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## Liquid Crystals

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## Molecular dynamics of a smectic liquid-crystalline side-chain polymer in its unaligned and aligned states as studied by dielectric relaxation spectroscopy

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Dielectric relaxation data are presented for unaligned, partially aligned and aligned thin films of a smectic liquid-crystalline side-chain polymer in the ranges 12 to  $10^5$  Hz and 299 to 343 K. The unaligned material exhibits a complicated dielectric absorption which has been resolved into two broad components ( $\delta$  and  $\alpha$  processes). The dielectric absorption changes remarkably on alignment of the material such that the  $\delta$  process is enhanced by a factor of three and the  $\alpha$  process is considerably diminished. A consideration is given of the molecular theory for dielectric relaxation in these materials and the variation in dielectric properties is shown to depend on the dipole components  $\mu_{\parallel}$  and  $\mu_{\perp}$ , the order parameter  $S$  for the mesogenic head groups and the order parameter  $S_d$  for the director alignment.

### 1. Introduction

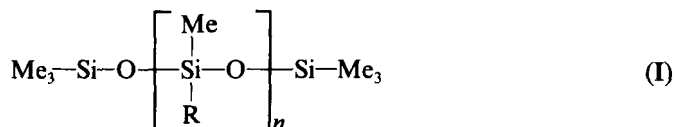
New comb-like polymers having mesogenic groups in the side chain which form liquid-crystalline materials were first reported by Ringsdorf, Finkelmann and co-workers [1, 2] and by Shibaev and Platé [3] in 1978. Since that time several hundred such polymers have been synthesized and investigated for their liquid-crystalline properties [4, 5]. The interest in these materials stems from the fact that they possess the remarkable electro-active, magneto-active and optical properties now familiar for thermotropic liquid crystals and have the good mechanical and film-forming properties of polymers. While their speed of response to applied electric fields is slow in comparison with liquid crystals of low molar mass, the new liquid-crystalline side-chain polymers show considerable promise as thin film media for reversible optical information storage [4-6]. Stable homeotropically-aligned films can be made by the combination of thermal and electrical treatment and information may be stored/retrieved at high density by addressing/reading with a laser beam.

Little information is available on the arrangement of molecules in these liquid-crystalline polymers, and little is known of the dynamics of the side chains in the unaligned and aligned states. In a recent publication [7] we reported the first study of the dielectric relaxation behaviour of a nematogenic siloxane polymer and showed that multiple relaxations ( $\delta, \alpha$  processes) occurred in the nematic state. These processes coalesced on raising the temperature to give a single, broad relaxation in the isotropic state.

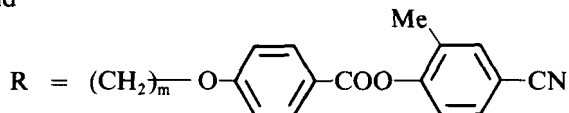
We subsequently showed [8] that multiple relaxations ( $\delta, \alpha$ ) were also observed for a smectic siloxane polymer and that remarkable changes in dielectric properties were observed when the material was homeotropically-aligned by a combined thermal/electrical treatment. We further showed [10] that the cooling rate was of great

importance when forming aligned thin films on cooling from the isotropic state in the presence of an applied a.c. voltage. These studies showed that the homeotropically-aligned smectic polymer retained its alignment in the liquid-crystalline state even for temperatures above the apparent glass transition  $T_g$ . This meant that the materials had dielectrically-variable properties in the liquid-crystalline state; i.e. the dielectric properties of a given sample can be systematically varied by changing the degree of alignment via different thermal/electrical histories. As such they represent a new class of dielectric materials of a kind quite different from those already known such as piezo-electric or electret materials. Note that low molar mass smectic liquid crystals also retain alignment when an aligning electric field is withdrawn but low molar mass nematics do not due to their low viscosity.

In our earlier communication [8] we gave preliminary dielectric data for the smectogenic polymer (I) in its aligned and partially aligned states



where  $n \approx 50$  and



with  $m = 8$ .

In the present paper we describe the dielectric relaxation behaviour for (I) in its unaligned and aligned states over a wide range of temperature and we consider the nature of the observed multiple relaxations and the variation of their frequency location, magnitude and lineshape with the extent of sample alignment.

