}$, the Brillouin line width will not reflect this motion.[8] But the Brillouin splitting will be increased by any slow process which contributes to K or G. The large loss due to vibrational specific heat relaxation in the pure polymer should persist in solution. This effect can also increase the Brillouin splitting since the sound velocity depends on the specific heat through γ.

The Brillouin frequencies f_B for the 40% solution are compared to the results for the pure solvent in Figure 2. The increase in the Brillouin splitting could be due to the increased modulus of compression of the solution or to viscoelastic effects. If the solution were in the viscoelastic regime, the temperature dependence of f_B would be expected[2] to be greater than that of the pure solvent, since both the modulus of compression and the relaxation strength of the viscoelastic processes increase with decreasing temperature. We attribute the increase in f_B to the decrease in free volume of the solution. This is confirmed by examining the line widths for the 40% solution which are presented in Figure 3. The 40% solution is still above the temperature of maximum hypersonic loss at room temperature, but the line width is over twice as large as that for the pure solvent. If the pure solvent is compared to the solution at constant Brillouin frequency, there is still a significant increase in Γ_l which is largely due to vibrational specific heat relaxation.

The 40% solution was then compared with a gel at the same concentration. The addition of the cross-links had no measurable effect on the Brillouin frequencies. This can be understood by considering the magnitudes of the compression and shear moduli for polymer fluids and gels. The modulus of compression for a typical fluid is of the order of 10^{10} dyn/cm^2. The shear modulus of a typical gel is in the range 10^6–10^7 dyn/cm^2. Thus a direct contribution to V_l due to the finite static shear modulus is ruled out.

The cross-links could still affect the hypersonic properties by changing the structural relaxation behavior of the gel. The Brillouin line widths for the 40% gel are plotted vs. temperature in Figure 4. They are all within experimental error of the results for the 40% solution. This confirms the fact that for typical gels, no effect of cross-linking should be apparent in the hypersonic properties.

In order to observe the region of the hypersonic loss maximum, a 65% gel was prepared. In the study of mechanical relaxation, the loss data are often[9] reported in terms of the quantity tan δ. For Brillouin scattering, this is given aproximately by

$$\tan\delta \approx 2\Gamma_l/\Delta\omega_l \qquad (7)$$

Values of tan δ determined for the 65% gel are plotted vs. temperature in Figure 5. A maximum is observed at approximately 80 °C. The frequency at the maximum was 5.9 GHz. This is within the normal range observed for many other polymeric systems. The magnitude of tan δ is also in the typical range, but this could be partially due to the loss contributed by specific heat relaxation.

Actual observations of Brillouin scattering in polymer solutions and gels confirm the general[2] picture developed

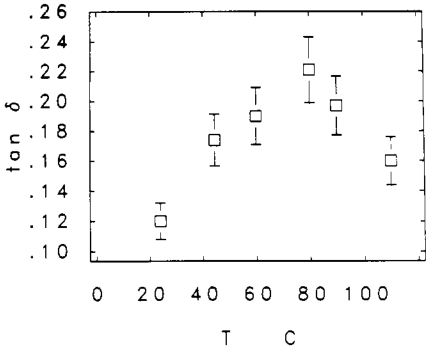

Figure 5. Mechanical loss tan δ plotted vs. temperature for the 65% gel. A loss maximum is observed at approximately 80 °C. The Brillouin frequency at this temperature was 5.9 GHz.

over the past few years. The primary variable which affects the hypersonic properties of polymeric systems is the local structural relaxation of the fluid. Long-range or other slow processes which may have dramatic effects on the low-frequency properties are often not observable at hypersonic frequencies.

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Depolarized Light Scattering from Macromolecules: Effects of Torsional Oscillations, Conformational Transitions, and Overall Rotations

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ABSTRACT: Depolarized dynamic light scattering spectra of dilute polymer solutions can be interpreted as due to the unequally weighted contributions of two processes: (1) a slow, molecular weight dependent contribution arising from the overall rotation of the molecule and (2) a fast, molecular weight independent process arising from some sort of local chain motions. To account for these observations we have derived an expression for the depolarized spectrum $I(\omega)$ of a schematic model consisting of a linear sequence of optically anisotropic segments, each of which is able to rotate about the chain axis. By coupling the rotations of adjacent segments harmonically, we mimic torsional oscillations of bonds about equilibrium rotation angles γ_i. Conformational transitions are mimicked by allowing the γ_i to be time dependent. Our results allow the assessment of the relative contributions to $I(\omega)$ of torsional oscillations, conformational transitions, and overall rotation; e.g., for the limiting case of a long rod with a large torsional potential, two unequally weighted Lorentzians occur only if conformational transitions are permitted.

Introduction

In addition to the now standard use of dynamic light scattering to obtain translational and overall rotational diffusion constants of macromolecules,[1] there is the additional possibility of obtaining rate constants for internal motions within the macromolecule. Although the customary polarized measurements can yield information about very slow intramolecular motions provided that the molecular weight is sufficiently high,[2] it is depolarized dynamic light scattering which is more promising for studying internal motions, irrespective of their time scale.[3-5]

The most suggestive study so far is that of Bauer, Brauman, and Pecora[3] (BBP) on dilute polystyrene fractions in CCl_4. Their spectra are reported in terms of the contribution of two unequally weighted Lorentzians. One of these is a slowly relaxing molecular weight dependent contribution which BBP identify with the overall rotation of the molecule. The other is a rapidly relaxing molecular weight independent contribution which they attribute to a local motion, viz., the rotation of phenyl groups about the main-chain axis. It is unclear wheather these features will be characteristic of the spectra of other polymer–solvent systems where the particular mechanism favored by BBP is less likely (or impossible).

Here we consider whether some simple idealized molecular model may, under certain conditions, exhibit the type of behavior observed by BBP. Evans[6] has used a dynamic theory of Fixman's[7] to treat interacting bond polarizabilities and has concluded that dipole-induced dipole interactions involving the substituents perpendicular to the main chain are responsible for the fast relaxation observed by BBP. We use a simpler model, which is of interest precisely because it is able to account for essentially those features which are experimentally observed, but without invoking either the mechanism suggested by BBP or that by Evans.

The model is similar to that employed by Shore and Zwanzig[8] in treating dielectric relaxation by means of a linear sequence of spins and to the linear elastic model employed both by Barkley and Zimm[9] and by Allison and Schurr[10] in their treatments of fluorescent depolarization