# Letter

## Multiple hypersonic relaxations and the $\alpha$-transition in poly(dimethyl siloxane).

In this Letter we report the first observation of multiple hypersonic relaxations in poly(dimethyl siloxane) (PDMS) using multipass Fabry–Perot spectroscopy[1,2]. Our data show evidence for loss maxima at 230, 250, 280 and 320K at a frequency of ~4 x $10^9$ Hz. Only one of these peaks, that at 320K has previously been reported[3], and this has been erroneously associated with the main $\alpha$-relaxation.

PDMS S 273-11-3 from ICI Ltd was used. The molecular weight was determined by g.p.c. to be 7.7 x $10^4$. Linewidths and Brillouin shifts of the longitudinal acoustic phonons were recorded as a function of temperature. The hypersonic velocity, $V_s$, and absorption per cycle, $\alpha\lambda_s$, can be calculated from these data as described elsewhere[1]. These measurements were performed at an internal scattering angle of 74° so that phonon frequencies ranged from 4.2 to 3.0 GHz over the temperature range investigated. The light source used was an argon ion laser operating at 5145 Å, and the sample refractive index (which showed a neglibible temperature variation) was measured as 1.40. In *Figure 1* the hypersonic velocity is plotted with temperature and there is a clear discontinuous change at ~240K which is evidence for a strong relaxation at that temperature. There is also some indication of a relaxation at ~330K. The hypersonic loss per cycle, $\alpha\lambda_s$, is plotted with temperature in *Figure 2*. Loss maxima are clearly seen at ~230, 250, 280 and 320K. In reporting the loss maximum at ~320K Patterson[3] tentatively assigned this peak to the main chain relaxation. (The $\alpha$- and $\beta$- processes are merged at these temperatures[4].) We believe that the main chain relaxation is most probably represented by the strongest loss peak at ~230K.

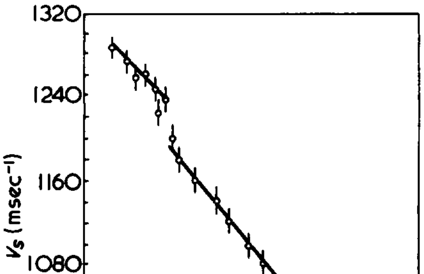

*Figure 1* Hypersonic velocity in PDMS plotted as a function of temperature. The frequency ranged from 4.2 to 3.0 GHz at the lowest and highest temperatures respectively. The discontinuities at ~240 and 330K are evidence of relaxations

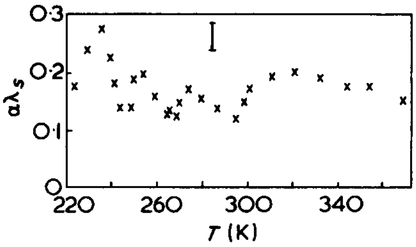

*Figure 2* Hypersonic loss per cycle in PDMS plotted as a function of temperature. Peaks are observed at 230, 250, 280 and 320K indicating the presence of relaxation processes. The frequences are as *Figure 1*.

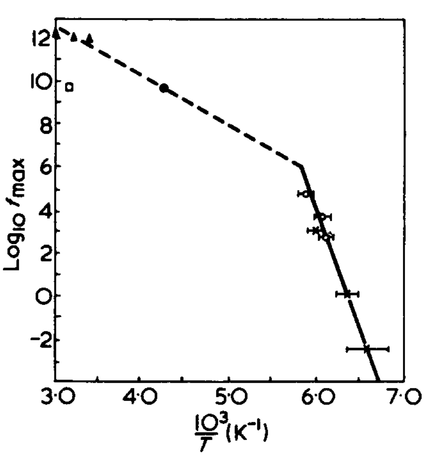

*Figure 3* Relaxation transition map for PDMS in which the log of the frequency of the main $\alpha$-relaxation is plotted *versus* reciprocal temperature. The data points are: □, 320K relaxation (ref 3); ▲, microwave relaxation (ref 7); ○, dielectric data (ref 6); x, dielectric data (ref 5); ●, 230K relaxation (present work). — — —, represents an activation energy of 10 Kcal/mol

A comprehensive transition map has not yet been published for PDMS. In *Figure 3* we have plotted the logarithm of the frequency of dielectric[5,6] and microwave[7] absorption peaks as a function of reciprocal temperature. In the case of the microwave data[7], we have plotted the logarithm of the reciprocal of the most probable relaxation time for the largest PDMS oligomers studied. We have estimated an activation energy for the 230K loss peak by measuring the loss maximum in an experiment with internal scattering angle of 158° (and corresponding maximum Brillouin shift of 6.6 GHz). The observed increase of approximately 5K in the temperature at which maximum loss occurred gives an activation energy of 10 Kcal/mol. Uncertainty in location of the loss peak gives rise to a maximum error of ±40% in this energy. The 230K relaxation is plotted in *Figure 3* with a broken line representing this activation energy. The microwave data fall on this line; the loss peak at 320K clearly does not. Further support for our interpretation comes from the temperature (~180K) at which the change over from Arrhenius to WLF behaviour occurs. This point, similar in most polymers[4], we believe to be the Debye temperature[8]. In addition a double loss peak at the main chain relaxation temperature appears to be a feature of the transition at hypersonic frequencies in several other polymers[1,9]. Further discussion of this and other hypersonic relaxation processes will appear in future papers.

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### *References*

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