Flow-modified permittivity of solutions of poly(n-butyl isocyanate) and poly(n-hexyl isocyanate)

H. Block, E. M. Gregson, A. Ritchie and S. M. Walker
Department of Inorganic, Physical and Industrial Chemistry, Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX, UK
(*Received* 8 *December* 1982)

The dielectric behaviour of solutions of poly(n-butyl isocyanate) and poly(n-hexyl isocyanate) in flow have been examined, including, for the latter polymer, fractions of differing molecular weight. The data are analysed in terms of established theories for changes in the permittivity of solutions of rigid macromolecules undergoing shear and are critically compared to dielectrically based information obtained from studies of still solutions. Rotational diffusion coefficients and dipole moments have been measured and the influence of heterogeneity in molecular weight on flow-modified permittivity is examined. The results obtained support the view that the theories for the flow-modified permittivity of rigid macromolecules are generally satisfactory in providing rotational diffusion coefficients and resolved dipoles, but that the influence of molecular shape on the effect is not simply obtained when polydisperse material is involved.

Keywords Flowing solutions; flow-modified permittivity; dielectric relaxation; poly(butyl isocyanate); poly(hexyl isocyanate)

INTRODUCTION

The measurement of the dielectric properties of liquids under shear (flow-modified permittivity, FMP) has been reported by us previously when the liquids were polymer solutions or dispersions[1-3]. The observed changes in permittivity of polymers are best understood for systems in which the macromolecules are not significantly deformed in flow and carry a permanent dipole whose relaxation involves whole-molecule rotational diffusion. Under such conditions the theories of Saito and Kato[4] and the much-simplified form due to Barisas[5] appear from previous studies[1,5] to be satisfactory. The observed reductions in the low-frequency relative permittivity (ε') of such solutions which occur over a range of shear rates (G) can be related to a rotational diffusion coefficient, to the magnitude and molecular orientation of the dipole involved and, in theory at least, to the shape of the macromolecules. However, we have reported some occasional discrepancies between rotational diffusion coefficients obtained from dielectric relaxation and FMP and in the locus of ε' as a function of G predicted theoretically and observed experimentally[1].

The poly(alkyl isocyanates) provide a class of macromolecules with considerable rigidity[5] and large dipole moments. Their synthesis[7] and conditions for fractionation[8] have been established. Dielectrically, the poly(alkyl isocyanates) have been extensively studied[9-19] and thus provide an excellent system for testing the applicability of the theory of FMP to rigid macromolecules. We report below on a dielectric and FMP study of poly(butyl isocyanate) and poly(hexyl isocyanate) in dilute solution. For the latter polymer molecular weight fractions have been examined. Good agreement between our results and those of other workers was found for the dielectric properties in still solution. In FMP the theory of Barisas was found to account for permittivity changes both qualitatively and, at low electrical frequency, quantitatively, particularly when the analysis is extended to take account of polydispersity in molecular weight. Such discrepancies as have been observed previously or in the present work, between dielectrically and FMP-derived diffusion coefficients, are shown to be largely due to polydispersity in molecular weight.

EXPERIMENTAL

Poly(n-butyl isocyanate) (PBIC) and poly(n-hexyl isocyanate) (PHIC) were prepared by the method of Shashoua *et al.*[7] using freshly distilled monomers, dry (vacuum, 100°C for 6 h) sodium cyanide as initiator and pure, dry *N,N*-dimethylformamide (DMF) (P_2O_5 for 24 h followed by fractionation at 10 Torr) as solvent. Polymerizations were carried out at −58°C and with the rigorous exclusion of moisture using glass apparatus which had previously been dried by flaming. The quantities employed were: for PBIC, NaCN (0.0272 g) in DMF (4 cm^3) added to monomer (40 cm^3) in DMF (120 cm^3); and for PHIC, NaCN (0.0678 g) in DMF (10 cm^3) added to monomer (80 cm^3) in DMF (240 cm^3). PHIC was fractionated from tetrachloromethane–methanol by the method of Rubingh and Yu[8], except that a somewhat higher initial concentration (0.6 g dm^{-3}) of PHIC was used. This, as the subsequent gel permeation chromatographs (g.p.c.) showed, resulted in only a marginal drop in the sharpness of fractions.

Except for fractions 2 and 6, weight and number

0032–3861/83/070859–06$03.00

average molecular weights ($\langle M_w \rangle$ and $\langle M_n \rangle$) were determined by g.p.c. using tetrahydrofuran as solvent and the calibration method of Benoit[20]. This was possible since the Mark–Houwink constants K and a are known, being respectively 4.57×10^{-6} g dm^{-3} and 1.18 for PBIC[21] and 2.2×10^{-5} g dm^{-3} and 1.06 for PHIC[22]. There was insufficient of fractions 2 and 6 to permit both the experiments described below and g.p.c. measurements, so in these cases $\langle M_w \rangle$ was estimated from the dielectric relaxation frequencies. *Table 1* shows the values for $\langle M_w \rangle$ and indicates the breadth of heterogeneity in terms of $\langle M_w \rangle / \langle M_n \rangle$. With unfractionated materials a sharp monodisperse peak of low molecular weight identified as trimer was observed in the g.p.c. This trimer is a known byproduct of the polymerization but has also been reported to result from degradation of the polymer particularly in the presence of trace acid[22]. However, no trimer was observed in the fractionated PHIC even after storing for five months, nor was there any observed decrease in the viscosity of solutions of PHIC in toluene over a period of five days. The values of $\langle M_w \rangle$ and $\langle M_w \rangle / \langle M_n \rangle$ quoted in *Table 1* refer only to the polymer peaks as illustrated in *Figure 1* and are exclusive of trimer.

