Effect of pressure on the dielectric-relaxation behaviour of a liquid-crystalline side-chain polymer

J. J. Moura-Ramos
Centro de Quimica-Fisica Molecular, Complexo Interdisciplinar, Instituto Superior Técnico, Av. Roviso Pais, 1000 Lisbon, Portugal

and G. Williams*
Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK

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The dielectric properties of a siloxane liquid crystal polymer have been studied over a range of frequencies (10–10^5 Hz), temperatures (50–75°C) and applied hydrostatic pressures (up to 1.5 kbar). The relaxation is due to the anisotropic motions of the dipolar mesogenic groups and its rate is strongly dependent upon the sample temperature and applied pressure. The δ- and α-relaxations are observed and are assigned to specific modes of motion of the dipolar groups, and their behaviour, with respect to temperature and pressure variations, are compared and contrasted with the relaxation of chain segments in amorphous solid polymers.

(Keywords: dielectric properties; liquid crystalline polymer; pressure effects)

INTRODUCTION

Molecular motions in solid polymers may be studied using a variety of spectroscopic, scattering or relaxation methods. One useful method is that of dielectric relaxation which may be used[1,2] to study the motions of dipolar groups in the frequency range 10^{-4}–10^{10} Hz. Using this method, amorphous and crystalline polymers have been studied over wide ranges of sample temperature[1,2] and pressure[3–9]. For such isotropic materials, the molecular mechanisms responsible for the multiple dielectric relaxations have been assigned[1,2]. In recent years, there has been an increasing interest in anisotropic polymers, notably liquid-crystalline side-chain (LC-SC) polymers. Several hundred such polymers have been synthesized (e.g. refs. 10–12 and references therein). For these materials the complex dielectric permittivity is a tensorial quantity. For a material having uniaxial symmetry (e.g. a nematic phase) the principal quantities are $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$ where $\parallel$ and $\perp$ refer to parallel with, or perpendicular to, respectively, the director axis n. Here $\omega = 2\pi f$ where f is the frequency of the measuring field. The dielectric properties of both unaligned[13–17] and aligned[18–30] LC-SC polymers have been studied over wide ranges of frequency and temperature. It is found that $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$ exhibit multiple relaxation regions arising from the anisotropic motions of the dipolar mesogenic head groups in the side chain and from the dipolar segments in the polymer backbone. The behaviour is understood, at least semi-quantitatively, in terms of a molecular theory for such motions in a LC phase[22,24,26].

Only limited studies have been made of the effect of an applied pressure on the dielectric relaxation behaviour of LC-SC polymers. Heinrich and Stoll[31] obtained dielectric data in the range 10^{-2}–10^6 Hz, 60–160°C and 1–5000 bar applied pressure for two unaligned LC polyacrylates which had p-cyano-phenyl benzoate groups in the side chain. Two loss peaks were observed, labelled δ and α, in ascending order of frequency, which exhibited large changes in their effective relaxation frequencies as pressure was increased at a fixed sample temperature. Attard and coworkers[23] briefly reported on the effect of pressure on the resolved δ-relaxation in a homeotropically aligned sample of a smectic siloxane LC polymer having p-cyano-phenyl benzoate groups in the side chain. It was shown that the effect of pressure was qualitatively similar to that observed for the α_a relaxation in amorphous solid polymers[2,4]. This material had been studied previously[19,20] in different states of macroscopic alignment over wide ranges of frequency and temperature. The present work gives extensive dielectric data for the same material in different states of alignment as studied over ranges of frequency, temperature and applied pressure.

EXPERIMENTAL

The LC siloxane polymer, structure shown below, was the same material as studied previously[19,20]. It had an S–I transition near 363K (differential scanning calorimetry (d.s.c.), heating) and an apparent glass transition temperature, T_g, about 274K (d.s.c., heating).

Dielectric studies were made with disc samples (1 cm diameter, 100 μm thickness), placed between the metal electrodes of a three-terminal high pressure cell whose construction and use have been described much earlier[7]. The pressure transmitting liquid was a light silicone oil,

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* To whom correspondence should be addressed

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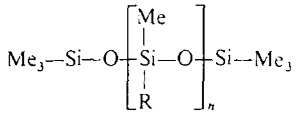

$$\mathrm{Me_3{-}Si{-}O}\left[\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{{-}Si{-}O{-}}\\ |\\ \mathrm{R}\end{array}\right]_n\mathrm{Si{-}Me_3}$$

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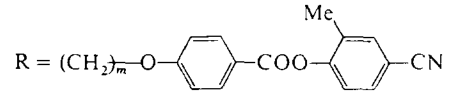
where $n \simeq 50$ and



with $m = 8$

and the pressure was measured using a standard gauge read in pounds per square inch*. The polymer film was aligned homeotropically by cooling from the melt in the presence of a saturating alternating current (a.c.) directing voltage of 300 V (r.m.s.) at 1 kHz. In the present work we show loss data in terms of $G/\omega = \varepsilon'' C_a$, where G is the measured equivalent parallel conductivity of the sample, ε'' is the dielectric loss factor and C_a is the inter-electrode geometric capacitance[17].

