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Hypersonic Attenuation in Poly(dimethylsiloxane) as a Function of Temperature and Pressure

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ABSTRACT: Hypersonic relaxation is studied in amorphous poly(dimethylsiloxane) (PDMS) as a function of temperature from 77 to 300 K and as a function of pressure at 296 K. A clear loss maximum as a function of pressure was found at 296 K. The loss maximum at 1 bar was found to be at 218 K at a frequency of 5.4 GHz. This is well below the melting point of PDMS (230 K), and the samples had to be carefully supercooled. Successful spectra were obtained down to 200 K. Shock-quenched amorphous samples could be studied up to 157 K. The present results were combined with dielectric relaxation studies of PDMS at 298 K and very high frequencies (159 GHz) and on shock-quenched samples at lower frequencies in the range of 150–160 K to calculate the empirical WLF parameters at the glass transition (146 K). The results were $c_1^g = 14.6$ and $c_2^g = 20$ K. This led to a fractional free volume at T_g of 0.030, which is quite normal. Previous WLF parameters for PDMS were based on an invalid extrapolation of viscosity data obtained above the melting point, where the local relaxation frequencies exceed 10 GHz. The present results place PDMS back within the normal range for polymers.

1. Introduction

Poly(dimethylsiloxane) (PDMS) has one of the lowest glass transition temperatures of all polymers[1] ($T_g \approx 146$ K). This corresponds to the temperature at which the volume or enthalpy relaxation time is near 10 s. Brillouin spectroscopy measures the velocity and attenuation of hypersonic (GHz) acoustic phonons. Light is scattered by thermal sound waves and the basic experiment consists of measuring the spectrum of the scattered light. A typical Rayleigh–Brillouin spectrum is shown in Figure 1. It consists of a central Rayleigh peak and two shifted Brillouin peaks with splitting $\Delta\omega_l$ and line width Γ_l. The longitudinal Brillouin splitting (frequency) is given by

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

where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector, n is the refractive index, λ is the wavelength of the incident light in a vacuum, θ is the scattering angle in the scattering plane, and $V_l(q)$ is the longitudinal velocity for phonons of wave vector magnitude q. The longitudinal Brillouin line width is given by

$$\Gamma_l = \alpha V_l(q) \tag{2}$$

where α is the attenuation coefficient. Hypersonic attenuation is also expressed in terms of the loss tangent

$$\tan\delta = 2\Gamma_l/\Delta\omega_l \tag{3}$$

When the local structural relaxation times are in the same range as the inverse Brillouin frequency, the hypersonic attenuation exhibits a maximum. Since the frequencies are so high (4–10 GHz), the temperature range in which the average relaxation time is comparable to the inverse Brillouin frequency is well above the usual glass transition. The temperature at which the hypersonic attenuation reaches a maximum at 1 bar is typically[2] 150–200 K above T_g. Thus, even for PDMS the hypersonic loss maximum might be expected to be near room temperature. The earliest study of PDMS by Brillouin spectroscopy[3] examined the hypersonic attenuation in the temperature range 273–373 K. No clear indication of a hypersonic loss maximum was observed in this range, and the Brillouin frequency remained lower than that usually associated with such a maximum (5–6 GHz). Measurements were extended to lower temperatures by Lindsay et al.,[4] but the precision of the results was limited. The lower limit was 220 K and an apparent maximum was reported at 230 K. However, PDMS is a crystallizable polymer and its melting point is 230 K. There is evidence that the sample was partially crystalline below this temperature[4] since the sound velocity showed a jump at the melting point. We can now obtain high-precision Rayleigh–Brillouin spectra at temperatures from 4 to 600 K. We can also measure the spectrum as a function of pressure. In the present paper we report the measurement of the Rayleigh–Brillouin spectrum of two molecular weight samples of PDMS as a function of temperature from 77 to 300 K and as a function of pressure at 296 K. The results are then discussed in terms of the full frequency dependence of the glass–rubber relaxation and compared to other measurements of viscoelasticity in PDMS.

