Dynamic Kerr-effect and dielectric relaxation studies of a poly(methylphenyl siloxane)

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Dynamic Kerr-effect and dielectric relaxation studies have been for a poly(methylphenyl siloxane) fluid in the region of its α relaxation process. The relaxations are broader than a single relaxation-time process and we find $\tau_{K,r} < \tau_{K,d} < \tau_{\epsilon}$ and $\beta_{K,r} \cong \beta_{K,d} < \beta_{\epsilon}$, where K, r; K, d and ϵ refer to Kerr-effect rise, decay and dielectric, respectively; τ and β are the relaxation time and the Williams–Watts relaxation parameter, respectively. It is suggested that the observed Kerr-effect relaxation is largely due to the motions of the phenyl group and that a substantial part of this process is due to motions about the bond joining the silicon atom to the aromatic ring.

INTRODUCTION

The dynamical behaviour of bulk amorphous polymers may be studied using dielectric, mechanical and n.m.r. relaxation techniques[1–4]. A complementary technique is that of Kerr-effect relaxation[5–8] for which the time-dependence of the optical birefringence of a medium is observed following the step application or withdrawal of a directing electric field E. This technique has been widely applied to polymers (mainly rod-like polymers or biopolymers) in solution[5–8], to liquid-crystal-forming materials (see e.g. ref 8) and to viscous molecular liquids[9–12]. Its application to bulk amorphous polymers was initiated by the present authors who studied both the Kerr-effect relaxation and dielectric relaxation of poly(propylene glycols) of different molecular weights. It was found[13,14] that two processes were observed by both techniques, the faster process being due to local segmental motions and the slower process being due to the longer-range motions[13–15] (and hence molecular-weight-dependent motions) of the chains in the bulk phase.

We have now extended our studies to the case of a bulk liquid poly(methylphenyl siloxane) and the present paper reports dielectric relaxation and Kerr-effect relaxation studies of the principal[1] (or α) relaxation process for this material. We note that dielectric relaxation[16] and visco-elastic relaxation studies[17] have been reported for certain poly(methylphenyl siloxane) liquids in the α-relaxation region.

EXPERIMENTAL

The sample of poly(methylphenyl siloxane), PMPS say, was the MS 350 material studied by Kim[17] and was kindly provided by Professor A. J. Barlow of the University of Glasgow. It has the same polymeric structure as poly(dimethyl siloxane) but with 25% of the methyl groups replaced by phenyl groups. It had a broad distribution of molecular weights (see ref 17) and $(M_w/M_n) = 27$. It was dried over zeolite and filtered before use.

Measurements of the Kerr-effect relaxation and dielectric relaxation were made using the equipment described earlier[9–14]. The Kerr-effect measurements were carried out using a He–Ne laser operated at 632.8 nm and using a linear detection technique[7,14]. Dielectric measurements were made concurrently with the Kerr-effect measurements on the same sample in the Kerr-cell, in order to optimize comparisons of relaxation times obtained from the two techniques. Sample temperatures were controlled to ±0.05K using a liquid circulation system and a Lauda Ultra Kryostat.

RESULTS

The static Kerr-constant, $B = \Delta n/(\lambda E^2)$ where Δn and λ are optical birefringence and optical wavelength, respectively, was measured in the range 230 to 210K. The values of B ranged from 2.75×10^{-15} V^{-2} m at 226K to 4.10×10^{-15} V^{-2} m at 211K. These are very small values and correspond to rotations of the analysing prism of up to 20 minutes of arc for the values of E used (0–20 kV cm^{-1}). For comparison, the static Kerr-constant of carbon tetrachloride is 0.88×10^{-15} V^{-2} m at room temperature[18].

In order to estimate the relative contributions to the Kerr-effect made by $[(CH_3)(Ph)Si–O]$ and $[(CH_3)_2Si–O]$ groups, B was measured for a sample of poly(dimethyl siloxane), PDMS*, and for a sample of PMPS†, MS 550. It was found that $(B_{PMPS}/B_{PDMS}) = 3.0$ at 295K, indicating that in our dynamic Kerr-effect studies of PMPS MS 350 the $[(CH_3)(Ph)–Si–O]$ groups make the major contribution to $B(t)$.

Figure 1 shows, as one example, the normalized time-dependent birefringence $(\Delta n(t)/\Delta n_{max})$ against time for PMPS MS 350 at 214.9K following the application of a rec-

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* This material had a molecular weight of 1.5×10^3, and was kindly provided by Dr J. A. Semlyen, University of York, UK.