RESULTS

It is well-known that surfaces may induce alignment in LC materials. In the present work it was found that the dielectric loss curves obtained at a fixed temperature in the LC state varied when the same sample was cooled repeatedly from the melt in the absence of an external electric field. These variations took the form of an increase or decrease in the height of the δ-process accompanied by a complementary decrease or increase, respectively, of the higher frequency shoulder (α-process). Such behaviour is consistent with a variable degree of surface-induced homeotropic alignment occurring when the LC phase is formed on cooling from the melt. As one example of our results, *Figure 1* shows loss data for a nominally unaligned material at 50°C for pressures in the range 1600–18 500 p.s.i. The curves resemble those obtained previously for this polymer in its unaligned state except that the high frequency shoulder is smaller, relative to the δ-process, than was observed earlier, indicating that the sample is slightly aligned homeotropically. Further loss spectra were obtained at 55, 60 and 65°C for different pressures. These data may be analysed to yield:

1. the effect of pressure on the overall shape of the loss spectra at each temperature;
2. the effect of temperature and pressure on the overall relaxation strengths;
3. the variation of the frequency of maximum loss, f_m, with temperature and pressure.

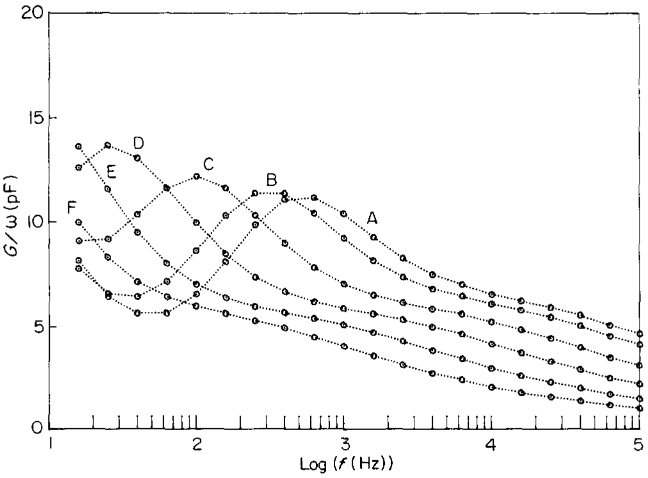


Figure 1 $\varepsilon'' C_a$ against log(f(Hz)) for a nominally unaligned sample at 50°C for different applied pressures. Curves A–F correspond to 1600, 3600, 7500, 11 000, 15 000 and 185 000 psi, respectively

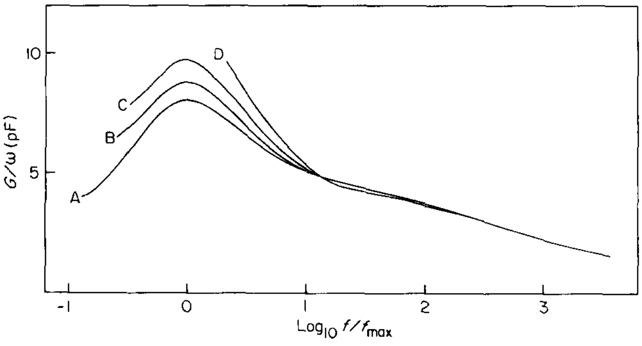


Figure 2 $\varepsilon'' C_a$ against log(f/f_m) as calculated from the data of *Figure 1*. Curves A–D correspond to 1600, 7500, 11 000 and 18 500 psi, respectively. The data for the three lowest pressures superpose at higher frequencies

