Molecular dynamics of liquid crystalline side-chain polymers: The dielectric relaxation behaviour of a siloxan polymer in the nematic and isotropic phases

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The dielectric relaxation behaviour of a liquid crystalline side-chain polymer having a siloxan backbone to which is attached an aromatic ester group via a C_5 methylene spacer has been studied in the nematic and isotropic phases. One process was observed in the isotropic phase and was characteristic of that of a glass-forming liquid. A composite process was observed in the liquid crystalline phase. In the transition range the dielectric behaviour changed continuously from that of the liquid crystal to the isotropic material. The characteristic features of the relaxations are described and their mechanisms are discussed in relation to earlier dielectric data for small molecule nematogens and for liquid crystalline side-chain polymers based on acrylate and methacrylate monomers.

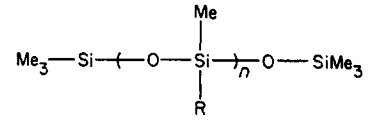
(Keywords: liquid crystalline polymers; dielectric relaxation; nematic)

INTRODUCTION

Following the pioneering works of Ringsdorf, Finkelmann and co-workers and of Shibaev, Platé and co-workers in the late 1970's, there has been great activity in the synthesis of thermotropic liquid crystalline side-chain polymers and the study of their physical properties. Several hundred such polymers have been synthesised, and the preparative methods used together with information on their phase behaviour have been reviewed[1-4]. These new materials are of interest to polymer science and to liquid crystal science. They are hybrid materials which share with polymers the property of viscoelasticity (see ref. 3, p. 159), while sharing with small-molecule liquid-crystals the formation of mesophases characterized by long-range orientational order. As a result these materials can be aligned in magnetic or electric fields[1-5] and are therefore interesting electro-optically active substances. It has been shown[1-5] that an aligned material may be prepared by cooling a melt into the liquid-crystalline phase in the presence of magnetic or electric fields. On removal of the field the alignment remains, so that these materials are of interest as reversible optical information media—as has been described by Shibaev and Platé (ref. 4, p. 235) and by Coles[5].

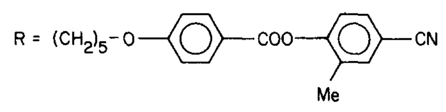
The optical textures observed under the polarizing microscope and X-ray scattering data indicate the presence of liquid-crystalline order. The measured order parameter appears to be lower than that in corresponding small-molecule liquid crystals[3]. The molecular dynamics of the liquid-crystalline phase may be studied by dielectric, n.m.r. and e.s.r. methods. Kresse and co-workers[6,7] observed the dielectric behaviour of methacrylate and acrylate polymers which have cyanobiphenyl groups in the side chain, while Zentel and co-workers[8,9] studied the dielectrical behaviour of a number of acrylate polymers with aromatic ester groups in the side chain. The loss peaks were attributed[6,9] to certain motions of the dipolar groups, as we shall describe further below.

In the paper presented here the dielectric properties of a siloxan polymer with the following structure will be described



$$\mathrm{Me_3{-}Si{-}\!\left(\!O{-}\overset{\displaystyle Me}{\underset{\displaystyle R}{Si}}\right)_{\!n}\!{-}O{-}SiMe_3}$$

where $n \simeq 50$ and



EXPERIMENTAL

The mesogenic pendant group R was prepared by the esterification of 4-hydroxy-3-methylbenzonitrile with 4-(n-pent-4'-enoxy)benzoic acid in the presence of triethylamine in dichloromethane[11]. The disubstituted benzonitrile was prepared by first monobrominating *o*-cresol, and then converting this compound to the nitrile using copper cyanide in 1-methyl-2-pyrrolidinone. The monosubstituted benzoic acid was made by alkylation of 4-hydroxybenzoic acid with 5-bromopent-1-ene in ethanolic sodium hydroxide solution. The polyhydrosilylation reaction was carried out in toluene by refluxing

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in an atmosphere of dry nitrogen using chloroplatinic acid as catalyst. The resultant polymer was nematic in character. A d.s.c. scan (10 K min^{-1}) gave a nematic-isotropic clearing point T_c at 325.7 K (heating) and 317.2 K (cooling). The transition range extended over about 5 K as judged by the range of the endo- or exotherms.