† Further details of this material are given in ref 17. Like MS 350, it has 25% of CH_3 groups replaced by Ph groups.

This material had a molecular weight of 4×10^3 and was kindly provided by Professor Barlow, University of Glasgow, UK.

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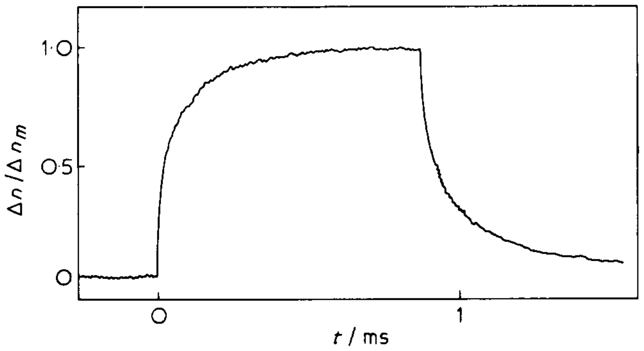


Figure 1 Normalized birefringence against time for PMPS MS 350 at 214.9K

Table 1 Kerr-effect and dielectric data for PMPS 350

T/K	$\langle\tau_{K,r}/\mu s\rangle$	$\langle\tau_{K,d}/\mu s\rangle$	$\beta_{K,r}$	$\beta_{K,d}$	$\langle\tau_\epsilon/\mu s\rangle$	β_ϵ
220.4	–	–	–	–	6.2	0.40
218.6	18.0	25.2	0.76	0.73	21.5	0.38
216.2	33.0	78.0	0.52	0.53	79.0	0.37
214.9	50.7	82.3	0.42	(0.61)	120	0.35
213.0	113	203	0.42	0.47	460	–

tangular pulse $E_p(t)$ of duration of 0.8 ms. The rise and decay transients are approximately equivalent in form and are far removed from a single exponential function of time – as evidenced by the rapid initial response followed by a slow approach to equilibrium in the presence or absence of the applied field. *Table 1* summarizes the $\tau_{K,r}$ and $\tau_{K,d}$ values where $\tau_{K,r}$ and $\tau_{K,d}$ are the times for the rise transient to reach $(1 - e^{-1})$ of its final value and for the decay transient to reach e^{-1} of its initial value. We note that $\tau_{K,r} < \tau_{K,d}$. Since the Kerr-effect is a non-linear electro-optical effect $\tau_{K,r}$ and $\tau_{K,d}$ may be quite different[5,7,19] but simple model theories[5–9] would predict $\tau_{K,r} > \tau_{K,d}$, in contrast to our observations on MS 350. With regard to the form of the rise and decay transients, it has been found that the dielectric α-relaxations for amorphous polymers[20–22] and for viscous molecular liquids[23] may be approximately represented by the empirical relaxation function of Williams and Watts[20,21]:

$$\varphi(t) = \exp(-t/\tau)^{\beta} \tag{1}$$

$0 < \beta \leqslant 1$. *Figure 2* shows, as an example, the Kerr-effect rise and decay data at 216.2K, which yield $\beta_{K,r} = 0.52 \pm 0.02$ and $\beta_{K,d} = 0.53 \pm 0.02$. *Table 1* gives the values of $\beta_{K,r}$ and $\beta_{K,d}$ determined over the temperature range and we note that (i) $\beta_{K,r} \simeq \beta_{K,d}$; and (ii) $\beta_{K,r}$ and $\beta_{K,d}$ decrease with decreasing temperature. Also included in the Table are values of τ_ϵ and β_ϵ obtained from dielectric loss curves which were measured concurrently with the Kerr-effect data. $\tau_\epsilon = (2\pi f_m)^{-1}$ where f_m is the frequency of maximum dielectric loss factor. $\beta_\epsilon < \beta_{K,r} \simeq \beta_{K,d}$ at each temperature and $\tau_{K,r} < \tau_{K,d} < \tau_\epsilon$ at each temperature. *Figure 3* shows the plot of $\log f_m$ against $(T/\mathrm{K})^{-1}$ for Kerr-effect rise and decay data and for the dielectric data. In converting the Kerr-effect data from the time-domain into the frequency domain (i.e. $\tau \to f_m$) there is a correction factor of 0.05 for $\log f_m$ (see ref 11) but this is small for the purposes of the present work and has been ignored in constructing *Figure 3*.