2. Theory

The phenomenological theory of Rytov[5] provides a complete framework for the description of Rayleigh–Brillouin scattering in amorphous liquids and solids. The

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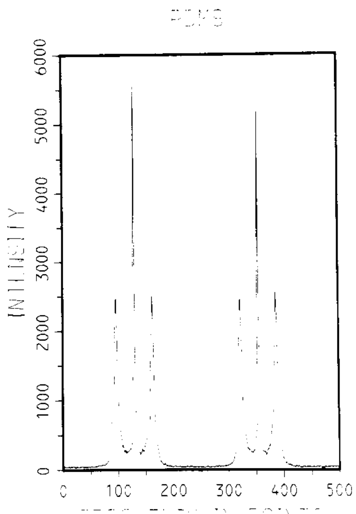

Figure 1. Rayleigh–Brillouin spectrum of PDMS at 296 K showing two Fabry–Perot orders. The free spectral range (distance between orders) was 27.1 GHz, and this allowed the digital locations of the peaks in points to be converted to absolute frequencies.

Brillouin splitting and line width can be expressed in terms of the frequency-dependent adiabatic longitudinal modulus $M = \gamma K + (4/3)G$, where K is the modulus of compression, G is the shear modulus, and $\gamma = C_p/C_v$ is the ratio of specific heats. A general representation of the longitudinal modulus is

$$M^*(\omega) = \gamma K_0 + M_R \int_0^\infty \frac{\rho(\tau) i\omega\tau}{1 + i\omega\tau} \, d\tau \tag{4}$$

where $K_0 = 1/\beta_T$ is the static modulus of compression, equal to the reciprocal of the isothermal compressibility, M_R is the total relaxation strength for all processes that couple to the longitudinal stress, τ is the relaxation time for these processes, and $\rho(\tau)$ is the distribution of relaxation strengths associated with each relaxation time. The longitudinal sound velocity is related to the real part of M^*

$$V_l(\Delta\omega_l) = \left[\frac{M'(\Delta\omega_l)}{\rho}\right]^{1/2} \tag{5}$$

where

$$M'(\Delta\omega_l) = \gamma K_0 + M_R \int_0^\infty \frac{\rho(\tau)(\Delta\omega_l\tau)^2}{1 + (\Delta\omega_l\tau)^2} \, d\tau \tag{6}$$

The static modulus of compression is a function of temperature and pressure. In order to cause dispersion in M', a process must have a relaxation time that is slow relative to $1/\Delta\omega_l$, and it must have a relaxation strength that is comparable to K_0.

The Brillouin line width is given by

$$\Gamma_l = \frac{q^2}{2\rho} M_R \int_0^\infty \frac{\rho(\tau)\tau}{1 + (\Delta\omega_l\tau)^2} \, d\tau \tag{7}$$

The Brillouin line width can also be formally expressed in terms of the frequency-dependent volume and shear viscosities

$$\Gamma_l = \frac{q^2}{2\rho}(\eta_V(\Delta\omega_l) + (4/3)\eta_S(\Delta\omega_l)) \tag{8}$$

In small-molecule liquids the Brillouin line width can be estimated very accurately from the zero-shear viscosity, unless there is a large contribution from the vibrational specific heat relaxation part of the volume viscosity.[6] For these liquids the volume and shear viscosity are usually comparable. If all the processes that couple to the longitudinal stress have relaxation times short relative to $1/\Delta\omega_l$, then the Brillouin line width in eq 7 is proportional to the average structural relaxation time

$$\Gamma_l = \frac{q^2}{2\rho} M_R \langle\tau\rangle \tag{9}$$

Processes with long relaxation times make little contribution to Γ_l because of the denominator in eq 7. In polymer fluids there are many processes that have relaxation times long relative to $1/\Delta\omega_l$ at all temperatures. These include the long-range chain entanglements that dominate the zero-shear viscosity in high-polymer fluids and the so-called Rouse modes for intramolecular conformational relaxation. Only the local intermolecular motions contribute significantly to Γ_l, but it is precisely these motions that determine the glass–rubber relaxation process. Although chain entanglements and Rouse modes are slow, the relaxation strength associated with these processes is small relative to K_0. As a result they are invisible to Brillouin scattering and make no measureable contribution to either the Brillouin splitting or line width.

