

## Low frequency multiple relaxation behaviour of poly(propylene glycol) as studied using dielectric and dynamic Kerr-effect techniques

It is now generally accepted that bulk poly(propylene glycols) may, in a certain range of molecular weight, exhibit two dielectric relaxation processes<sup>1-3</sup>. The higher frequency process (*A*-process say) carries with it most of the available relaxation strength and is not very sensitive in its frequency-temperature location to variation in molecular weight<sup>1</sup>. It is thought<sup>1-3</sup> that this process is due to the local reorientations of the ether-group dipoles. The small lower-frequency dielectric process (*B*-process, say) has a frequency-temperature location which is strongly-dependent upon molecular weight and Baur and Stockmayer<sup>1</sup> have suggested that this process is due to Bueche-Rouse-Zimm-type modes of motion of whole chains, the magnitude of this process being related to the cumulative dipole moment along the chain-contour.

Considerable interest has been shown concerning mechanisms for the internal motion and long-range diffusional motion of polymer chains in concentrated solutions and in the bulk<sup>4-8</sup>. De Gennes<sup>7</sup> and Edwards and co-workers (see e.g. reference 8) have proposed a 'reptation' mechanism for the translational diffusion of whole chains in the melt in which a representative chain moves as if it were constrained to a tube partially defined by its own contour and by the surrounding polymer molecules. Experimental evidence for such a process is given by Klein<sup>9</sup>. He found that the translational diffusion coefficient  $D_t$  for fractions of low-molecular weight deuterio-polyethylene dispersed in the melt of a high-molecular weight polyethylene followed the relation  $D_t = CM_w^{-2}$  where  $C$  is a constant and  $M_w$  is the weight-average molecular weight. Such behaviour is in accord with that predicted by De Gennes<sup>7</sup> using a model representation of the reptation process. Similarly, the <sup>1</sup>H n.m.r. data for poly(ethylene glycols), obtained over a range of frequency and temperature, have been interpreted by Kimmich and Schmauder<sup>10,11</sup> in terms of three processes, each of different time-scale: (a) local motions of chain segments; (b) reptational motions in a 'tube' whose coordinates do not change within the time-scale of the reptational motion; (c) random motions of the coordinates of the tube (slowest process).

During extensive investigations concerning several liquid poly(propylene glycols) it became apparent that there were two optical relaxation processes and that these might be similar in origin to the fast (*A*) and slow (*B*) dielectric processes which we also observed (in confirmation of the dielectrics data of Baur and Stockmayer<sup>1</sup> and Alper and co-workers<sup>2</sup>).

Essential details of the techniques we have used to measure the dynamic Kerr-effect and dielectric relaxation for viscous liquids, over a range of time, frequency and temperature, have been described previously<sup>12,13</sup>. Since poly(propylene glycols) exhibit very small static Kerr-constants it was necessary to modify the apparatus, and the details will be given in a later publication. The stainless-steel Kerr-cell, which also acts as the dielectric cell, was fitted with rectangular electrodes of length 7.45 cm and separation 0.115 cm. The temperature of the cell was controlled to  $\pm 0.05$ K over the range 198-310K with the aid of a Lauda Ultrakryostat.

Figure 1 shows normalized dielectric loss factor curves for poly(propylene glycol) (PPG) of nominal molecular weight 2025 (from BDH Chemicals Ltd., Poole, Dorset). The two relaxation regions *A* and *B* are clearly observed and our

data are in agreement with those of Baur and Stockmayer<sup>1</sup> for this material. Figure 2 shows the plot  $\log f_m$  vs.  $T^{-1}$  for the dielectric data for Figure 1. Here  $f_m = (2\pi\tau_D)^{-1}$  where  $f_m$  is the frequency of maximum dielectric loss-factor and  $\tau_D$  is the effective dielectric relaxation time.

Optical birefringence transients resulting from the application of rectangular shaped high voltage pulses were monitored with the aid of a He-Ne 2mW polarized laser and a Mullard Type 56TVP photomultiplier tube and a Datalab Type DL 920 transient recorder. Figure 3 shows a representative optical transient for poly(propylene glycol) 2025 at 231.4K. It is apparent that both the rise and decay transients are composed of a fast negative component and a slower positive component. The birefringence plateau with field on is thus the resultant obtained from the addition of negative and positive contributions. Such behaviour was observed at all temperatures for this polymer, and was confirmed to be the intrinsic behaviour of the material using linear and quadratic detection techniques for a range of applied electric fields.

