

Brillouin scattering from oligomers of polydimethylsiloxane and the assignment of the hypersonic α loss peak in polymers

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Hypersonic sound speed and loss have been measured in poly(dimethylsiloxane) fluids of viscosities 0.65 to 3.5×10^4 centistoke. Both rise to a plateau level for viscosity values in excess of ~ 10 centistokes. Loss measurements as a function of temperature indicate that the α loss temperature (T_α) in the dimer is depressed below 180K compared to 230K in the high molecular weight materials. This molecular weight dependence of T_α is used to account for the hypersonic loss as a function of molecular weight in polystyrene and polypropylene glycol in addition to the assignment of the α loss peak in polydimethylsiloxane.

INTRODUCTION

Hypersonic loss peaks have been reported in many polymers¹ and when the temperature and frequency of the observed maximum loss are plotted on a transition map together with loss data from a variety of other techniques (e.g. n.m.r. dielectric and mechanical loss studies) the hypersonic loss appears to lie on the so-called 'merged' α - β high temperature relaxation line².

Patterson³ has recently reported the observation of an apparently distinct α loss peak at a temperature above the major hypersonic loss peak in polypropylene oxide (PPO) which lies on an extrapolation of the β -line on the transition map. Whilst posing some theoretical difficulties², the observation of a distinct α loss process at high temperatures must cast doubt on the assignment of the hypersonic loss in other polymers where minor loss peaks are observed at temperatures above the major hypersonic loss. In an earlier paper reporting hypersonic loss in polydimethylsiloxane (PDMS)⁴ we assigned the major loss peak at ~ 230 K to the 'merged' α - β process, whilst Patterson¹ has suggested this assignment for the minor loss peak at ~ 320 K. Patterson's assignment of the loss peaks in PPO suggests the possibility that the 230K loss in PDMS is due to a β relaxation, whilst the weaker peak at ~ 320 K is due to the α process. A correct assignment is important in interpreting measurements we have made on PDMS networks⁵, and there is insufficient reliable high frequency loss data on PDMS to permit an unequivocal assignment through a transition map².

In this paper we report Brillouin measurements on a series of PDMS oligomers in which both the sound speed and loss have been found to vary strongly with molecular weight, and some measurements in polypropylene glycol (PPG) in which they do not. A molecular weight dependence of these

parameters in Brillouin studies of polystyrene has been reported by Patterson⁶ whilst behaviour similar to that observed by us has been reported in ultrasonic studies of PDMS oligomers⁷. We believe that the Brillouin measurements may be accounted for, at least qualitatively, by a movement in the α loss temperature with molecular weight, and that the effects of this movement at a given temperature and frequency may be used to aid assignment of the hypersonic loss peaks.

THEORY

Brillouin scattering is but one of many forms of inelastic light scattering, in which an incident photon is inelastically scattered by a phonon. This process gives rise to two peaks in the scattered light spectrum shifted from the elastically scattered light by an amount $\pm \nu_B$. The Brillouin shift (ν_B) is related to the speed of sound in the scattering medium v_s , by the well known relationship.

$$v_s = \frac{\nu_B \lambda_0}{2n \sin(\theta/2)} \quad (1)$$

where λ_0 is the wavelength *in vacuo* of the incident radiation, n is the index of refraction in the scattering medium, and θ the scattering angle in the material.

Several relationships between acoustic loss and Brillouin linewidth appear in the literature^{8,9,10}, the form used in this work is stated for clarity. Acoustic attenuation of the phonons gives rise to lines which are approximately Lorentzian in profile having a halfwidth at half height $\nu_{1/2}$. This is equal to the temporal decay coefficient, Γ , for amplitude fluctuations which decay as

$$A(t) = A_0 e^{-\Gamma t} \quad (2)$$

In most sound attenuation measurements the quantity

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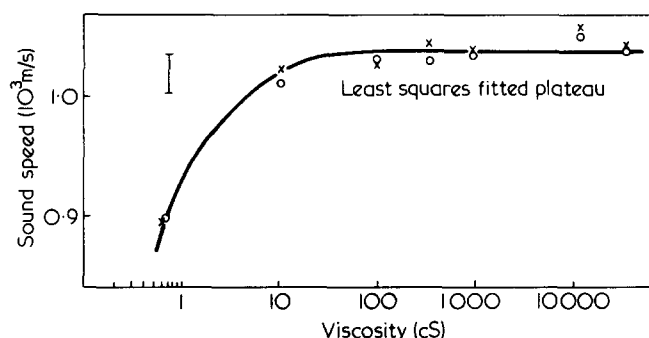