The dielectric measurements were made in the range 12–10^5 Hz using a Gen Rad 1689 precision RLC digibridge which was computer controlled. The equivalent parallel capacitance C_p and conductance G_p of the sample was measured at twenty spot frequencies by a substitution method involving first zeroing the Gen Rad unit without the sample and then measuring with sample present. A complete frequency scan required approximately 15 min. The disc sample (120 μm thick and 10 mm diameter) was contained in a three terminal cell previously[12] described. The values of C_p and G_p are related to the dielectric permittivity ε' and loss factor ε'' according to the relations[10]

$$C_p = \varepsilon' C_a + C_1 \tag{1a}$$

$$\frac{G_p}{\omega} = \varepsilon'' C_a \tag{1b}$$

where C_a is the geometrical capacitance of the interelectrode space, C_1 is the fringing capacitance and $\omega = 2\pi f$ is the angular frequency of the measurement. Thus plots of C_p and G_p/ω against frequency are sufficient to indicate the dielectric relaxation behaviour of the liquid-crystalline polymer.

RESULTS

Figures 1 and *2* show plots for fixed temperatures in the range 313.0–348.0 K. *Figure 1* shows that relaxation occurs in this frequency range which is broader in the liquid-crystalline range (curves 1–3) than in the isotropic range (curves 6–9). The loss data shown in *Figure 2* indicate the following: (i) In the liquid-crystalline state (curves 1–3) the loss peak is bimodal and extremely broad, implying overlapping processes which we shall call the δ and α processes in order to conform with the nomenclature of Zentel *et al.*[8,9]. The curve at 313.0 K clearly has two components, but this becomes less evident as the temperature is raised in the liquid-crystal range, suggesting that the apparent activation energy for the δ-process is greater than that for the α-process (in this temperature range). (ii) In the isotropic state (curves 6–9) the loss peak is narrow and asymmetrical in the Davidson–Cole sense[10] with a half width of $\simeq 1.72$ units of $\log_{10}(f/\text{Hz})$. Such curves may be fitted using the Kohlrausch–Williams–Watts relation with an exponential factor of 0.67.

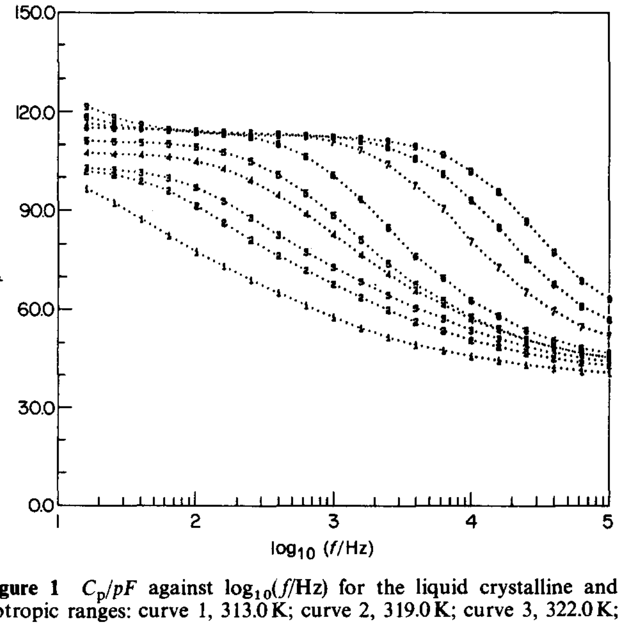

Figure 1 C_p/pF against $\log_{10}(f/\text{Hz})$ for the liquid crystalline and isotropic ranges: curve 1, 313.0 K; curve 2, 319.0 K; curve 3, 322.0 K; curve 4, 325.4 K; curve 5, 326.5 K; curve 6, 330.0 K; curve 7, 338.0 K; curve 8, 343.0 K; curve 9, 348.0 K