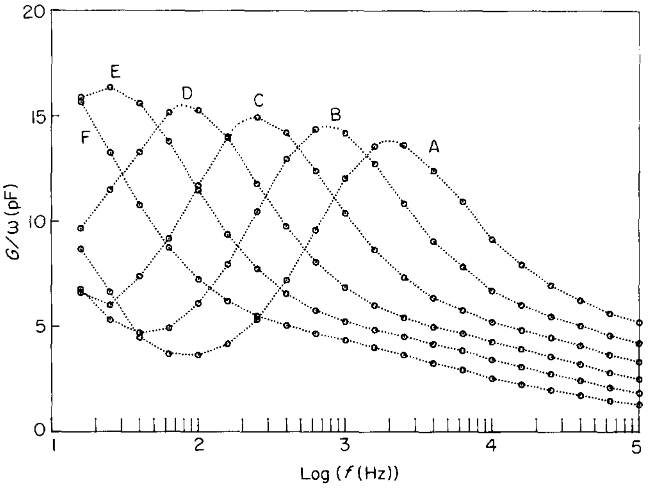


Figure 3 $\varepsilon'' C_a$ against log(f(Hz)) for a partially aligned sample at 55°C for different applied pressures. Curves A–F correspond to 0, 3.7×10^3, 7.4×10^3, 1.1×10^4, 1.47×10^4 and 1.85×10^4 psi, respectively

In order to investigate (1) for this sample we constructed a set of loss curves at 50°C in which each curve is referenced to its frequency of maximum loss, f_m. *Figure 2* shows the curves derived in this way from *Figure 1* and it is apparent that the height of the δ-process increases steadily with increasing pressure while the shoulder (α-process) is hardly changed. Such behaviour also shows that the δ- and α-processes have approximately the same dependence of f_m on applied pressure in this range. Similar behaviour was obtained using the data at 55, 60 and 65°C.

In a further study, a sample was cooled from the melt in the absence of a directing electric field and gave the loss spectra shown in *Figure 3* for the sample at 55°C and different applied pressures. Comparison with *Figure 1* shows that this sample is partially aligned homeotropically, as was discussed above (increase in δ-process, decrease in the high-frequency shoulder). The values of

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* 1 p.s.i. = 0.06895 bar; 1 bar = $1.0133 \times 10^5\ \mathrm{N\,m^{-2}}$

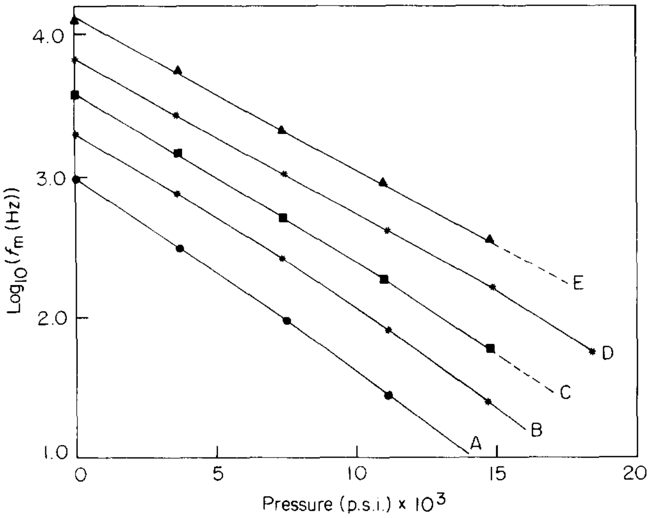

Figure 4 Log(f_m(Hz)) *versus* pressure (psi) for the partially aligned sample. A–E correspond to 50, 55, 60, 65 and 70°C, respectively

f_m for the δ-process are approximately the same for both samples at given temperature and pressure (T, P) conditions. The variation of $\log f_m$ with pressure for this sample is shown in *Figure 4*. The plots are curved, with $|(\partial \log f_m/\partial P)|_T = \chi_{T,P}$ say, increasing with increasing pressure at a fixed temperature. We obtained $\chi_{T,P\to 0}$ values from *Figure 4*: $\chi_{T,P\to 0}$ is 1.87, 1.74, 1.71, 1.61 and 1.58 kbar^{-1} for temperatures of 50, 55, 60, 65 and 70°C, respectively. For comparison, Heinrich and Stoll[31] obtained a linear plot for $\log f_m$ *versus* P at 120°C for the δ-process in P/H/6CN with $\chi_{T,P} = 1.30\,\mathrm{kbar}^{-1}$.

The same sample as that used to obtain the data for *Figures 3* and *4* was aligned fully homeotropically by cooling from the melt in the presence of a saturating a.c. electric field applied at 1 kHz[19,20]. The dielectric loss spectra were obtained at 5°C intervals in the range 50–75°C and at different applied pressures. In *Figures 5* and *6* we show a portion of our data and note that the loss-peak is dominated by the δ-process, as we have discussed earlier[19,20]. The peak moves rapidly to lower frequencies on raising the pressure at each sample temperature, and *Figure 7* shows these variations (c.f. *Figure 4*). As before, the plots are curved downwards at the higher pressures. The derived values for $\chi_{T,P\to 0}$ are 1.88, 1.80, 1.71, 1.55, 1.45 and 1.39 kbar^{-1} at 50, 55, 60, 65, 70 and 75°C, respectively. These values are not strictly comparable with those obtained from *Figure 4* due to the presence of the α-process in the latter loss curves. The shape of the loss curves for the homeotropically aligned sample may be examined conveniently by forming the 'master curves' of $\varepsilon''/\varepsilon''_m$ against log (f/f_m) at each temperature. As one example, *Figure 8* shows our results at 70°C. The data form a well-defined master curve having a half-width of 1.46 which is to be compared with 1.14 for a single relaxation time process. At high frequencies there is a long 'tail' which may be due to the presence of a high-frequency process.