Dielectric and FMP measurements

Dielectric measurements were made on solutions of PBIC in tetrachloromethane and PHIC in toluene using three terminal measurements and a frequency range 10^2 to 10^6 Hz. For the unfractionated materials a Tinsley 4536-A concentric cylinder cell was used and a similar gold-plated home-made cell of smaller capacity (4.24 cm^3) was used for the fractions. In the frequency range 10^2 to 2×10^4 Hz measurements were made with a Wayne–Kerr Autobalance Universal Bridge (B642) energized externally with a Venner TSA 625/2 oscillator. The position of balance was detected with a Brookdeal type 464 null detector. From 2×10^4 to 10^5 Hz a Wayne–Kerr type B601 bridge was used with the above oscillator–detector system and from 10^5 to 10^6 Hz the B601 bridge was energized and the null point detected using a Wayne–Kerr radiofrequency source-detector.

The self-centring shear cell used for FMP measurements has been described previously[23]. It enables both relative permittivity (ε') and dielectric loss (ε'') of liquids in flow to be determined as a function of shear rate (G) in a defined range. The lower limit of this range is set by the requirement for flow to centre the stator and the upper limit by the onset of turbulence. The positions of both limits are influenced by the viscosity, but for dilute polymer solutions in liquids of average viscosity such as tetrachloroethane or toluene used here the effective range is $5 \times 10^2 \leqslant G \leqslant 2 \times 10^5$ s^{-1}. Permittivity measurements using this cell were made on solutions of PBIC and PHIC at 20°±2°C, in some cases over the frequency range 10^2 to 2×10^4 using the Wayne–Kerr B642 bridge.

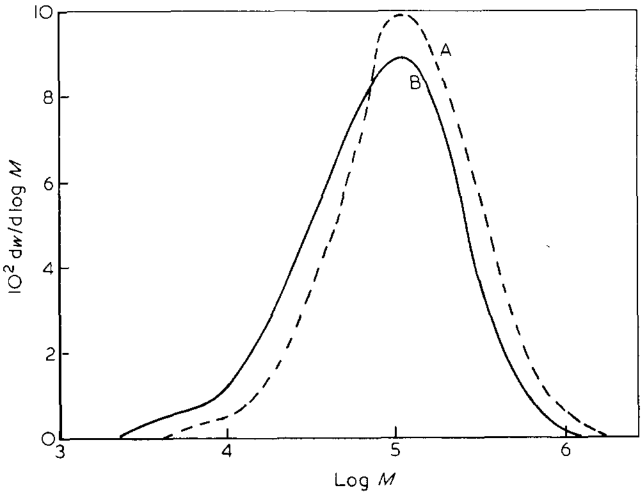

Figure 1 Normalized molecular weight (M) distribution curve (weight fraction w) for unfractionated (A) PBIC and (B) PHIC. Peaks for low molecular weight trimers occur at a nominal log M~2.3 and are not shown

RESULTS AND DISCUSSION

Figure 2 shows the frequency dependence of the dielectric increment $\Delta\varepsilon'$ (the difference between solution and solvent relative permittivity) and ε'' as a function of frequency f for the still solutions of the poly(isocyanates) studied. The extrinsic relaxation times $\tau - 1/2\pi f_c$ (where f_c is the critical frequency) can be obtained from these dielectric data and are given in *Table 1*. Since the solvents are of low polarity these will be very close to the intrinsic relaxation times[24]. The behaviour shown in *Figure 2* has been observed previously by other workers[9–19] and it is generally agreed that the molecular process responsible for the relaxations is an end-over-end rotational diffusion. A consequence of this common mechanism is that solvent viscosity (η_0), τ and the degree of polymerization, taken as the most generally available weight average $\langle p_w \rangle$, are interrelated in a universal dependence of τ/η_0 on $\langle p_w \rangle$. This should be so regardless of which poly(isocyanate) homologue is involved provided the same diffusion process is involved. *Figure 3* illustrates that this is indeed the case for the data that we and others have obtained. Individual workers do report data which show a degree of divergence but the

Table 1 Molecular weight and other data for the poly(alkyl isocyanates)