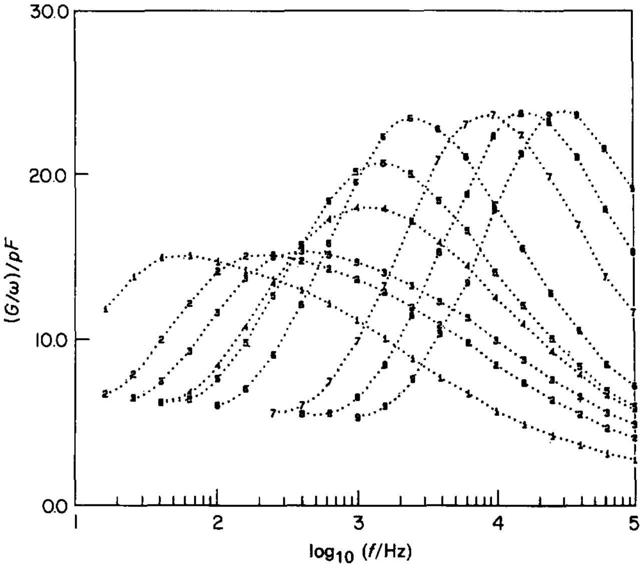

Figure 2 $(G_p/\omega)/pF$ against $\log_{10}(f/\text{Hz})$ for the liquid-crystalline and isotropic ranges. Curves 1–9 correspond to the temperatures indicated in *Figure 1*

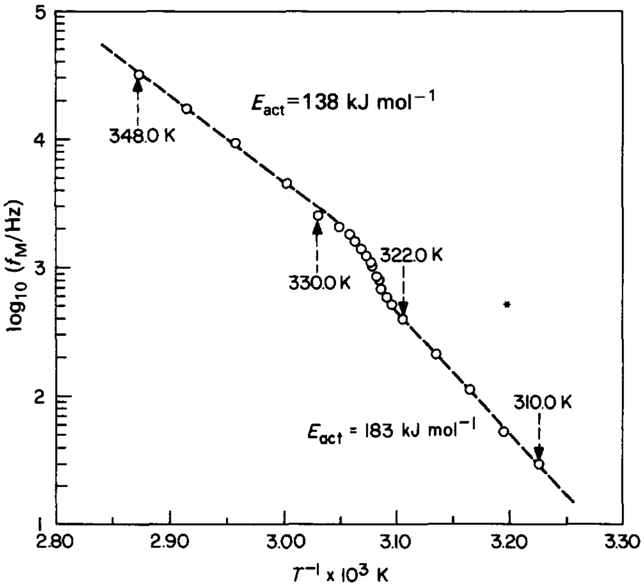

Figure 3 $\log_{10}(f_{max}/\text{Hz})$ against $(T)^{-1} \times 10^3$ K for the data of *Figure 2*

The apparent activation energy for the loss peak in the isotropic phase is determined from the plot of $\log_{10}(f_{max}/\text{Hz})$ *versus* $(T/\text{K})^{-1}$ shown in *Figure 3*. The points actually indicate a curve, with E_{act} increasing with decreasing temperature. This is behaviour typical for a glass-forming isotropic liquid[12]. The linear broken line through the points shown in *Figure 3* gives an average value of $E_{\mathrm{act}} \simeq 138\,\mathrm{kJ\,mol^{-1}}$. Such a large value is typical[10,12] for relaxation in a glass-forming isotropic liquid when $\log_{10}(f_{\max}/\mathrm{Hz})$ is in the range 3–5. Thus the broad asymmetric loss profile and the frequency–temperature variation for the process in the isotropic state indicates a cooperative reorientation of the dipolar mesogenic groups in a normal glass-forming isotropic liquid. (iii) In the transition range (curves 4–6) the dispersion (*Figure 1*) and absorption (*Figure 2*) curves show a continuous variation. The magnitude of the loss peak grows and the curves narrow as the bimodal loss curve of the liquid crystalline phase gradually transforms into the single loss curve of the isotropic phase. The results in this range were reproducible for heating and cooling cycles: no hysteresis or time effects were observed.

DISCUSSION

These data may be discussed by considering, in turn, the magnitude, location and shape of the relaxation curves in the liquid-crystalline, bi-phasic and isotropic ranges.