DISCUSSION

The dielectric α relaxations for bulk amorphous polymers[1–4,22] and for small-molecule viscous liquids[23] are commonly fitted using the W–W function with β_ϵ in the range 0.4–0.8. For many of these systems β_ϵ lies in the range 0.5–0.6. Baird and Sengupta[16] studied the dielectric α relaxation of a narrow fraction of the homopolymer poly(phenylmethyl siloxane) which had $M_n = 1060$ and $M_w = 1330$. They found $\beta_\epsilon = 0.62$ for this material. In contrast, the dielectric relaxation data for PMPS MS 350 gives β_ϵ in the range 0.35 to 0.4, i.e. far broader loss curves than those observed by Baird and Sengupta. Two sources of the increased breadth are: (a) the distribution of molecular weights for MS 350; and (b) that the $[(CH_3)_2Si{-}O]$ units relax at a different rate from the $[(CH_3)(Ph)Si{-}O]$ units. A comparison of the data of ref 16 and the present work indicates that the motions of $[(CH_3)(Ph)Si{-}O]$ dipole units

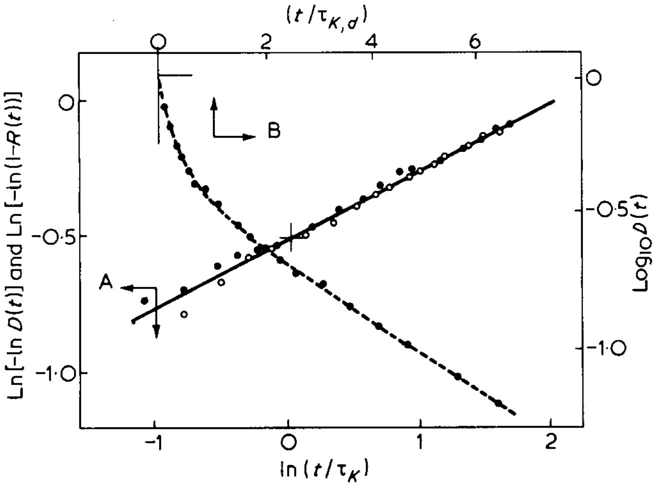


Figure 2 A, Ln[-ln[1 – $R(t)$]] against ln($t/\tau_{K,r}$) and ln[–ln$D(t)$]] against ln($t/\tau_{K,d}$) for PMPS MS 350 at 216.2K. $R(t)$ and $D(t)$ are the normalized rise and decay birefringence, respectively. ● and ○ refer to rise and decay data, respectively; B, log$D(t)$ against ($t/\tau_{K,d}$) for PMPS MS 350 at 216.2K

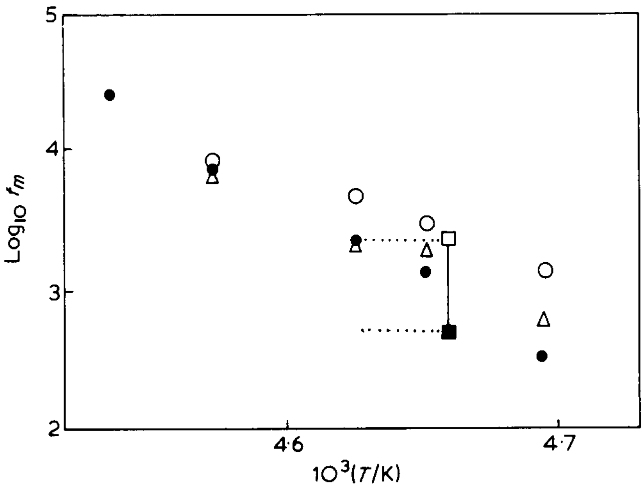


Figure 3 Log f_m against $(T/\mathrm{K})^{-1}$ for PMPS MS 350. ○, △ and ● refer to Kerr-effect rise, Kerr-effect decay and dielectric data, respectively. □ and ■ refer to the major and minor processes resolved for the decay transient at 216.2K assuming two single-exponential components

occur, on average, at a slower rate than that of the dimethyl siloxane units. Thus if the increased breadth is due to (b) then the [$(CH_3)(Ph)Si-O$] dipole units would contribute at the lower frequency end of the overall loss curves.