A feature of the data of *Figures 5* and *6* is that the peak height, h, for the δ-process increases markedly with increasing pressure. The plots of h *versus* P were approximately linear, giving $(1/h_0)\cdot(\partial h/\partial P)_T \simeq 1.20\,\mathrm{kbar}^{-1}$ (or 20% kbar^{-1}). This large effect is not due to a change in the shape of the δ-peak (*Figure 8*) as pressure is varied. If the sample dilated uniformly in response to the applied

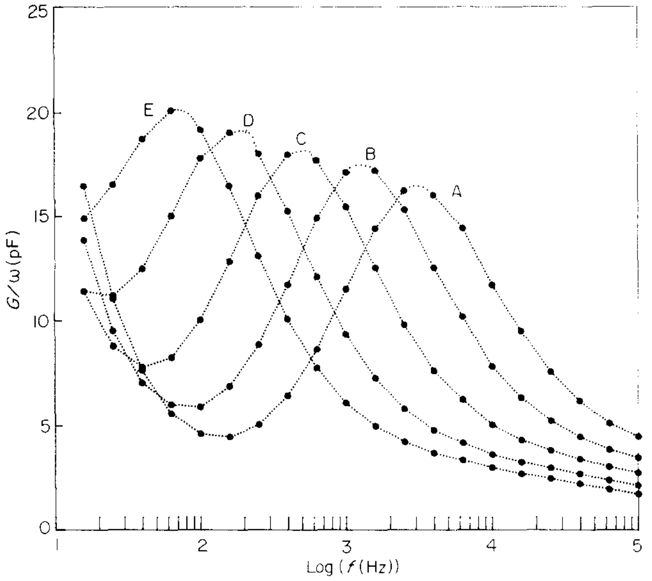

Figure 5 $\varepsilon''C_a$ against log(f(Hz)) for homeotropically aligned sample at 60°C and different applied pressures. Curves A–E correspond to 0, 3.7×10^3, 7.4×10^3, 1.1×10^4 and 1.41×10^4 psi, respectively

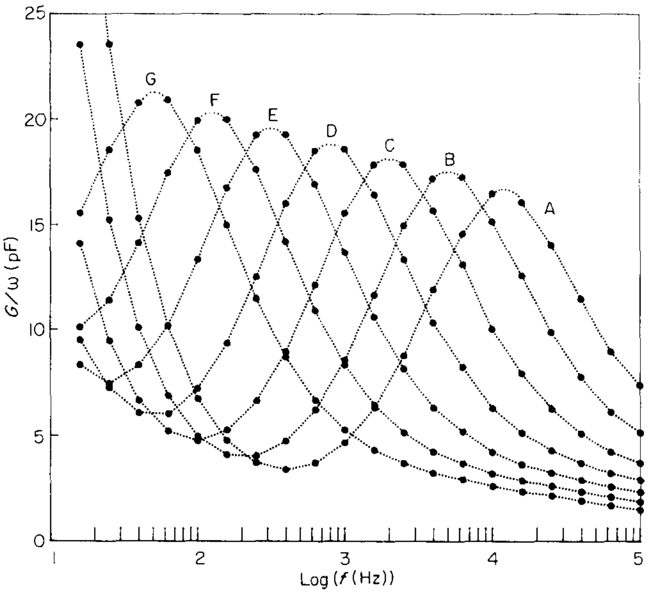

Figure 6 $\varepsilon''C_a$ against log(f(Hz)) for homeotropically aligned sample at 70°C and different applied pressures. Curves A–G correspond to 0, 3.6×10^3, 7.4×10^3, 1.1×10^4, 1.48×10^4, 1.85×10^4 and 2.2×10^4 psi, respectively