Material*	$10^{-5}\langle M_w \rangle$	$\langle M_w \rangle / \langle M_n \rangle$	τ (μs)	$\langle \mu^2 \rangle^{1/2}/10^{-27}$ (C m)	$D/10^3$ (s^{-1}) Dielectric	$D/10^3$ (s^{-1}) FMP
PBIC	2.12	3.3	85	5.2	5.9	6.0
PHIC	1.61	5.1	73	–	6.9	12.6
PHIC 1	2.33	2.0	110	4.5	4.5	8.7
PHIC 2	1.29†	–	43	3.3	12	17
PHIC 3	0.856	1.4	16	2.8	31	33
PHIC 4	0.516	1.2	10	1.8	50	50
PHIC 5	0.439	1.5	5.0	1.5	100	78
PHIC 6	0.39†	–	1.6	1.5	310	–

* Numbers following PHIC indicate fractionated polymer
† Obtained from dielectric relaxation time

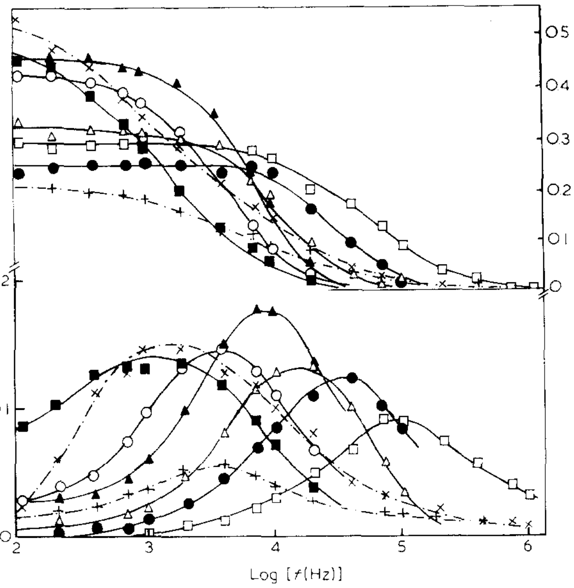

Figure 2 Frequency dependence of dielectric increment (Δε') and loss (ε'') of the poly(isocyanates) at a common concentration of 4 x 10^{-4} g cm^{-3} and at 20°C: x, PBIC in tetrachloromethane; +, PHIC unfractionated; ■, PHIC 1; ○, PHIC 2; ▲, PHIC 3; △, PHIC 4; ●, PHIC 5; □, PHIC 6; all in toluene

linear trend up to $\log\langle p_w\rangle \simeq 3.3$ is generally observed. In this region a mean dependence of the form

$$\tau/\eta_0 = 1.47\times10^{-9}\langle p_w\rangle^{2.53}\ \mathrm{ms^2\ kg^{-1}}$$

is shown in *Figure 3* and this relation was used to estimate $\langle p_w\rangle$ for fractions PHIC 2 and PHIC 6. Beyond $\langle p_w\rangle \simeq 2000$ a change of slope has been observed by Bur and Roberts[9] and their data are shown in *Figure 3*. The dependence of τ/η_0 on $\langle p_w\rangle$ at both low and high degrees of polymerization is consistent with whole-molecule rotational diffusion, the change in curvature at high molecular weights reflecting a measure of flexibility for such long chain macromolecules. Root-mean-square average dipole moments $(\langle\mu^2\rangle^{1/2})$ obtained by applying the Debye equation to the dielectric increments at a common concentration of 0.04 g cm^{-3} are given in *Table 1* for PBIC and PHIC fractions. Examination of the concentration dependence of Δε' for PBIC had indicated that failure to extrapolate to infinite dilution results in an underestimate in $\langle\mu^2\rangle^{1/2}$ of ~8%. Limits on the amounts of material available for the PHIC fractions, together with other sources of error such as an unknown internal field correction ignored by the Debye equation, made such an approximation necessary but only of minor significance. The $\langle\mu^2\rangle^{1/2}$ value for unfractionated PHIC was low, reflecting a low value of Δε' resulting from significant contamination by cyclic trimer.

The dependence of $\langle\mu^2\rangle/\langle p_w\rangle$ on $\langle p_w\rangle$ is illustrated in *Figure 4* which also shows values obtained by other workers. There is considerable scatter in these data due to several possible causes. There are problems in relating Δε' to $\langle\mu^2\rangle$ because of uncertainty in the internal field correction, errors associated with comparing $\langle\mu^2\rangle$ for not truly monodisperse fractions as well as general experimental errors. Nevertheless general trends can be discerned. Initially $\langle\mu^2\rangle/\langle p_w\rangle \propto \langle p_w\rangle$ but between $\langle p_w\rangle$ of 500 and 1000 the curve bends finally reach a plateau. This again is indicative of the onset of flexibility, the square dipole moment per residue $(\langle\mu^2\rangle/p_w)$ finally becoming independent of chain length.