The rise and decay transients were obtained with good precision at each temperature using a scale-expansion of each region and recording, on paper-tape, 2048 equally-spaced data points. The rise and decay functions are written as  $F_r(t)$  and  $F_d(t)$  respectively where:

$$F_r(t) = -\mathcal{A}f_{Ar}(t) + \mathcal{B}f_{Br}(t) \quad (1a)$$

$$F_d(t) = -\mathcal{A}f_{Ad}(t) + \mathcal{B}f_{Bd}(t) \quad (1b)$$

$\mathcal{A}$  and  $\mathcal{B}$  denote the magnitudes of the *A* and *B* processes respectively,  $f_{Ar}(t)$  and  $f_{Br}(t)$  are the normalized rise func-

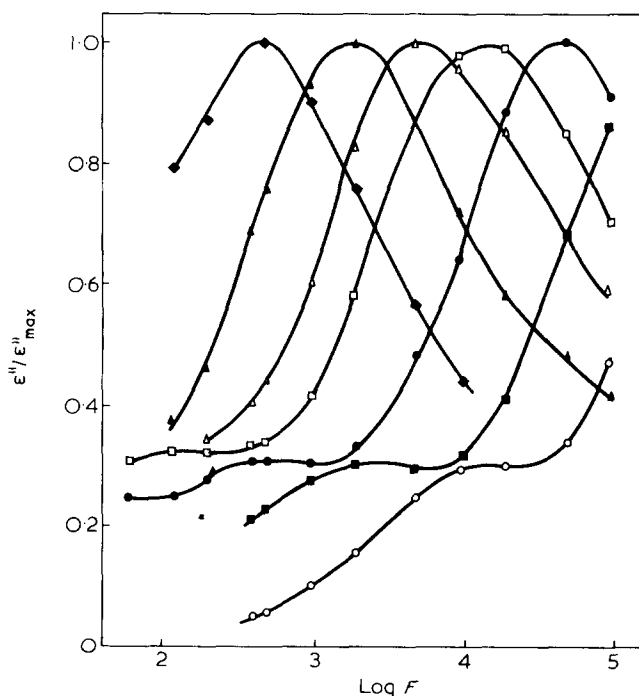


Figure 1 Normalized dielectric loss-factor ( $\epsilon''/\epsilon_m$ ) as a function of  $\log$  (frequency/Hz) for PPG 2025 at different temperatures.  $\circ$ , 247.8K;  $\blacksquare$ , 238.3K;  $\bullet$ , 231.4K;  $\square$ , 227.4K;  $\triangle$ , 224.9K;  $\blacktriangle$ , 221.4K;  $\blacklozenge$ , 217.5K

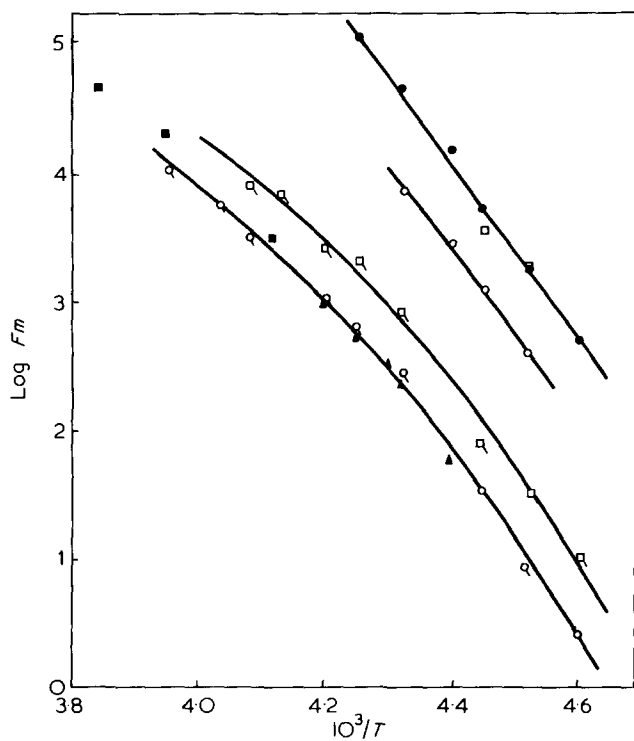


Figure 2 Log( $f_m$ /Hz) against  $T^{-1}$  for PPG 2025.