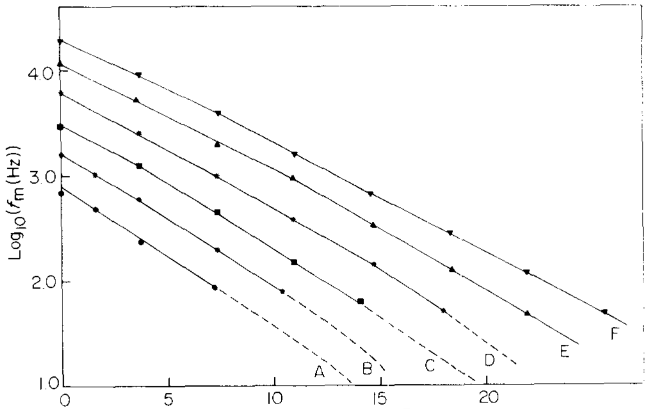

Figure 7 Log(f_m(Hz)) against pressure (psi) for the homeotropically aligned sample. A–F correspond to 50, 55, 60, 65, 70 and 75°C, respectively

hydrostatic pressure, as it should do, then for a typical bulk compressibility of 6×10^{-5} bar^{-1} we would expect a 2% *decrease* per kbar in the measured loss factor due to changes in sample dimensions. If the sample adhered to the electrodes so that all the volume change appeared as a change in sample thickness (an unlikely occurrence) then we would expect a 6% *increase* per kb in the measured loss factor, which is far less than the 20% increase we observed.

Figure 9 shows plots of log f_m(Hz) against reciprocal temperature for the homeotropically aligned sample. The plots exhibit an increase in initial slope, and an increased curvature, as the pressure is increased, which is consistent with WLF behaviour[1,20] in which the apparent 'Vogel' temperature T_0 increases with increasing pressure. Similarly, we are able to construct (T, P) plots at constant relaxation frequency, f_m, and these are shown in *Figure 10*.

DISCUSSION

We have shown earlier[22] that the complex dielectric permittivity $\varepsilon(\omega)$ for a partially aligned LC polymer is given, approximately, by the relation

$$\varepsilon(\omega) = (1 + 2S_d)\cdot\varepsilon_{\parallel}(\omega)/3 + 2(1 - S_d)\cdot\varepsilon_{\perp}(\omega)/3 \quad (1)$$

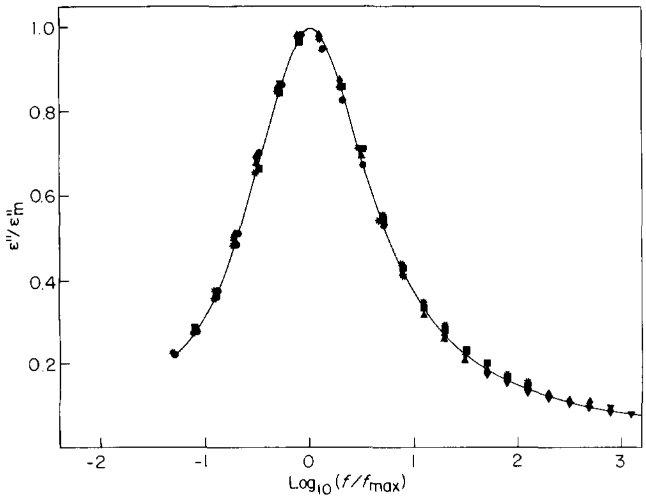

Figure 8 Master curve for the data of *Figure 6*. Symbols ●, ★, ■, *, ▲, ◆ and ▼ correspond to 0, 3.6×10^3, 7.4×10^3, 1.1×10^4, 1.48×10^4, 1.85×10^4 and 2.20×10^4 psi, respectively

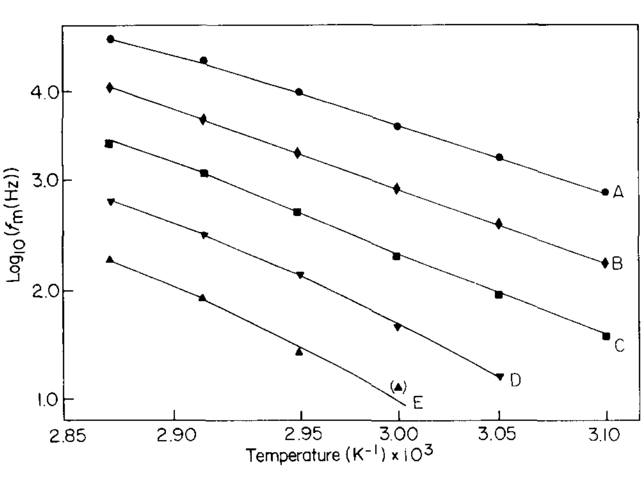

Figure 9 Log(f_m(Hz)) against the reciprocal of temperature (K^{-1}) for the homeotropically aligned sample. A–E correspond to 0, 5.0×10^3, 1.0×10^4, 1.5×10^4 and 2.0×10^4 psi applied pressure, respectively