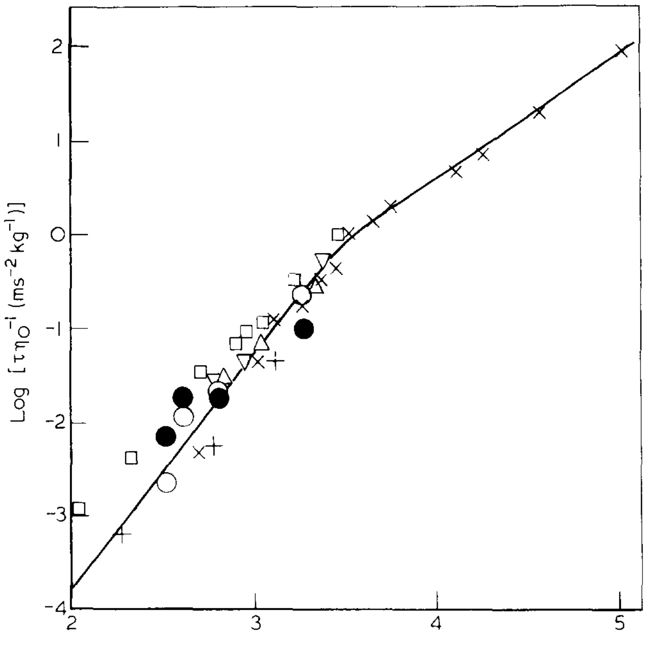

Figure 3 Universal interdependence of relaxation time (τ), solvent viscosity (η_0) and weight average degree of polymerization ($\langle p_w\rangle$) of some poly(isocyanates) of narrow molecular weight distribution. Present dielectric (○) and FMP results (●) for PHIC fractions in toluene. Data for PHIC from Coles *et al.*[12] (△). Data for PBIC from Bur and Roberts[9] (X), from Tsvetkov *et al.*[10,11] (□), from Jennings and Brown[25] (+), and from Troxell and Scheraga[26] (▽)

With FMP measurements the variation of permittivity with *f* or *G* can be studied and sensibly so when either one is kept constant, the other being the experimental variable. For PBIC in tetrachloromethane *Figures 5* and *6* respectively show the variation of Δε' and ε'' as a function of *f* and ε' as a function of *G*, at a number of preset values for the other variable. In the frequency plane at constant *G* the loss process is shifted to higher frequencies with increasing *G* (*Figure 5*). This type of behaviour has been observed previously by us[1] to occur with solutions of α-helical poly(γ-benzyl-L-glutamate) and reflects a hastening of the rotation in flow. Maxima also appear in Δε' and such shifts in ε'' and maxima in Δε' have been predicted by Barisas[5] for spherical macromolecules. In the shear plane

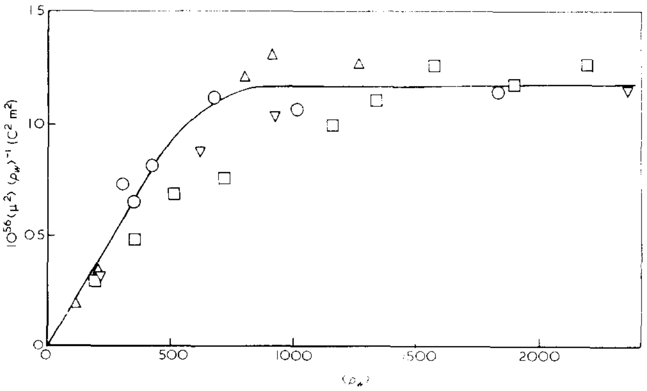

Figure 4 Universal dependence of mean-square residue dipole ($\langle\mu^2\rangle/\langle p_w\rangle$) on the weight average degree of polymerization. Present PHIC fractions (○). Results of Tsvetkov *et al.*[10,11] (△), Bur and Roberts[9] (□), and Troxell and Scheraga[26] (▽) for PBIC fractions