Magnitude

The dielectric increment[10] $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is not easily obtained from the data of *Figures 1* and *2* since the loss curves are broad. A rough estimate of the variation of $\Delta\varepsilon$ on passing through the liquid-crystalline, bi-phasic and isotropic ranges may be made as follows. For a broad loss curve the product $\varepsilon''_{\max} \times \Delta_{\frac{1}{2}}$, where $\Delta_{\frac{1}{2}}$ is the half-width of the loss curve, is proportional to $\Delta\varepsilon$ (see Ref. 13, eqn. 8), the proportionality factor being dependent on the form of the distribution. For the data of *Figure 2*, $(G/\omega)_{\max} \times \Delta_{\frac{1}{2}}$ for the entire range was found to very by less than 3% from a constant value. This shows that $\Delta\varepsilon$ is approximately the same value in the liquid-crystal, bi-phasic and isotropic states, despite the large variations in $(G/\omega)_{\max}$ and $\Delta_{\frac{1}{2}}$ seen in *Figure 2*. Thus the effective mean square dipole moment being relaxed is approximately the same in all three ranges, the variations in loss profile reflecting the modes of relaxation being used. Note that the plot of $(G/\omega)_{\max}/pF$ against $(T/\mathrm{K})^{-1}$ shown in *Figure 4* gives a good indication of the transition from isotropic to liquid-crystalline phase through the bi-phasic region. Thus the dielectric method provides a simple and direct method of following the phase behaviour. This is in contrast with volume or specific heat studies for which the liquid-crystal→isotropic transition is detected only using high precision (dilatometry) or under poorly defined dynamic conditions (d.s.c.). Note also that in *Figure 4*, $(G/\omega)_{\max}$ refers to the single broad loss peak for the isotropic range, and mainly to the δ-peak for the liquid-crystalline range. Our results for this nematic siloxan material are qualitatively different from those of Kresse and Talroze[6] for nematic poly[1-[5-(4′-cyano-4-biphenyloxy)-pentyloxycarbonyl]ethylene]. They found that in the liquid-crystalline phase a single broad loss curve was observed (with $\Delta_{\frac{1}{2}} \simeq 1.6$) which is *smaller* and slightly *broader* ($\Delta_{\frac{1}{2}} \simeq 1.8$) than that obtained in the isotropic phase. Thus, in this case $\Delta\varepsilon$ appears to fall on passing from the liquid-crystalline to isotropic states. This is confirmed by inspection as seen in *Figures 1* and *2* where ε_0, the low frequency permittivity, falls from 135–122 pF through the transition range[6].

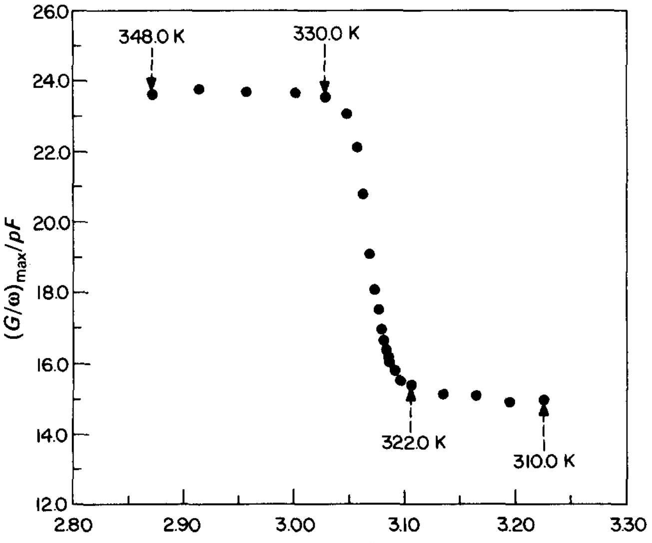

Figure 4 $(G/\omega)_{\max}/pF$ against $T^{-1} \times 10^3$ K showing the transition from the isotropic to liquid-crystalline states