Figure 1 Hypersonic sound speed at 2.5 GHz (O) and 5.0 GHz (x) as a function of viscosity in PDMS at 293K. For clarity a single representative error bar is shown

measured is the linear intensity decay coefficient, α , and this is related to Γ by

$$\alpha = \frac{2\Gamma}{v_s} \quad (3)$$

The loss per cycle, $\alpha\lambda_s$ (where λ_s is the wavelength of the hypersound) is

$$\alpha\lambda_s = \frac{2\nu_{1/2}}{\nu_B} \quad (4)$$

This quantity is identical to the ratio of the real and imaginary components of the complex modulus, that is the loss tangent. In the absence of a viscoelastic loss mechanism $\alpha\lambda_s$ is only weakly temperature dependent having a value between 0.1 and 0.05 which arises from structural⁸ or phonon-phonon scattering⁹. When the loss temperature (for the frequency of measurement) is reached, visco-elastic relaxation leads to an increase in $\alpha\lambda_s$. In the case of large $\alpha\lambda_s$ Montrose *et al.*¹¹ have shown a better form to be

$$\alpha\lambda_s = \frac{2\Gamma_+}{\nu_B} \left(1 + \frac{\Gamma_+}{2\nu_B} \right) \quad (5)$$

where Γ_+ is the half width of the Brillouin line measured on the high frequency side of the peak.

EXPERIMENTAL

Several samples of PDMS, each of different molecular weight, were obtained from Dow Corning Limited and ICI Limited. The Dow Corning samples were characterized by their viscosity and were of 0.65, 10, 100, 350, 1000 and 12 500 centistokes. The weight average molecular weight was found by gel permeation chromatography (g.p.c.) to be 2.2×10^2 , 1.4×10^3 , 35.8×10^3 , 1.2×10^3 , 1.2×10^4 , 2.1×10^4 and 7.0×10^4 , whilst the ICI material (S273-11/3) had a molecular weight of 7.7×10^4 . The viscosity of this sample was found from the data of Barlow *et al.*¹² to be 35 000 cS. The polypropylene glycol had weight average molecular weights of 400, 1500 and 4000 found by g.p.c.

The refractive index of all the PDMS samples was measured using an Abbé refractometer and found to be 1.402 ± 0.001 at 291K except the 0.65 cS sample which had an index of refraction at this temperature of 1.376 ± 0.001 . The refractive index of the PPG sample was found to be

1.446 ± 0.001 (400), 1.449 ± 0.001 (1500) and 1.450 ± 0.001 (4000).

The temperature variation in the refractive index was measured and although only small this correction has been included in our data.

Brillouin spectra were obtained using a triple pass Fabry-Perot spectrometer, described in detail elsewhere¹³, using the 5145 Å line of an argon ion laser. Approximately 100 mW of radiation was incident on the sample, no local heating of the sample was detected. The spectrometer was operated at an optimised free spectral range in all cases to avoid shrinkage effects¹⁴, and the collection aperture was sufficiently small to neglect the broadening of linewidths caused by a finite collection aperture¹⁵. The effect of instrumental broadening is corrected using the deconvolution procedure of Lindsay *et al.*¹⁶.

The finesse of the spectrometer was never less than 30 and at least six good spectra have been recorded for each experimental point at the two angles of scatter, 51° and 128° in PDMS and 53° in PPG. The sound speed is accurate to ~2% whilst the loss data is only good to ~20%, and by using the six spectra this is reduced to ~8%.