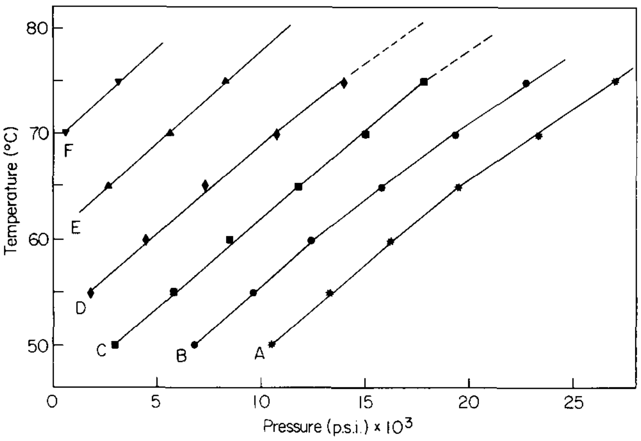

Figure 10 Plots of temperature (°C) against pressure (psi) for different constant relaxation frequencies for the homeotropically aligned sample. A–F correspond to log(f_m(Hz)) equal to 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0, respectively

where $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$ are related to the longitudinal (μ_l) and transverse (μ_t) components of the dipole moment μ of the mesogenic group, and S the local order parameter of the LC phase, according to the following equations

$$\varepsilon_{\parallel}(\omega) = \varepsilon_{\infty\parallel} + \frac{G}{3kT}\cdot[(1 + 2S)\mu_l^2\cdot F^l_{\parallel}(\omega) + (1 - S)\mu_t^2\cdot F^t_{\parallel}(\omega)] \quad (2a)$$

$$\varepsilon_{\perp}(\omega) = \varepsilon_{\infty\perp} + \frac{G}{3kT}\cdot[(1 - S)\mu_l^2\cdot F^l_{\perp}(\omega) + (1 + S/2)\mu_t^2\cdot F^t_{\perp}(\omega)] \quad (2b)$$

and where the $F^i_j(\omega)$ are given by Fourier transforms of time-correlation functions for the angular motions of μ_l and μ_t. Using this theory it was considered[19,22] that the low frequency peak (δ-peak) in this polymer in its unaligned state was due to the $F^l_{\parallel}(\omega)$ process (00-relaxation mode[24,32]) and that the high frequency shoulder (or α-process) arose from the superposition of the remaining processes (01, 10 and 11 relaxation modes). For the aligned specimen, the spectrum is dominated by the δ-process (00-mode) and the high frequency tail is assigned to the 01 relaxation mode[19,22]. In the present work we observed a marked increase, with pressure, of the height of the δ-process in both unaligned and H-aligned samples. The increase for the δ-process in the H-aligned sample was ~20% per kbar, which could not be explained by a geometrical change in the sample. In an earlier study[4] it was found for amorphous poly(methyl acrylate) that the α_a-relaxation (segmented chain motions associated with the apparent glass transition) also showed an increase in peak height of ~20% kbar^{-1}. In that case it was considered that the mean-square dipole moment $\langle\mu^2\rangle$ for the polymer chain increased with the increasing pressure. This was possible since $\langle\mu^2\rangle$ is dependent on the conformation of the chain via the Kirkwood g-correlation terms[1,4,33] for the angular correlations between chain dipoles. Thus we could interpret the apparent large increase in the relaxation strength for the present polymer as being due to an increase in the effective g-factor with increasing pressure. An alternative source of an increase in relaxation strength for the δ-process for the LC polymer would be if S increased with increasing pressure (see equation (2a)). While a contribution from this source is possible, it seems unlikely that this is the dominant factor, for the following reasons:

1. the increase of 20% in relaxation strength for the δ-process per kbar increase in pressure would give an increase of S from 0.5 (assumed, say) at $P = 0$–0.7 at 1 kbar. Such a large increase in S seems unrealistic;
2. the relaxation strength of the δ-process increases approximately linearly with applied pressure (e.g. *Figure 6*) with no evidence of saturation at the highest pressures. If the ratio of relaxation strengths at a pressure P_1, say, to that at $P = 0$ reaches 1.5 then for $S(P = 0) \simeq 0.5$ (assumed) then $S(P_1) = 1.0$ which again seems unrealistic for an LC polymer;
3. for the unaligned sample $S_d = 0$ so

$$\varepsilon(\omega) = [\varepsilon_{\parallel}(\omega) + 2\varepsilon_{\perp}(\omega)]/3 \tag{3}$$

from equation (2) it follows that the combined contribution to $\varepsilon(\omega)$ from the 01 and 11 processes is proportional to $\mu_t^2 \cdot [F^t_{\parallel}(\omega) + F^t_{\perp}(\omega)]$ i.e. it is independent of S. Thus any variation in strength of the overall α-process arises from the 10 process, which is proportional to $(1 - S)\mu_l^2 \cdot F^l_{\perp}(\omega)$. Thus as pressure is increased, if S increases then this contribution to the strength of the overall α-process would show a decrease. There is no evidence for such a decrease in *Figure 2*. Therefore, it seems likely that the variation in the relaxation strength with pressure for the δ-process is due to a change in $\langle \mu^2 \rangle$ for the LC polymer chain due to a change of conformation with pressure which leads to an enhancement of the overall dipole moment.