Location and shape

It is not possible to resolve the bimodal peak in the liquid-crystalline phase (*Figure 2*) into its component δ and α processes. A rough estimate shows that the α-peak occurs at about one unit of $\log_{10}(f/\mathrm{Hz})$ above that of the δ-peak at 313.0 K, and this is indicated in *Figure 3* as the single starred point. Linear extrapolation of the locus for the isotropic data in *Figure 3* would give a value of $\log_{10} f_{\max}$ at 313.0 K, slightly lower than that for the α-peak (* point). Such an extrapolation seems unreasonable, since, as we indicated above, the isotropic data are typical for a glass-forming liquid so that extrapolation would be expected to follow a Vogel-type curve[10] and give a value of $\log_{10} f_{\max}$ in the supercooled isotropic liquid well below the value observed for the α-peak. Therefore it seems likely that the α-peak in the liquid-crystalline material is not to be correlated with the peak in the isotropic phase: i.e. the α-peak is not due to cooperative motions in an amorphous phase in a partially crystalline material (for such examples in solid polymers see the accounts for nylon and poly(ethylene terephthalate) in ref. 10). We note that the siloxan backbone has only a small mean square dipole moment per repeat in comparison with that for the mesogenic head group, so that both δ- and α-processes observed for polymer (**I**) arise principally from the motions of the mesogenic head group. It is likely that the δ- and α-processes are different kinds of motion of the head group in the liquid-crystal environment. These in turn may be tentatively assigned to longitudinal (δ-process) and transverse (α-process) motions of the (non-linear) mesogenic head group. The group R in structure I above has longitudinal and transverse dipole moment components so that it is likely that these components are the source of the δ- and α-processes respectively. Kresse and co-workers[6,7] found no evidence of composite δ and α loss peaks in the liquid-crystalline phases for acrylate and methacrylates with cyanobiphenyl head groups. Their peaks are δ-peaks, and the absence of an α-process is due to the absence of a transverse dipole moment component in those polymers. Both the polymers of Kresse and co-workers[6,7], and of Zentel and co-workers[8,9] have ester groups which attach the side chain to the main chain, and whose motions, if detected in a dielectrics experiment, would give information on the main-chain motions of the polymer. Such motions were not observed by Kresse and co-workers[6,7] in their temperature range of study. Zentel and co-workers observed δ, α, β, γ_1 and γ_2 processes in acrylate polymers which have as the mesogenic group an aromatic ester group O–Ø–COO–Ø–R′, where R′ is CN or alkoxy. They assigned their α-process to motions of the ester group linking main and side chains; i.e. to backbone chain motions. Their β-process, which occurs at very low temperatures, was assigned to motions of the bridge ester group between the aromatic rings in the mesogenic head group. Thus whereas we have assigned the α-process for polymer (I) to be transverse dipole motions of the aromatic ester groups, the α-process in the polymers studied by Zentel and co-workers is assigned to main chain motions (and hence is to be associated with the apparent glass transition temperature of the polymer). For polymer (I), the d.s.c. data suggest that T_g is in the range 20–30°C. However, the frequency–temperature location of the present α-process is not sufficiently well defined, experimentally, to correlate it to T_g. Also, as we have already indicated, the lack of sufficiently large dipole moment in the siloxan chain backbone does not allow us to see those motions directly.