The data obtained at room temperature were taken with the samples contained in standard 1 cm square glass spectrophotometer cells, whilst an Oxford Instruments CF104 light scattering cryostat was used for the low temperature work where the sample was contained in a sealed glass phial. Temperature measurement was by a thermocouple inserted in the sample near the scattering volume and is accurate to ± 0.1 K.

RESULTS AND DISCUSSION

Values of sound speed, v_s , and loss per cycle, $\alpha\lambda_s$, are plotted in Figures 1 and 2 as a function of PDMS viscosity. The two sets of data correspond to measurement at internal scattering angles of 51° and 128° (giving maximum Brillouin shifts of 2.5 and 5.0 GHz). Both v_s and $\alpha\lambda_s$ rise to a plateau beyond viscosities of ~10 cS. The velocity data show little evidence of dispersion – least squares fits to plateau values of v_s are 1025 ms^{-1} (2.5 GHz) and 1040 ms^{-1} (5.0 GHz), equal within experimental error, $\alpha\lambda_s$ reaches plateau values of 0.14 (2.5 GHz) and 0.20 (5.0 GHz).

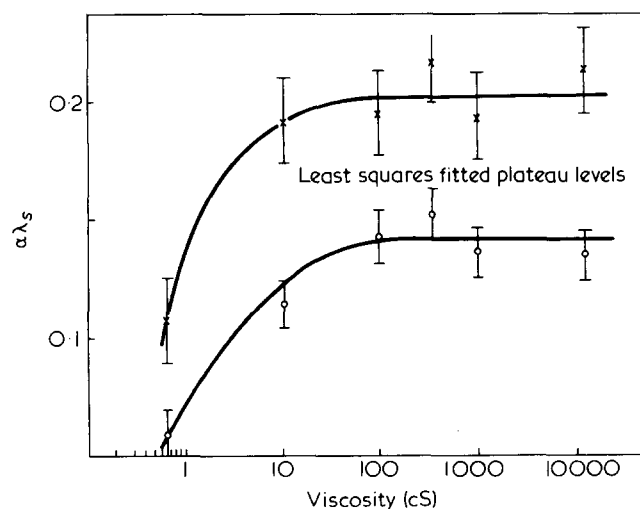


Figure 2 Hypersonic loss at 2.5 GHz (O) and 5.0 GHz (x) as a function of viscosity in PDMS at 293K

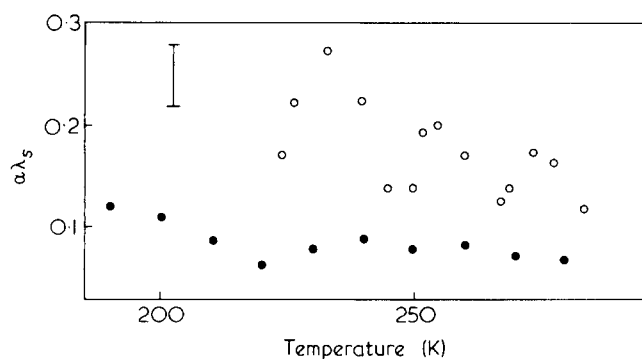


Figure 3 Hypersonic loss in a high molecular weight PDMS ($M_w = 7.7 \times 10^4$) (●) and in the dimethylsiloxane dimer (○) measured as a function of temperature at the same frequency. One representative error bar is shown for clarity

We believe these results reflect a movement of the α relaxation temperature, T_α with molecular weight in a manner analogous to the molecular weight dependence of the quasi static glass transition where¹⁷

$$T_g = T_{g\infty} - \frac{K}{M}$$

Here $T_{g\infty}$ is the limiting value of the glass transition temperature, M , the molecular weight and K is a constant. It is reasonable to assume that at high frequencies T_α depends on molecular weight in much the same way. The limiting value of T_α may be reached at lower molecular weights, that is when chain length is large compared with the extent of mechanical fluctuations associated with the driving excitation. It is probably also true that in polydisperse samples such as ours the limiting value of T_α is reached more quickly as high molecular weight components begin to dominate the relaxation spectrum. Thus in the PDMS dimer T_α is depressed below the value of $\sim 230\text{K}$ we measure in the high molecular weight material⁴. As chain length is increased, T_α is raised nearer room temperature causing $\alpha\lambda_s$ to rise until the high molecular weight limit is reached.