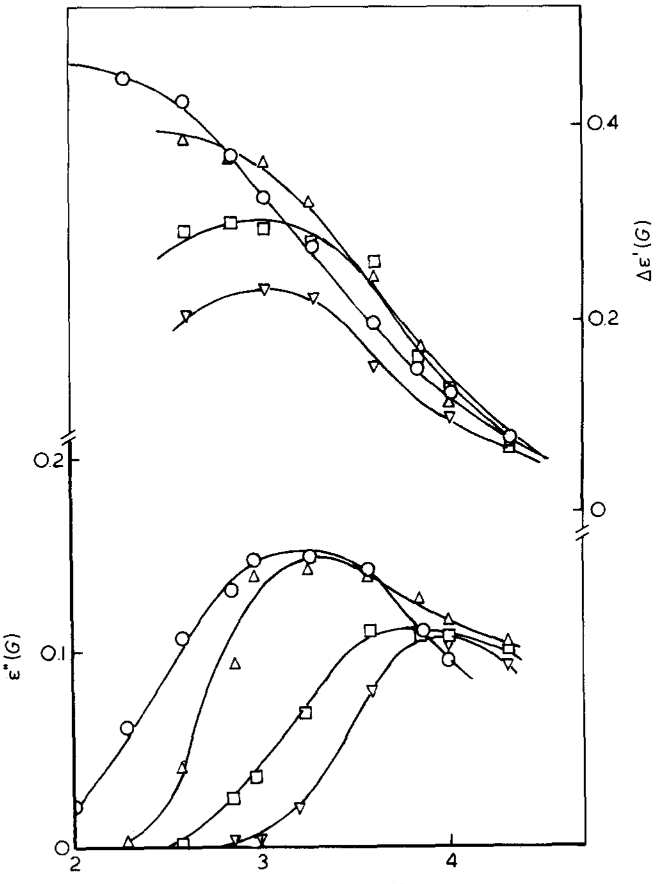

Figure 5 Variation of dielectric increment ($\Delta\varepsilon'(G)$) and loss ($\varepsilon''(G)$) with frequency (f) at various shear rates (G). Data refer to PBIC in tetrachloromethane (4×10^{-4} g cm^{-3}) at 20°C. Values of G (s^{-1}) where 0 (○), 10^4 (△), 5×10^4 (□) and 10^5 (▽)

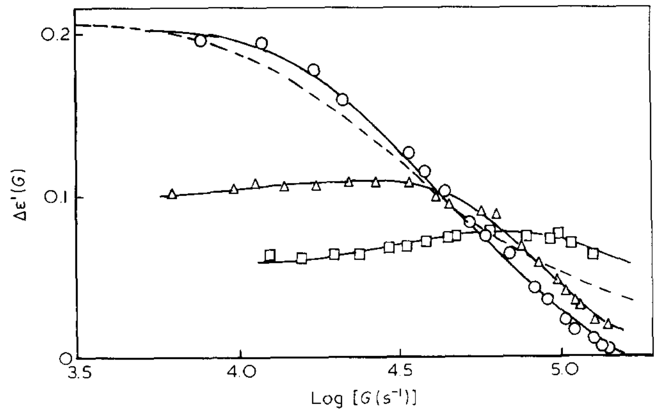

Figure 6 Variation of dielectric increment ($\Delta\varepsilon'$ (G)) with shear rate (G) at various frequencies (f). Data refer to PBIC in tetrachloromethane (4×10^{-4} g cm^{-3}) at 20°C. Values of f (Hz) were 400 (○), 1591 (△) and 4000 (□). The broken curve is a fitted Barisas[5] dependence with a rotational diffusion coefficient of 6×10^3 s^{-1}

no maxima occur in $\Delta\varepsilon'(G)$ at low f but maxima develop at higher f as shown in *Figure 6*.

The low-frequency behaviour illustrated in *Figure 6* is reminiscent of the relaxation of $\Delta\varepsilon'$ in the frequency plane in still solution. Indeed there is a mechanistic interrelation of both effects. In dielectric spectroscopy the drop in $\Delta\varepsilon'$ over the relaxation reflects the rate of the natural process of dipole orientation. In flow-modified permittivity it is the influence of flow on the particle rotation which causes the decrease in $\Delta\varepsilon'$, because as G increases a situation is reached where the flow enhancement of natural rotation is such as to diminish and finally prevent the establishment of polarization. This simple situation in the G plane applies only when the electrical sensing frequency is sufficiently low so that the process of dipole orientation is much faster than changes in the polarity of the electrical field (that is, at frequencies well below the relaxation frequency). If in such a situation whole-molecule rotation is the only dielectrically active process and if the molecule either has spherical symmetry or the dipole is parallel to the axis undergoing reorientation, then $\Delta\varepsilon'$ will tend to zero at high G. This is the behaviour observed with PBIC at 400 Hz shown in *Figure 6* but as can also be seen in *Figure 6* this simple behaviour is not maintained as G approaches the critical angular frequency of 1.2×10^4 s^{-1} when maxima appear in $\Delta\varepsilon'(G)$. Barisas[5] has analysed the dielectric behaviour of rigid spheroids in flow at the low frequency limit of permittivity. His analysis provides a series solution for the polarization per particle at any G in terms of the parameters

$$p = (r^2 - 1)/(r^2 + 1) \quad \text{and} \quad \mu E/kT$$

where r is the axial ratio for the spheroid, μ the major-axis dipole and E the field intensity which is such that $\mu E/kT \ll 1$. In the particular case of spherical symmetry ($p = 0$) an analytic solution for the polarization per particle was established in t terms of both f and G, and the restriction to a time-invariant field need not be made. However, solutions in terms of the frequency dependence of the polarization of spheroidal particles in shear have not been derived to date. In the absence of such a solution we have used Barisas' analytical expressions, which apply strictly only to spherical symmetry and to a non-distributed single orientational relaxation process, to analyse the variation of position of the various maxima shown in *Figures 5* and *6*. The theoretical equations governing these are:

$$\xi_1^6 - (\alpha^2 - 1)\xi_1^4 - (\alpha^4 + 10\alpha^2 + 1)\xi_1^2 + (\alpha^2 - 1)(\alpha^2 + 1)^2 = 0 \tag{1}$$