3. Experimental Section

The poly(dimethylsiloxane) samples were Dow Corning 200 fluids of viscosity 50 and 100 000 cP. The number-average molecular weights of these materials have been determined before and are reported to be[7] 3800 and 68 000, respectively. The lower molecular weight sample was high enough to give the asymptotic value for the Brillouin splitting in PDMS but was of low enough viscosity to be filtered easily. It serves as the pressure fluid in our[8] high-pressure light scattering cell. The liquid was quenched into the glassy state, and the T_g was determined by differential scanning calorimetry to be 146 K based on the onset point for the jump in C_p. This value was also obtained for the high molecular weight sample. The low molecular weight sample could be essentially fully crystallized, and the melting point was consistent with that for PDMS (230 K). The low molecular weight sample was filtered directly into the scattering cell. It was then pumped down for several days to remove residual gases and moisture and sealed under vacuum. The higher molecular weight sample could not be filtered, but it was sealed under vacuum after extended pumping.

Rayleigh–Brillouin spectra were obtained with a Fabry–Perot interferometer with a free spectral range of 27.1 GHz. The incident light was at 5145 Å and the scattered light was observed at 90°. The finesse of the system was very high (>100), and a typical Rayleigh–Brillouin spectrum of PDMS at room temperature is shown in Figure 1. The sample was free of particulates and yielded the intrinsic spectrum due to density fluctuations. As the temperature was lowered below 258 K small particles appeared and the central line was increased due to elastic scattering by these impurities. This did not prevent an accurate analysis of the Brillouin splitting and line width, but it did mar the pretty spectra. Both samples could be supercooled for periods long enough to obtain spectra. However, there was a temperature gap over which the sample was not stable relative to crystallization for sufficient periods. Nevertheless enough data were obtained to fully illustrate the behavior of the Brillouin splitting and line width. Temperatures were controlled with a Janis SuperVeritemp optical Dewar. Control could easily be maintained to ±1 K, which was adequate for this work. The pressure studies were carried out with the same cell described previously.[8] The pressure was applied directly to the fluid with a piston and measured with a precision gauge.

4. Results

As noted above, the 50-cP fluid serves as the pressure fluid in our high-pressure light scattering cell. As an initial

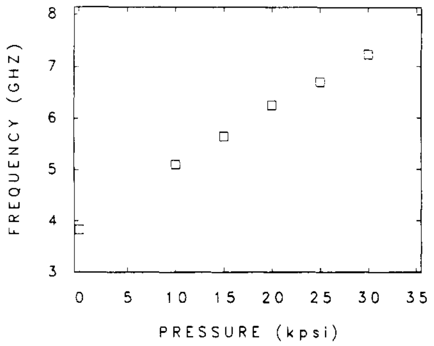

Figure 2. Brillouin frequency in gigahertz as a function of pressure up to 2 kbar (30 kpsi) for 50-cP PDMS at 296 K.

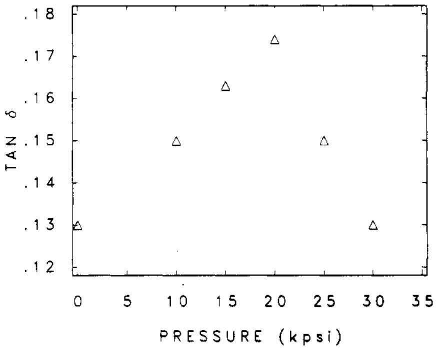

Figure 3. Hypersonic loss (tan δ) as a function of pressure for 50-cP PDMS at 296 K.

experiment when it was constructed we measured the Rayleigh–Brillouin spectrum at 296 K of the pressure fluid up to 3 kbar. The 1-bar spectrum was identical with Figure 1 (even the small Rayleigh peak). As the pressure increased, the splitting and line width both increased. The line width reached a maximum at 1.33 kbar. Above 2 kbar the sample crystallized. The results are shown in Figures 2 and 3.