The data of *Figures 1* and *2* suggest that the frequency–pressure variations of δ- and α-processes are approximately the same. In our earlier study[20] for this polymer it was shown that the temperature dependence of the frequency locations of the resolved δ- and α-processes were approximately the same for measurements made in the frequency range 10–10^5 Hz. Therefore, it is not surprising to find that the pressure- dependencies of the two processes are similar. At lower temperatures, we found that the α- and δ-processes tend to coalesce[20] in the region where the plots of $\log f_m$ *versus* T^{-1} are strongly curved in anticipation of the apparent glass transition (WLF behaviour[1]). In *Figure 9* we see, for the δ-process in the H-aligned specimen, that the apparent activation energy increases with increasing pressure and that the curvature in the plots becomes more pronounced at the higher pressures, being indicative of an increase in T_g as the pressure is raised. In an earlier study of the effect of T and P on the α_a-relaxation in amorphous polymers we considered the significance of the apparent activation energies $Q_V(T, V)$ and $Q_P(T, P)$ derived from constant volume or constant pressure experiments. Here

$$\begin{aligned} Q_V(T, V) &= -R(\partial \ln f_m/\partial 1/T)_V, \\ Q_P(T, P) &= -R(\partial \ln f_m/\partial 1/T)_P \end{aligned} \tag{4}$$

where

$$Q_V(T, V) = Q_P(T, P) + (\partial P/\partial T)_V \cdot RT^2 \cdot (\partial \ln f_m/\partial P)_T \tag{5}$$

Thus data for the thermal pressure coefficient, $(\partial P/\partial T)_V$, are required to calculate $Q_V(T, V)$ knowing $Q_P(T, P)$ and $(\partial \ln f_m/\partial P)_T$. In the case of poly(methyl acrylate), both $Q_V(T, V)$ and $Q_P(T, P)$ were determined for different (T, P) conditions. It was found that $Q_V(T, V)/Q_P(T, P) \simeq 0.7$–0.8 for the α_a-relaxation in this polymer. We do not have thermal pressure coefficient data for the present LC polymer. If we assume that the $(\partial P/\partial T)_V = 1.5$ bar K^{-1} (as for poly(methyl acrylate)) then we would calculate $Q_V(T, V)/Q_P(T, P)$ values which are very similar to those for poly(methyl acrylate). The question arises—what is the molecular significance of $Q_V(T, V)$ compared with $Q_P(T, P)$ for the δ-relaxation in the LC polymer? The simplest free volume theories for relaxation predict that $Q_V(T, V)$ is zero or negative[34,35] which is inconsistent with experimental data for amorphous and crystalline polymers[2–9] and for LC polymers (see ref. 31 and the present work). It is evident that any theory for dielectric relaxation must involve the time-dependence of the motions of dipoles (as expressed by a time-dependent rotational diffusion equation, say, or as time-dependent fluctuations of local thermodynamic quantities, including local volume) and that such features are absent when a relaxation time is related to a time-averaged free volume, as is the case for the simple free volume theories[2,4,34,35]. Motion in LC phases is usually modelled using theories due to Martin *et al.*[36] and Nordio and coworkers[37,38]. For the δ-relaxation it was shown that the relaxation time $\tau = (2\pi f_m)^{-1}$ was given by

$$\tau = J\tau_0 \tag{6}$$

where τ_0 is the effective relaxation time for rotation in the isotropic state, extrapolated to the required temperature in the LC state and J is a retardation factor given by

$$J = \frac{kT}{q}\,[\exp(q/kT) - 1] \tag{7}$$

where q is the height of the nematic potential barrier. This is the result for small-step rotational diffusion in the effective nematic potential. It is usual to ignore changes in q with volume when constant pressure activation energies are determined, so for $q \gg kT$ equations (6) and (7) give