We cannot explain the result $\tau_{K,r} < \tau_{K,d}$ in terms of available models for relaxation[5–7,9] but note that the Kerr-effect transients are broad and in the frequency domain would have a half-width of the imaginary component of $B(\omega)$ of $\Delta \log f_m = 2.0$. The difference of $\log f_m$ between rise and decay data ranges from 0.1 to 0.3 (see *Figure 3*) and whilst it is real, it is rather small for such broad transients. It is evident from *Figure 3* that the Kerr-effect relaxation (rise and decay) is close to, but faster than, the dielectric relaxation.

For small molecule viscous liquids[4,9–11,23] we have found that the dielectric and Kerr-effect data for the α relaxation are consistent with a 'fluctuation-relaxation' model for motion. This model considers that groups randomize via angular jumps of arbitrary size, and this leads to the result that the rise and decay functions for the Kerr-effect are equivalent (in contrast to the small-step rotation of a dipole[5,9]) and are equivalent to the dielectric relaxation function. This leads to (i) $\tau_{K,r} = \tau_{K,d} = \tau_\epsilon$ and (ii) $\beta_{K,r} = \beta_{K,d} = \beta_\epsilon$ (if the W–W function applies). Whilst it appears that (i) may be *approximately* true for PMPS MS 350, (ii) is certainly not true. Thus our interpretations of the data are made complicated by the presence of broad relaxation features, this being a common problem in relaxation phenomena. This brings into question the analysis of broad relaxation features. We have analysed our data using the W–W function, yielding results shown in *Figure 3* and *Table 1*. However, given the qualitative feature of *Figure 2* that the rise (or decay) function has a 'short-time' part and a 'longer-time' part, we may choose to analyse the data into two component processes. *Figure 2* includes the plot $\log [\Delta n(t/\tau)/\Delta n_m]$ against (t/τ) for the decay process at 216.2K. Such data may be analysed as a 'fast' process, which accounts for about (2/3) of the total process, and a 'slower' process which accounts for the remainder. The resulting values for $\tau_{K,r}$ or $\tau_{K,d}$ for the 'fast-process' are rather similar to the original $\tau_{K,r}$ and $\tau_{K,d}$ values, but $\tau_{K,r}$ and $\tau_{K,d}$ for the 'slower' process are about four times larger. *Figure 3* includes these points for the Kerr-effect decay transient at 216.2K. A similar result is obtained for the rise-transient at this temperature and for the rise and decay transients at the other temperatures. The main component (faster component) for data resolved in this way still relaxed more quickly than the dielectric process – as seen in *Figure 3*.

The dielectric process is due to the motions of the [Si–O–Si] dipolar groups. The Kerr-effect process is due to the motions of the ellipsoids of optical polarizability which are associated with the [$-(CH_3)PhSiO-$] and [$-(CH_3)_2SiO-$] groups but with the relaxation data dominated by the motions of the former groups. The principal optical polarizabilities of alkyl C–H bonds[24] are:

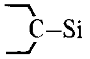
$$\alpha_1 = \alpha_2 = \alpha_3 = 0.7 \times 10^{-40}\ \mathrm{C\,m^2\,V^{-1}}$$

which may be compared with principal optical polarizabilities for the phenyl group[24] of:

$$\alpha_1 = \alpha_2 = 13 \times 10^{-40}\ \mathrm{C\,m^2\,V^{-1}},$$

$$\alpha_3 = 8 \times 10^{-40}\ \mathrm{C\,m^2\,V^{-1}}.$$

Thus, the methyl groups are essentially optically isotropic in contrast to the phenyl groups which exhibit marked optical anisotropy. This is consistent with the static Kerr-constant results described above. The present dielectric data, when compared with that of Baird and Sengupta[16], indicates that the [$(CH_3)(Ph)SiO$] group dipoles move, on average, more slowly than the [$(CH_3)_2SiO$] groups; thus we would have expected the Kerr-effect relaxation to have been slower than the dielectric relaxation. Since the converse is true, we are led to suggest that the local reorientation of the Ph ring about the



bond makes an appreciable contribution to the Kerr-effect relaxation and that this process is faster than the reorientational motions of the [Si–O–Si] dipoles. This would also help to explain the observation that β_ϵ is less than $\beta_{K,r}$ and $\beta_{K,d}$ since we would suggest that the dielectric process is averaged over the motions of the dipoles associated with each of the two monomer units whilst the Kerr-effect process is primarily due to the internal motions and overall motions of the phenyl ring which is associated with the [$(CH_3)(Ph)Si-O$] group.

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