This explanation may be checked by looking for movement at T_α in the low molecular weight materials, and in Figure 3 values of $\alpha\lambda_s$ are plotted with temperature for the dimer over the range 180–300K. We are currently extending this range of measurement, however the extreme flammability and volatility of the dimer impede high temperature measurements. Also shown is loss data for a high molecular weight material ($M_w = 7.7 \times 10^4$) displaying the previously reported broad loss peak at $\sim 230\text{K}$ ⁴. Both sets of data were taken at internal scattering angles of 71° . In the dimer $\alpha\lambda_s$ only begins to rise significantly below $\sim 200\text{K}$. Low temperature measurements are needed to cover the relaxation and establish that crystallization is occurring below T_α . However there is little increase in the intensity of elastic scattering down to the lowest temperature, and we therefore conclude that the observed increase in loss is due to a merged α – β relaxation below 180K and not to the onset of crystallization.

The rise in $\alpha\lambda_s$ with frequency at a given molecular weight (Figure 2) is also consistent with our assignment of T_α . A higher measurement frequency implies a higher T_α with a corresponding increase in $\alpha\lambda_s$ measured at a temperature above T_α .

Had the α relaxation been above room temperature as indicated by Patterson's tentative assignment¹ we might ex-

pect just the reverse molecular weight dependence – that is a fall in $\alpha\lambda_s$ as T_α is moved still further above our measurement temperature with increasing molecular weight. An example of such behaviour is to be found in polystyrene where the temperature of maximum hypersonic loss is $\sim 513\text{K}$ ¹. In Figure 4 we have redrafted the loss data obtained by Patterson for polystyrene oligomers⁶ to show isothermal plots of $\alpha\lambda_s$ with molecular weight.

An example of intermediate behaviour is PPG where the loss spectrum is dominated by a broad feature centred around room temperature² and attributed to the β relaxation whilst the α relaxation is reported as a minor loss peak at $\sim 370\text{K}$ ³. We would not therefore expect variations in chain length to affect $\alpha\lambda_s$ significantly, and indeed we measure a constant value of 0.3 ± 0.03 in samples of molecular weight 400 (~ 6 atom chain), 1500 (~ 25 atom chain) and 4000 (~ 68 atom chain). (The measurements were carried out at 293K).

Finally we note that ultrasonic measurements (30–270 MHz) of α and ν_s in PDMS oligomers show these parameters to vary with molecular weight in a qualitatively similar manner to the behaviour we observe at hypersonic frequencies. The ultrasonic data are accounted for by a postulated low temperature relaxation in both shear and compressional viscosities⁷. The relaxation temperature determined in this ultrasonic work is well above T_α at ultrasonic frequencies and the apparent activation energies (~ 3 kcal/mole in a 10 atom polysilicone and ~ 6 kcal/mole in a 6 atom polysilicone) well below the value expected for the α relaxation². Although the molecular weight behaviour is similar in the ultra and hypersonic experiments the origin of the relaxation controlling the ultrasonic behaviour is not clear.

On the other hand we note a surprising connection between plateau values of α measured by the two techniques. Hunter *et al.*⁷ find that plateau values of α fall below the expected Stokes values, and do not scale with the square of frequency, f^2 , as would be expected from the Stokes relationship. Plotting their data on a logarithmic scale we find that α is proportional to $f^{1.5}$ and that Brillouin measurements of α (as determined by equation (3)) at the plateau values fit an extrapolation of the ultrasound data well