$$\xi_2 = [2\alpha(\alpha^2 + 1)^{1/2} - (\alpha^2 + 1)]^{1/2} \tag{2}$$

and

$$\alpha_1 = [2\xi(\xi^2 + 1)^{1/2} - (\xi^2 + 1)]^{1/2} \tag{3}$$

where $\xi = \pi f/D$ and $\alpha = G/4D$. ξ_1 and ξ_2 relate to ξ with f values corresponding to the maxima in ε'' and $\Delta\varepsilon'$ respectively at set shear rates and α_1 relates to α with G values corresponding to the maxima in $\Delta\varepsilon'$ at set frequencies. D is the rotational diffusion coefficient obtained from $D = \pi f_c = 5.9 \times 10^3$ s^{-1} assuming spheroidal symmetry. *Figure 7* shows the loci for these equations and the data experimentally obtained. The predictions of equation (1) are upheld and those for (3) are not greatly divergent from the experimental observations, indicating that the influence of shape on the positions of these maxima is only marginal, since PBIC is far removed from being a spherical molecule. In contrast, the positions of the maxima in $\Delta\varepsilon'$ in the frequency plane at various shear rates do not follow equation (2). If this discrepancy is due to the extended nature of the PBIC molecules, then it would seem that a study of the position of these peaks with shear rate would be sensitive to axial ratio. However, investigation of this prediction awaits a solution of the

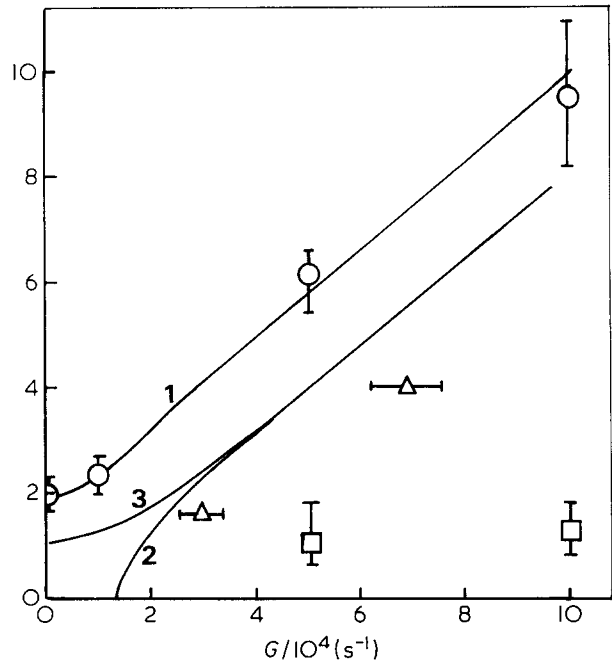

Figure 7 Experimental maxima in dielectric increment ($\Delta\varepsilon'$) or loss (ε'') in the shear (G) or frequency (f) plane for PBIC in tetrachloromethane and the loci theoretically predicted by Barisas[5] for spherical molecules. Curve 1 from equation (1) relates to the G dependence of the frequency for maxima in ε'' and symbols ○ to the data from *Figure 5*. Curve 2 from equation (2) relates to the G dependence of the frequency for maxima in $\Delta\varepsilon'$ and symbols □ to the data from *Figure 5*. Curve 3 from equation (3) relates to the f dependence of the shear rate for maxima in $\Delta\varepsilon'$ and symbols △ to the data from *Figure 6*

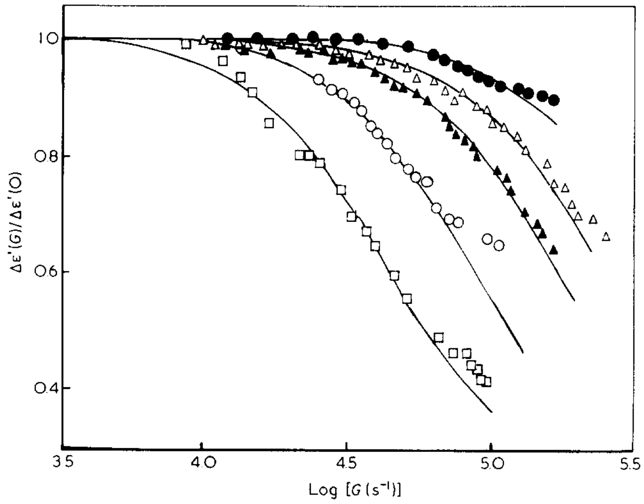

Figure 8 Ratio ($\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$) of dielectric increment under shear rate (G) to that in its absence of PHIC fractions in toluene measured at 400 Hz: □, PHIC 1; ○, PHIC 2; ▲, PHIC 3; △, PHIC 4; ●, PHIC 5. Curves are calculated for needle geometry and the best-fit rotational diffusion coefficients are given in *Table 1*

diffusion equation for spheroids under conditions of variable frequency.