The demonstration of a clear line width maximum as a function of pressure at 296 K suggested that there should also be a hypersonic loss maximum at 1 bar at temperatures well below ambient. The question was whether it would lie too far below the melting point. The PDMS was quenched into the glassy state and studied from 77 K up to a temperature where the sample crystallized (160 K). The hypersonic loss was very low over this region, but it did start to increase from 150 to 160 K. The value of the Brillouin frequency in the glassy state was comparable to that for other polymers. The 50-cP fluid could be cooled to 208 K. The Brillouin line width reached an apparent maximum in this temperature region. The 100 000-cP fluid was supercooled successfully to 200 K, and the location of the hypersonic loss maximum was confirmed to be at 218 K. The two PDMS fluids yielded identical Brillouin splittings and line widths within experimental error. Although data could not be obtained in the gap between 160 and 200 K, the behavior in this region can confidently be interpolated. The results are shown in Figures 4 and 5.

The Brillouin frequency at the maximum (5.4 GHz) is well within the usual limits for such a result.[2] There is only a small interval between T_g and the hypersonic loss maximum ($\Delta T = 68$ K). The average relaxation time in PDMS changes by more than 10 decades over this interval. However, the change in $1/T$ is more comparable to other polymers.

5. Discussion

Remarkably little relaxation data on purely amorphous PDMS has been reported in the literature. The reason for this is now quite apparent. The liquid is not stable relative to crystallization over the region where the loss maximum would occur for most frequencies. Recently, dielectric relaxation in amorphous PDMS was studied from 150 to 160 K.[9] The loss maximum at 100 Hz was at 152.5 K, and at 1000 Hz it was at 155.2 K. This leads to an apparent activation energy of approximately 40 kcal/mol. At the other end of the frequency spectrum, oligomers of PDMS were studied[10] near room temperature at frequencies up to 136 GHz. The average relaxation time of the pentamer at 298 K was approximately 1 ps. This corresponds to a frequency of 159 GHz. Although there is no a priori reason why the dielectric loss maximum at some frequency would occur at the same temperature as the mechanical loss maximum determined by Brillouin spectroscopy, it has been observed empirically[6] that this is often the case. If we combine these dielectric relaxation results at the two extremes with the Brillouin results at 5.4 GHz, we can obtain the best fit to the empirical parameters in the equation

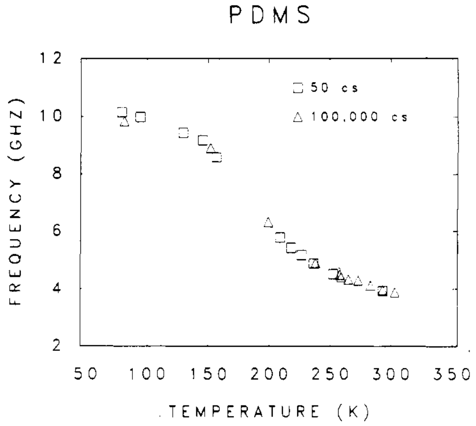

Figure 4. Brillouin frequency in gigahertz as a function of temperature at 1 bar for two molecular weights of PDMS.

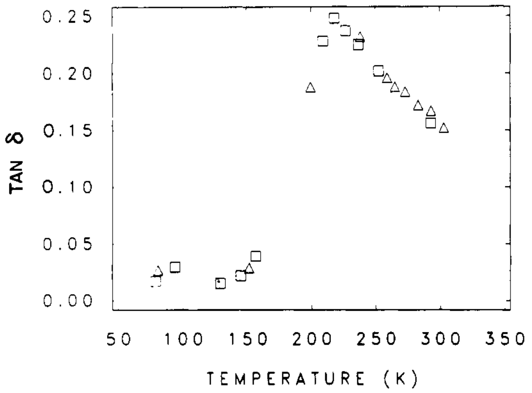

Figure 5. Hypersonic loss (tan δ) as a function of temperature at 1 bar for two molecular weights of PDMS. The maximum loss occurs at 218 K at a frequency of 5.4 GHz.