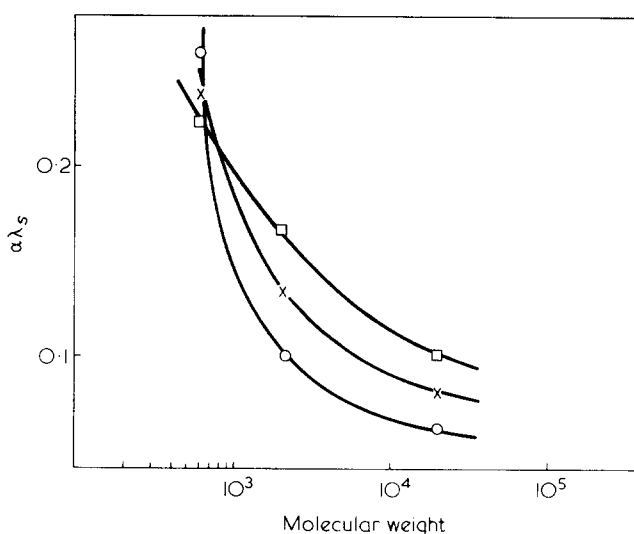


Figure 4 Hypersonic loss as a function of molecular weight in attactive polystyrene at 410K (○), 430K (x) and 450K (□) after Patterson⁶

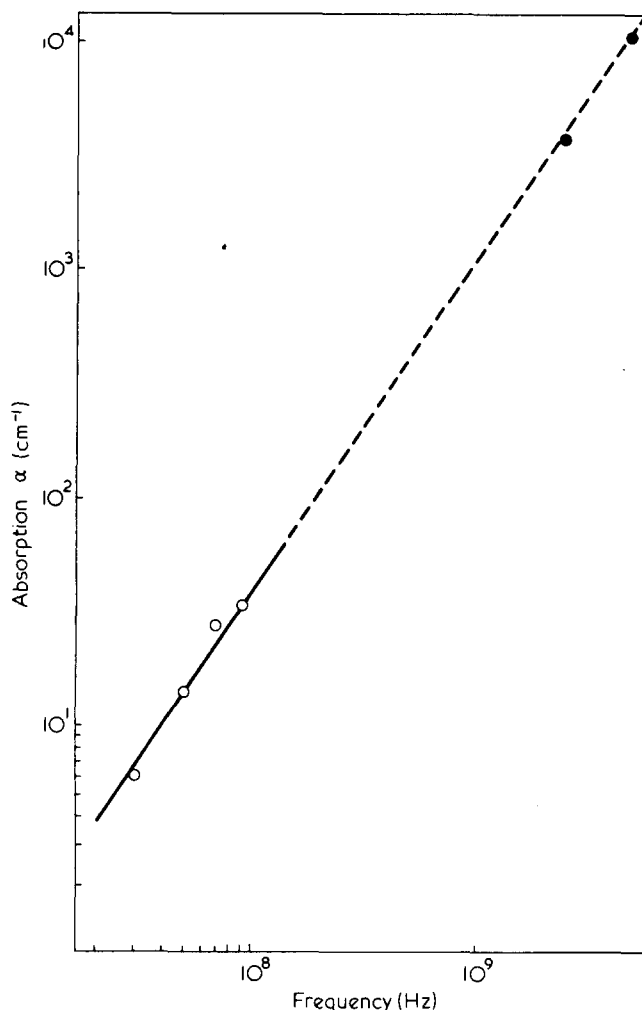


Figure 5 Plateau absorption levels as a function of frequency in PDMS from Brillouin data (●) and the ultrasonic studies of Hunter et al.⁷ (○)

(Figure 5). We are not aware of any theoretical justification of such a power law. Since absorption appears to be dominated by different relaxation processes in each case it is difficult to see how plateau values of α might be connected, though we mention the relationship because it appears unlikely to be coincidental and indicates that further theoretical understanding is required.

CONCLUSIONS

Previously published data on the molecular weight dependence of hypersonic absorption may be accounted for by a movement of T_α with molecular weight. This dependence is useful in assigning the α relaxation in a complex loss spectrum, and we have used it to lend support to our earlier assignment of T_α at hypersonic frequencies in PDMS. Further measurements are in hand to determine T_α in a series of PDMS oligomers in order to establish the functional form of the dependence of T_α on molecular weight at hypersonic frequencies.

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