For macromolecules where a hydrodynamically equivalent spheroidal shape is appropriate, the investigations of Barisas provide a theoretical foundation for the dependence of the low-frequency $\Delta\varepsilon'(G)$ upon G. In such cases the form that $\Delta\varepsilon'(G)$ takes can be expressed most directly in terms of its ratio to the increment in still solution $\Delta\varepsilon'(0)$. Provided the increments refer only to contributions from orientational diffusion of the major axis,

$$\Delta\varepsilon'(G)/\Delta\varepsilon'(0)=\Gamma(p,G/2D)$$

where $\Gamma(p, G/2D)$ is the ratio of the polarization per macromolecule in shear of rate G to its still solution or Debye value. $\Gamma(p, G/2D)$ is obtainable from coefficients involving the associated Legendre polynomials making up the space-time distribution function descriptive of the orientation of the major axis. Barisas gives the data for Γ at selected p and $G/2D$ values. The functionality of Γ in terms of p and $G/2D$ enables universal curves of Γ as a function of $G/2D$ to be constructed for any value of p. By matching such curves to the experimental $\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$ values, D can be estimated, for example by finding the value of G at which $\log(G/2D)=0$ in the Γ dependence. For the poly(isocyanates) a value $p\simeq 1$ (needle geometry) is appropriate, particularly as the dependence of Γ on p is not very marked. *Figure 5* shows such an analysis for PBIC on results obtained at 400 Hz and *Figures 8* and *9* provide a similar analysis for the PHIC fractions and unfractionated PHIC at the same frequency. The quality of fit for PHIC fraction and for PBIC is within experimental uncertainty but for unfractionated PHIC this is not the case. However, for all polymers a mean diffusion coefficient estimated by superposition of the Barisas curve for $\Gamma(G)$ dependence was estimated and these are listed in *Table 1* together with the dielectrically estimated rotational diffusion coefficient $D=\pi f_c$. Bearing in mind the width of both the shear and dielectric relaxations, the agreement seems acceptable, a contention supported by the position of individually estimated τ/η_0 as shown in *Figure 3* using diffusion coefficients based on FMP for τ estimates. For unfractionated PHIC the theoretical decay in Γ with G is much steeper than the observed reduction in $\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$. It is unlikely that the choice of needle geometry can cause such discrepancy since the gentlest decay in Γ occurs for $p=1$ if spheroidal geometry is appropriate. We believe that the discrepancy originates in

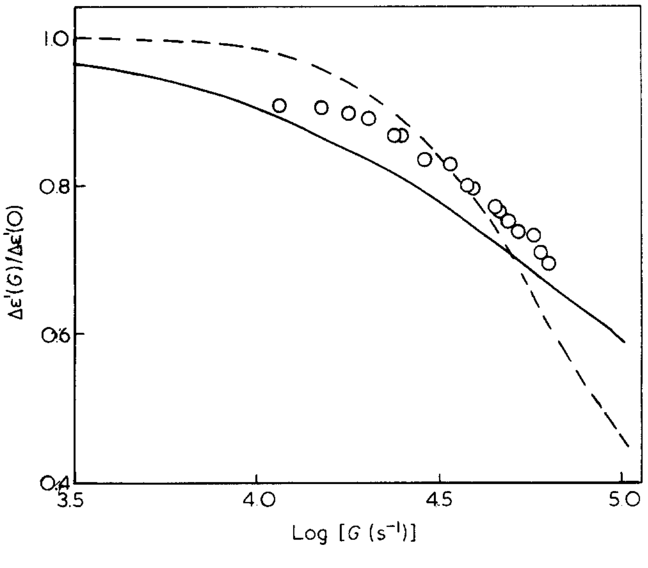

Figure 9 Ratio ($\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$) of dielectric increment under shear rate (G) to that in its absence of unfractionated PHIC in toluene measured at 400 Hz. The broken curve was calculated for needle geometry and the best-fit rotational diffusion coefficient of 12.6×10^3 s^{-1} without correction for polydispersity in molecular weight. The full curve was calculated from equation (5), thereby allowing for polydispersity

polydispersity of molecular weight which is greatest with unfractionated PHIC, being significantly larger than for PBIC (*Table 1*).

The hypothesis that polydispersity is involved can be tested using known data, since for a polydisperse sample each i-mer contributes individually to $\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$ via Γ_i, its dipole μ_i and its molar concentration C_i. Thus

$$\frac{\Delta\varepsilon'(G)}{\Delta\varepsilon'(0)}=\frac{\Sigma\mu_i^2C_i\Gamma_i}{\Sigma\mu_i^2C_i} \qquad (4)$$

where the summation is taken over all i present. Since $C_i = w_ic/M_i$, where w_i is the weight fraction of i-mer in the mass concentration c, expression (4) can be written as

$$\frac{\Delta\varepsilon'(G)}{\Delta\varepsilon'(0)}=\frac{\displaystyle\int\frac{\mu_i^2}{M_i}\frac{\mathrm{d}w_i}{\mathrm{d}\log M_i}\Gamma_i\mathrm{d}\log M_i}{\displaystyle\int\frac{\mu_i^2}{M_i}\frac{\mathrm{d}w_i}{\mathrm{d}\log M_i}\mathrm{d}\log M_i} \qquad (5)$$

The integrands given in expression (5) are known since individual components are known. Data for $\mathrm{d}w_i/\mathrm{d}\log M_i$ were obtained from the curve in *Figure 4*. To obtain Γ_i we used Barisas' data with $p=1$ and an estimated D_i from the curve in *Figure 3* with $\eta_0=5.8\times10^{-4}$ kg m^{-1} s^{-1} for toluene at 20°C. Numerical integration of (5) for individual values of G gave the solid curve in *Figure 9*.