The main relaxation observed in the liquid crystalline phase for the present siloxan polymer (I) and for the polymers studied by Kresse[6,7] and by Zentel[8,9] is the δ-relaxation. It is the slowest process at a given temperature for all systems studied. The locus of $\log_{10} f_{\max}$ *versus* T^{-1} for the liquid-crystal phase in *Figure 3* is mainly due to the δ-process while similar plots for refs. 6–9 are also largely determined by the δ-process. We obtain $E_{\text{act}} \simeq 183\,\text{kJ}\,\text{mol}^{-1}$, which is to be compared with $220\,\text{kJ}\,\text{mol}^{-1}$ and $190\,\text{kJ}\,\text{mol}^{-1}$ for the nematic[6] and smectic[7] phase acrylate polymers studied by Kresse. Similar values are obtained for the δ-process for the polymers studied by Zentel *et al.*[8,9] It has been suggested[6–9] that the δ-process is due to the rotation of the mesogenic group as a whole (head + tail) around the main chain. Small molecule nematics such as the alkylcyanobiphenyls exhibit a large (near the single relaxation time) dielectric relaxation process in the nematic phase. The process occurs in the frequency range 10^5–10^7 Hz for $T_c - 50 \leqslant T < T_c$ and has an apparent activation energy of $\sim 60\,\text{kJ}\,\text{mol}^{-1}$. This process is usually assigned as the small-step rotational diffusion of the elongated molecules in a P_2-type nematic potential, i.e. individual molecules undergo a 'flip-flop' rotation in the nematic phase which reverses the longitudinal component of the dipole moment vector. For the alkylcyanobiphenyls the lateral dipole moment component is absent[14]. However for the benzylideneaniline derivatives[15] (e.g. MBBA) and aromatic esters[16], there are significant longitudinal and transverse dipole moments. Bone *et al.*[16] studied the dielectric relaxation of several aromatic esters which had been aligned with a magnetic field. It was shown for *n*Pr–Ø–COO–Ø–*n*Pentyl that two loss peaks occurred in the isotropic phase at 302 K, the lower frequency process was small and peaked at $10^{7.3}$ Hz, while the higher frequency process was larger, carrying with it most of the mean square dipole moment, and peaked at $10^{8.5}$ Hz. In its liquid-crystal (nematic) phase at 291 K, the aligned material gave two peaks for ε (parallel to E) at $10^{6.3}$ and $10^{8.5}$ Hz respectively, while ε (perpendicular to E) gave one peak at $10^{8.5}$ Hz. Such behaviour shows that two dipole moment components, longitudinal (L) and transverse (T), are being relaxed, and that the L process is the slower process of the two. Again, it is thought that the L process is the 'flip-flop' motion and the T process is motion about the long axis of the small molecules nematogen. If we now consider the siloxan or acrylate polymers, the end of the flexible alkyl spacer is tied to the polymer chain. Motions of the mesogenic group (which contains the dipole moment) around the long axis of the mesogenic head group in the nematic phase would be expected to occur in a similar manner, but at a much slower rate than the corresponding motions in the small molecule nematic—owing to the larger local viscosity in the polymer system. However, the decrease in the frequency of maximum loss for the transverse motion from $10^{8.5}$ to $\simeq 10^3$ on passing from a small molecule system to a polymeric system is very large and raises again the question of the origin of the α-process in the siloxan polymer (I). This can only be resolved experimentally, e.g. by measuring ε(parallel) and ε(perpendicular) for a sample which has been aligned by a magnetic field. If the α-process is the dominant relaxation affecting ε(perpendicular) then its mechanism is due, like the small molecule system, to the motions of the transverse dipole moment.

A comparison of the 'flip-flop' process in the small molecule nematogens[14–16] with the δ-process in the siloxan polymer (I) and the acrylate polymers[6–9] is important. For the aromatic ester ME35 Bone *et al.*[16] obtained $f_m \simeq 10^{6.3}$ Hz at 291 K and $E_{\text{act}} \simeq 90\,\text{kJ}\,\text{mol}^{-1}$, which we may compare with the locus (dominated by the δ-process) in *Figure 3*. It thus appears that the longitudinal relaxation is decreased in rate by $\simeq 10^8$ on passing from a small molecule system to a polymeric system and the apparent activation energy for the process is doubled. The longitudinal relaxation in the polymer (δ-process) is evidently more cooperative, and such cooperation effects must arise from the fact that the flexible spacer is tied to the siloxan chain. This is clear evidence that the polymer chain influences the properties of the mesogenic head group—an aspect of liquid-crystalline polymers which is discussed continually[3,4]. While it is possible for small molecules to undergo 'flip-flop' motion in the nematic state, it is likely that the topological constraints in the polymer systems will hinder such a motion, suggesting that the longitudinal relaxation in the polymers (δ-process) has a different mechanism. One possibility is that a representative dipolar mesogenic head group undergoes large fluctuations in its direction with respect to the local director prescribed by the adjacent mesogenic head groups, but does not reverse its dipole vector. Such motions of the mesogenic head group may be described as motions in an effective cone of cone angle θ_0 say. Such a motion may be modelled in terms of rotational diffusion, for which several models are available: e.g. small step diffusion in a cone, as described by Wang and Pecora[17] and applied to the motion of rod-like polymers in the lyotropic liquid-crystalline state by Moscicki, Aharoni and Williams[18–21]. Further dielectric studies of liquid crystalline side chain polymers in their unoriented and oriented states are required to establish the mechanisms for the δ- and α-processes described here.

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