$$Q_P(T, P) \simeq E_\eta(T, P) + q \tag{8}$$

where $E_\eta(T, P)$ is the apparent activation energy for viscous flow at constant pressure (derived from $(\partial \ln f_{mo}/\partial 1/T)_p$ for the isotropic motion), $\tau_0 = (2\pi f_{mo})^{-1}$. Thus the slopes of the lines in *Figure 9* yield values of $Q_p(T, P)$ which may be interpreted in terms of equation (8), i.e. in terms of E_η and q, but it is not possible at this stage to separate the terms experimentally in order to further quantify such an analysis. Similarly, the variations in $\log f_m$ with pressure for fixed temperatures (*Figure 7*), when considered in terms of equation (6), would give information on the effect of pressure on both τ_0 (increase in apparent rotational diffusion relaxation time τ_0 with pressure due to increase in local viscosity), and on q (increase in barrier height when system is compressed). Again it is not possible to quantify this analysis due to insufficient information being obtainable from the dielectric experiments.

Finally, we note that the cross-plot of $\log f_m$ *versus* $1/T$ (*Figure 9*) gives the plots shown in *Figure 10* of the (T, P) conditions for constant relaxation frequency. Such plots were constructed previously for the α_a-relaxation in amorphous solid polymers[4,39], and express the variation of the apparent dynamic T_g with pressure at constant relaxation frequency. Similar plots were made by Heinrich and Stoll[30] for unaligned LC polymers at a relaxation frequency of 10^{-3} Hz (for comparison with long time (e.g. dilatometric) T_g behaviour). Our data in *Figure 10* give parallel lines at low pressures, all having slopes $(\partial T/\partial P)_{f_m}$ of 26.0 ± 0.5 K kbar^{-1} ($1.78 \pm 0.03 \times 10^{-3}$ K p.s.i.$^{-1}$), which are to be compared with 20.0 K kbar^{-1} for P/H/6/CN and 23.0 K kbar^{-1} for P/H/2/CN by Heinrich and Stoll[30]. The constancy of $(\partial T/\partial P)_{f_m}$ for our data in *Figure 10* contrasts sharply with our observations for the α_a-relaxation in poly(methyl acrylate)[4] and poly(propylene oxide)[39] where we found $(\partial T/\partial P)_{f_m}$ increased markedly with increasing values for f_m. For example, for poly(methyl acrylate)[4] the values increased from 14.7 K kbar^{-1} at $\log f_m = 2.0$ to 21.7 K kbar^{-1} at $\log f_m = 5.0$. This difference in behaviour arises from the fact that the plots of $\log f_m$ *versus* P for the LC polymers show only a small variation in slope as temperature is varied when compared with the variation observed for poly(methyl acrylate). This serves to emphasize that the mechanism for the α_a-relaxation in amorphous polymers[1-6,39] and the δ-relaxation in LC polymers are fundamentally different. The difference is evident from a comparison of the shapes of the α_a and δ processes. The α_a relaxation gives a characteristically broad asymmetric loss peak, which may be fitted approximately using the KWW (or 'stretched-exponential') relaxation function[40,41]. For poly(propylene oxide) and poly(methyl acrylate), the half widths of the loss curves are approximately 2.6 units of $\log_{10}$ frequency and the loss curves are skewed to high frequencies. For the present LC polymer the δ-relaxation has a half width of only 1.46 units (but is also apparently skewed due to the presence of the 01 relaxation mode[19]). For amorphous polymers it is considered that the dipole-group motions occur by strongly co-operative motions within and between chains by a process similar to that observed in low-molar-mass glass-forming molecular liquids (i.e. chain connectivity is not a prerequisite for KWW behaviour[42]). The fact that the δ-process in the LC polymer lies close to a single relaxation time process indicates a different mechanism for motion from that for the α_a-process in amorphous polymers. We note also that the corresponding δ-process in low molar mass thermotropic liquid crystals has a loss-factor-contour similar to that for a single relaxation time process, indicating a similar mechanism for motion[43,44]. However, the attachment of the mesogenic group to a polymer chain means that its motions in the LC potential are strongly coupled to the main chain motions so that on decreasing the temperature towards T_g (or increasing the pressure) the decrease in relaxation rate of the chain backbone also decreases the relaxation rate of the mesogenic group. It is perhaps surprising that we have not observed a marked increase in the half width of the dielectric loss curve for the δ-process in LC polymers as T_g is approached[20] or as pressure is increased (as in the present study).

CONCLUSIONS

The dielectric relaxation behaviour of a LC siloxane polymer in its unaligned and aligned states has been studied over a range of temperatures and pressures. The variations of relaxation strength, relaxation frequency and shape of relaxation curves with changes of sample temperature and pressure have been determined and have been discussed in terms of anisotropic molecular relaxation of the dipolar mesogenic groups of the polymer. The essential similarities and differences in the relaxation behaviour of amorphous solid polymers and LC side chain polymers have been discussed.

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