It can be seen that the width in the $\Delta\varepsilon'(G)/\Delta\varepsilon'(0)$ curve is reproduced although there is a slight mismatch of the curves, the decay in the predicted behaviour occurring at lower shear rates than that experimentally observed. The broadening of Γ decay due to polydispersity is clearly visible and for this reason in particular we concur with Barisas that analysis of FMP for rigid macromolecules in terms of the low-frequency shear dependence is not very sensitive to shape.

Finally, all the FMP measurements show, within experimental error, the expected drop in $\Delta\varepsilon'(G)$ over the shear rates achievable with our equipment. This indicates that the total dielectric increment $\Delta\varepsilon'(0)$ is involved in the rotational process and that in consequence there is no component of dipole normal to the major axis of the particle. Thus the *cis*-amide bond structure of poly(isocyanates) provides only a summative dipole along this major axis and any perpendicular components must, because of symmetry, cancel in the chain conformation. The implication is that the chain has a helical twist.

ACKNOWLEDGEMENTS

We wish to acknowledge a grant from the SERC in support of this work and for the assistance of the Rubber and Plastics Research Association in providing the g.p.c. data.

REFERENCES

1 Block, H., Ions, W. D., Powell, G., Singh, R. P. and Walker, S. M. *Proc. R. Soc. London, A* 1976, **352**, 153

2 Block, H., Ions, W. D. and Walker, S. M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 989

3 Block, H., Goodwin, K. M. W., Gregson, E. M. and Walker, S. M. *Nature* 1978, **275**, 632

4 Saito, N. and Kato, T. *J. Phys. Soc. Jpn.* 1957, **12**, 1393

5 Barisas, B. G. *Macromolecules* 1974, **7**, 930

6 Bur, A. J. and Fetters, L. J. *Chem. Rev.* 1976, **76**, 727

7 Shashoua, V. E., Sweeney, W. and Tietz, R. F. *J. Am. Chem. Soc.* 1960, **82**, 866

8 Rubingh, D. N. and Yu, H. *Macromolecules* 1976, **9**, 681

9 Bur, A. J. and Roberts, D. E. *J. Chem. Phys.* 1969, **51**, 406

10 Tsvetkov, V. N., Ryumtsev, Ye. I., Aliyev, F. M. and Shtennikova, I. N. *Eur. Polym. J.* 1974, **10**, 55

11 Tsvetkov, V. N., Ryumtsev, Ye. I., Aliyev, F. M., Shtennikova, I. N. and Savvon, S. M. *Polym. Sci. USSR* 1974, **16**, 1627

12 Coles, H. J., Gupta, A. K. and Marchal, E. *Macromolecules* 1977, **10**, 182

13 Yu, H., Bur, A. J. and Fetters, L. J. *J. Chem. Phys.* 1966, **44**, 2468

14 Bur, A. J. *J. Chem. Phys.* 1970, **52**, 3813

15 Lochhead, R. Y. and North, A. M. *J. Chem. Soc. Faraday Trans.II* 1972, **68**, 1089

16 Ryumtsev, Ye. I., Aliev, F. M. and Tsvetkov, V. N. *Polym. Sci. USSR A* 1975, **17**, 1967

17 Tsvetkov, V. N., Ryumstev, E. I., Pogodina, N. V. and Shtennikova, N. *Eur. Polym. J.* 1975, **11**, 37

18 Anderson, J. S. and Vaughan, W. E. *Macromolecules* 1975, **8**, 454

19 Beevers, M. S., Carrington, D. C. and Williams, G. *Polymer* 1977, **18**, 540

20 Grubisic, Z., Remp, P. and Benoit, H. *J. Polym. Sci. B* 1967, **5**, 753

21 Burchard, W. *Makromol. Chem.* 1963, **67**, 182

22 Berger, M. N. and Tidswell, B. M. *J. Polym. Sci., Polym. Symp. Edn.* 1973, **42**, 1063

23 Block, H., Gregson, E. M., Ions, W. D., Powell, G., Singh, R. P. and Walker, S. M. *J. Phys. E* 1978, **11**, 251

24 Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M. 'Dielectric Properties and Molecular Behaviour', Van Nostrand Reinhold, London, 1969

25 Jennings, B. R. and Brown, B. L. *Eur. Polym. J.* 1971, 7, 805

26 Troxell, T. C. and Scheraga, H. A. *Macromolecules* 1971, **4**, 528