Process	Dielectric	Kerr-rise	Kerr-decay
A	●	○	□
B	▲, ■ (ref 1)	◊	◻

tions for the A and B processes while  $f_{Ad}(t)$  and  $f_{Bd}(t)$  are the corresponding normalized decay functions. The data for the B-process was found to be adequately represented by

$$f_{Br}(t) = [1 - \exp - (t/\tau_{K,r}^A)]$$

and

$$f_{Bd}(t) = \exp - (t/\tau_{K,d}^B)$$

Subsequent analysis using equation (1) showed that the rise and decay functions for the A-process were broader than the single exponential function of time. Adequate representations of these data were obtained using the empirical representation due to Williams and Watts<sup>14,15</sup> so that

$$f_{Ar}(t) = [1 - \exp - (t/\tau_{K,r}^A)^{\beta r}]$$

and

$$f_{Ad}(t) = \exp - (t/\tau_{K,d}^A)^{\beta d}$$

We find  $\beta_r \approx \beta_d \approx 0.7$  for PPG 2025 for the range studied here. The correlation times  $\tau_{K,r}^A$ ,  $\tau_{K,d}^A$ ,  $\tau_{K,r}^B$  and  $\tau_{K,d}^B$  obtained at each temperature were used to calculate corresponding log  $f_m$  values using the relation  $f_{mi} = (2\pi\tau_i)^{-1}$ . These data are included in Figure 2 and it is clear that dielectric and Kerr-effect data for both A and B processes are to be correlated. The important result is that the dynamic Kerr-effect measurements appear to be detecting the slow, long-range motions (B-process) seen earlier by dielectric measurements<sup>1,2</sup>. Detailed interpretations of such data will be given in a later publication, which will include results for a range

of molecular weight. For the present, we make the following comments.

The relationship between the rise and decay functions for Kerr-effect relaxation is dependent on the model for molecular motion<sup>12</sup>, in contrast with dielectric relaxation where the linear response condition ensures that rise and decay functions are governed by the same time-function. Similarly, the relationships between correlation times for Kerr-effect decay and those for dielectric relaxation are dependent upon the model for motion<sup>12</sup>. For polymers, cross-correlation functions of different order are involved in dielectric and Kerr-effect relaxations, as has been outlined by Kielich (see reference 16 p 293), and therefore complicate the interpretations of experimental data. For the simple model of the motion of an axially-symmetric dipolar and polarizable group, it may be shown<sup>12</sup> that the dielectric relaxation and Kerr-effect decay yield the auto-correlation functions  $\langle P_1(\cos \theta(t)) \rangle$  and  $\langle P_2(\cos \theta(t)) \rangle$  for the angular motions of the axis of the group\*. For small-step angular diffusion these correlation functions are  $\exp - 2D_R t$  and  $\exp - 6D_R t$  respectively† leading to  $\tau_{K,d} = (1/3)\tau_D$  and a Kerr-effect rise-transient which is slower than the decay transient if the dipolar term dominates<sup>16</sup>. The observations that  $\tau_{K,d} \approx (1/3)\tau_D$  and  $\tau_{K,r} > \tau_{K,d}$  for the B-process (Figure 2) indicates a small-step diffusional process.

With regard to the mechanisms of the A- and B-processes, all the evidence suggests that the A-process is due to the anisotropic segmental motions of the main-chains. Baur and Stockmayer<sup>1</sup> have analysed the dielectric B-process in terms of the Bueche-Rouse-Zimm model in which normal modes of diffusional motion of a spring-bead chain are considered. The fact that the dipole situated on each monomer unit does not precisely bisect the C-O-C bond-angle leads to a cumulative dipole-moment along the chain contour<sup>1</sup> and so produces a dielectric activity for the long-range motions of the chain. It is interesting to note that Doi and Edwards<sup>8a</sup> have analysed a model for the reptational motions of a chain. In their model the internal segmental motions are assumed to occur at a rapid rate compared with that for the reptational motions (as would be the case for PPG). They find

\*  $P_n(X)$  is the  $n$ th Legendre polynomial of  $X$ .