$$f = f_0 \exp\left[\frac{-A}{T - T_0}\right] \tag{10}$$

The results are $f_0 \approx 10^{13}$ Hz, $A = 672$ K, and $T_0 = 126$ K. The limiting frequency is very reasonable and is typical of many polymers. The characteristic temperature A corresponds to an apparent activation energy at 298 K of approximately 4 kcal/mol. This is calculated as $\Delta H = RAT^2/(T - T_0)^2$, where R is the gas constant. This is at least in reasonable agreement with the measured activation energy[11] for viscous flow (3.65 kcal/mol). The value of T_0 given in ref 12 (81 K) is based on a study of the viscoelastic properties of PDMS in the temperature range 223–323 K.[7] As shown in ref 11, this is barely into the temperature interval where any deviation from a simple Arrhenius behavior is detected and surely cannot be used to estimate T_0. More recent attempts[13] to determine T_0 from viscosities produced even more outrageous results (T_0 = 67 K). The very rapid change in relaxation frequency with temperature near 150 K demands that T_0 be well above 81 K.

The empirical parameters in eq 10 can also be interpreted in terms of the free volume of the liquid according to the WLF[12] equation. PDMS was thought to have an unusually high fractional free volume at the glass transition.[12] The WLF parameters calculated from our results are $c_1^g = 14.6$ and $c_2^g = 20$ K. This leads to a calculated fractional free volume at the glass transition of $f_g/B = 0.030$. This is higher than some polymers, but well within the normal range.

The value of T_g listed in ref 12 is 150 K. It now appears that this value was obtained with semicrystalline PDMS. The value reported by Yim and St. Pierre[1] was obtained with shock-quenched amorphous PDMS. The difference can be rationalized by the results of Adachi et al.[9] obtained by dielectric relaxation on both amorphous and crystalline PDMS. The dielectric loss maximum shifts by approximately 2 orders of magnitude when the sample crystallizes. This corresponds to approximately 4 K in the region of T_g. The elevation of the glass transition temperature of the amorphous part in a semicrystalline polymer is a common phenomenon, but for PDMS little notice of this effect has been made. When the truly amorphous T_g is used for PDMS (146 K), the calculated freqency of maximum dielectric loss at the glass transition is approximately 0.02 Hz, which is quite reasonable.

Acknowledgment. We gratefully acknowledge many fruitful discussions with S. M. Lindsay.

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Viscoelastic Properties of Star-Shaped Polymers[†]

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ABSTRACT: A theory is presented to describe the viscoelastic properties of star-shaped polymers. Disentanglement processes are considered to be dominated by diffusion of the ends of the arms in a (free energy) potential field. The existence of the potential function is supported by recent work of Helfand and Pearson on random walks entangled with a fixed obstacle net. When compared with new and existing experimental data on well-characterized polymeric stars, the theory predicts the correct molecular weight dependence of the viscosity and the steady-state shear compliance, as well as the frequency dependence of the dynamic moduli, $G'(\omega)$ and $G''(\omega)$. Useful variables for plotting time- or frequency-dependent relaxation data of star polymers are suggested by the theory and are considered.

During the past few years important advances have been made in understanding the rheological properties of high molecular weight polymers. Using concepts originally suggested by Edwards[1] and de Gennes,[2] Doi and Edwards[3] developed a theory that describes the response of polymeric fluids when subjected to an external strain. Although improvements are still needed,[4,5] their theory has been remarkably successful in describing complex viscoelastic behavior.[6,7]

The theory, as originally presented, applies to concentrated solutions of linear molecules. For this case it is assumed that polymer chains are hemmed in by their neighbors and that they move by translating in a curvilinear fashion roughly paralleling their own contour. The time dependence of their escape from present surroundings to new surroundings can be obtained from a solution to the first-passage time problem[8] for a diffusing chain.[3] If the polymer molecule is branched, it is expected that this simple snake-like motion will be highly suppressed. The resulting change in the mechanism of diffusion will alter the rate of stress relaxation and, in general, all rheological properties.

The simplest type of branched polymer is the star-shaped molecule for which f chains are connected to a central point. Using small-strain deformation measurements, the time-dependent response of this type of polymer has been found to be quite different from linear polymer.[9-11] Approximate theories for describing the observed behavior were proposed by de Gennes,[12] Doi and Kuzuu,[13] and Graessley.[7]

[†] This paper is dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday. We appreciate both the knowledge and the wisdom he has shared with us.

0024-9297/84/2217-0888$01.50/0