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Anomalous dielectric relaxation in poly(dimethyl siloxane) polymers

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The dielectric relaxation in poly(dimethylsiloxane) of viscosity 10^5 CSt at around the melting point is found to deviate from the existing theory. Although the position of maximum loss is insensitive to changes in temperature in the range −40°C to −54°C, the magnitude of the loss changes by about 50%.

Keywords Absorption curves; anomalous behaviour; α-relaxation; loss peak; spherullites; rotator phase

Dielectric behaviour in siloxane polymers was previously studied around room temperature[1-2] and little was known about the low temperature region above and around the glass transition where the loss peaks appear in the audio frequency region[3-5]. Studies of poly(dimethylsiloxane) fluids ranging in viscosity from 100 cSt to 10^5 cSt (1 cSt $=10^{-6}$ m^2 s^{-1}) at room temperature were reported[6] earlier. Broad loss peaks in the audio frequency region due to micro-Brownian motion were observed in the temperature range −120°C to −100°C. However for poly(dimethylsiloxane) of viscosity 10^5 cSt which crystallizes at around −50°C, the curves in the α relaxation region are highly skewed towards the low frequencies. These features are typical of the crystalline polymers[7]. As the temperature is raised, the absorption curves move to the higher frequencies and the locus of $\log_{10}f_m$ (frequency of maximum loss) against $\frac{1}{T}k$ curves is predicted by the WLF equation[8].

As the temperature is raised near the melting point at about −50°C where poly(dimethylsiloxane) becomes opaque due to the crystallization and growth of spherulites[9], anomalous behaviour of the relaxation was observed in the temperature region −60°C to −40°C as shown in *Figure 1*. The thermal treatment of the sample was carefully controlled and the rate of cooling was maintained practically the same in all observations. A striking feature is that although the position of the loss peak is apparently insensitive to changes in temperature in the range −40°C to −54°C, the magnitude of the loss changes by about 50%.

These peaks cannot be associated with electrode difficulties. A three terminal dielectric cell, used in this study, was constructed so that the electrodes followed any contraction of the sample as the temperature was lowered. The loss peaks may not be attributed to the contaminated water vapour, since the samples of poly(dimethylsiloxane) were dried for several hours *in vacuo*

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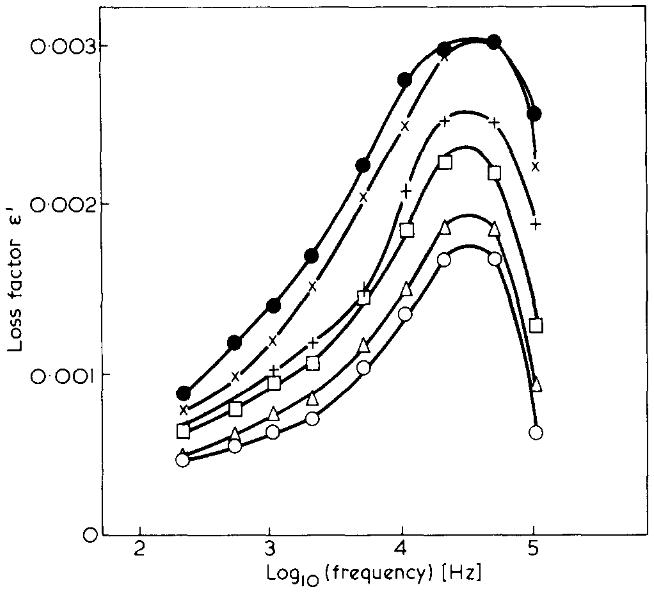

Figure 1 Plots of loss factor against $\log_{10}$ frequency for poly(dimethylsiloxane) of viscosity 12 500 cSt (○) −40°C; (△) −43°C; (□) −45.5°C; (+) −48°C; (X) −51°C; (●) −54°C

over P_2O_5. The normal picture of relaxation of a dipole due to thermal agitation from one equilibrium position to another over an energy barrier is not applicable to this particular absorption, since this would be temperature dependent. However, for bulk polymers at temperatures well above their T_g's (as is the case here) the activation energies can become quite small. A further study over a greater span of temperature and with different thermal treatment of the sample is currently going on. The results will be reported later.

Most probably the origin of the loss peaks are due to the interfacial polarization at the solid–liquid boundary. As the temperature is raised the relaxation time need not shorten, since it may depend, in a complex manner, on the dielectric constants and the conductivities of solid and liquid phases. It has been found in polyethylene[10] that addition of 1% imadazoline amphoteric surface active agent, loss peaks arising due to crystalline and amorphous region moved to lower frequencies as the temperature was raised to a certain value. Such unusual behaviour was explained in terms of the variation in size of the crystalline regions with temperature in accordance with existing theory. However the magnitude of loss peaks in *Figure 1* increases in a monotonic way with decreasing temperature and therefore with increasing crystallinity. This behaviour suggests that the relaxation process could be associated with the crystalline phase.

This leads us to speculate that some form of 'rotator' phase may exist for poly(dimethylsiloxane) in which rotational motions are restricted by a very small energy barrier. This would give rise to a relaxation time insensitive to changes in temperature over the range of temperatures considered here.

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