†  $D_r$  is the rotational diffusion coefficient.

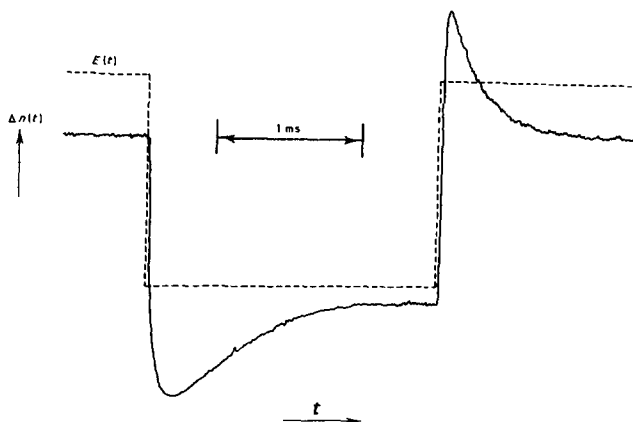


Figure 3 A representative pair of transients for PPG 2025 at 231.4K showing the birefringence ( $\Delta n(t)$ ) and applied electric field ( $E(t)$ ). Data obtained using linear detection and fast and slow components are seen as negative and positive contributions to  $\Delta n(t)$  for both rise and decay functions

that the time-correlation functions for the tangent vector of the primitive chain, for the centre of mass diffusion and for the diffusion of a monomer in the chain are formally similar to those for a Rouse chain, although the underlying models for reptation and diffusion of a spring-bead chain are quite different. Thus it is interesting to speculate that the *B*-process observed in dielectric and Kerr-effect studies for PPG 2025, and for PPG of different molecular weight, is due to reptation. Thus the rotational motions would be achieved by a combination of rotation and translation, as is envisaged in the reptation process. The Bueche–Rouse–Zimm models and those of De Gennes, Edwards and their coworkers predict that the correlation times for the *B*-process will be strongly dependent upon molecular weight, at a given temperature, and this has been observed experimentally using dielectric techniques<sup>1,2</sup> and using the Kerr-effect technique, as will be discussed by us in a separate publication.

#### ACKNOWLEDGEMENTS

M. S. B. and D. A. E. gratefully acknowledge the financial support grants provided by the SRC and we gratefully acknowledge the award of an equipment grant from the SRC.

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#### REFERENCES

- 1 Bauer, M. and Stockmayer, W. H. *J. Chem. Phys.* 1965, **43**, 4319
- 2 Alper, T., Barlow, A. J. and Gray, R. W. *Polymer*, 1976, **17**, 665
- 3 Williams, G. *Trans. Faraday Soc.* 1965, **61**, 1564
- 4 Rouse, P. E. *J. Chem. Phys.* 1953, **21**, 1272
- 5 Zimm, B. H. *J. Chem. Phys.* 1956, **24**, 269
- 6 Bueche, F. J. *J. Chem. Phys.* 1952, **20**, 1959
- 7 De Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
- 8 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. II* (a) 1978, **74**, 1789, (b) 1978, **74**, 1802, (c) 1978, **74**, 1818
- 9 Klein, J. *Nature*, 1978, **271**, 143
- 10 Kimmich, R. *Polymer* 1977, **18**, 233
- 11 Kimmich, R. and Schmauder, Kh. *Polymer* 1977, **18**, 239
- 12 Beevers, M. S., Crossley, J., Garrington, D. C. and Williams, G. *J. Chem. Soc., Faraday Trans. II*, 1976, **72**, 1482
- 13 Crossley, J. and Williams, G. *J. Chem. Soc. Faraday Trans. II*, 1977, **73**, 1651
- 14 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80
- 15 Williams, G., Watts, D. C., Dev, S. B. and North, A. M. *Trans. Faraday Soc.* 1971, **67**, 1323
- 16 Kielich, S. in 'Dielectric and Related Molecular Processes', Spec. Period. Rep. (Ed. M. Davies) (Chem. Soc. London 1972) Vol 1, p 192–387