## 2. Experimental

The material was the same as that described earlier [8] and was provided by Professor G. W. Gray and Dr. D. Lacey of Hull University. The D.S.C. scan ( $10 \text{ K min}^{-1}$ ) showed a smectic-isotropic transition near 363 K (heating) and 358 K (cooling): the transition extended over about 7 K as judged by the widths of the exo and endotherms. The apparent glass transition temperature, as estimated from the D.S.C. scan was approximately 274 K. The dielectric measurements were made in the range 10 to  $10^5 \text{ Hz}$  using a fully automated dielectric measuring assembly which comprised a GenRad 1689 Digibridge, a Hewlett-Packard 87B computer and associated peripherals, and a thermostatted water bath. The polymer sample was contained in a three-terminal dielectrics cell described previously [9] and was in the form of a disc about 1.1 cm diameter and  $120 \mu\text{m}$  in thickness. The temperature stability of the sample was estimated to be of the order of 0.02 K. The equivalent parallel capacitance  $C_p$  and conductance  $G_p$  were measured at each frequency and these are related to the dielectric permittivity  $\epsilon'$  and loss factor  $\epsilon''$  by

$$C_p = \epsilon' C_a; \quad G_p/\omega = \epsilon'' C_a, \quad (1 a, b)$$

where  $C_a$  is the geometric capacitance of the space occupied by the sample and  $\omega$  is the angular frequency  $2\pi\nu$ .

The sample was aligned *in situ* in the dielectric cell by the following procedure. The cell was heated to 370 K in order to melt the polymer into its isotropic state, and was

maintained at this temperature for 15 min before an a.c. electric voltage  $V$  at 3 kHz was applied using a signal generator and a power transformer. With the voltage maintained the cell was cooled slowly to 343 K at a rate of about  $0.5 \text{ K min}^{-1}$  at which temperature the polymer was well within its smectic range. We note that cooling more quickly reduces the degree of alignment achieved [10]. The source of  $V$  was removed, the cell was short-circuited to remove any extraneous polarization and was connected to the Digibridge for the dielectric measurements to be made at any desired temperature. By varying  $V$  different degrees of homeotropic alignment were achieved [8, 10] as we shall now describe.

### 3. Results

#### 3.1. Unaligned material

Figure 1 shows plots of  $G/\omega$  against  $\log_{10} \nu$  for polymer (I) obtained at given temperatures in the range 305 to 344 K. At a fixed temperature the absorption curve shows a distinct low frequency peak and a higher frequency shoulder indicative of at least two broad component processes. We label these as the  $\delta$  and  $\alpha$  processes in increasing order of frequency. Since the mesogenic head group contains most of the mean square dipole moment per repeat unit of the polymer chain ( $\langle \mu_r^2 \rangle$ ) the relaxation behaviour shown in figure 1 gives direct information on the angular motions of the different components of  $\langle \mu_r^2 \rangle$  with respect to the local director in the smectic liquid-crystalline state.

#### 3.2. Aligned materials

Specimens having different degrees of homeotropic alignment were prepared by cooling with 50 V (rms) and 300 V (rms) applied. Our earlier studies showed that the extent of alignment was essentially complete for  $V > 150 \text{ V}$  (rms) for this material

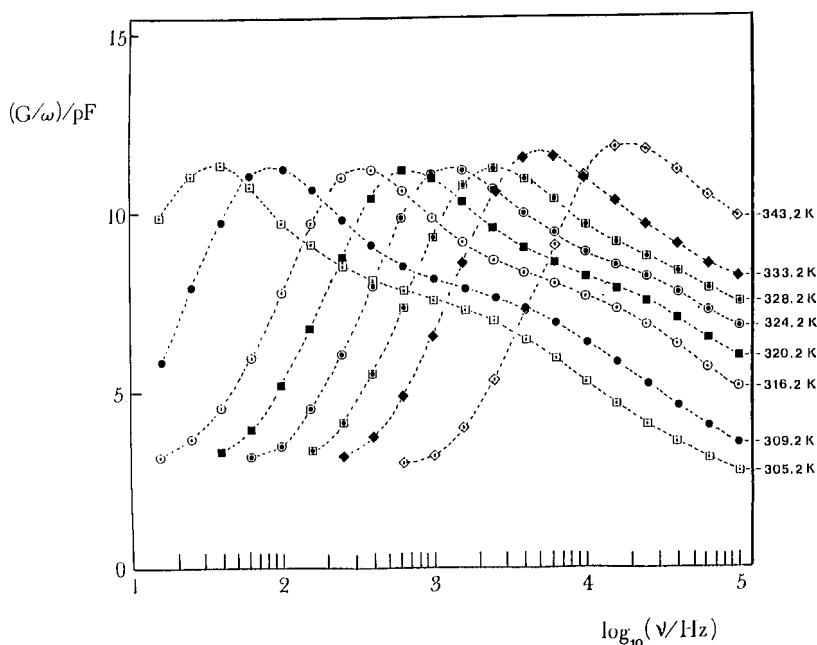


Figure 1.  $(G/\omega)$  shown as a function of  $\log_{10}$  (frequency) for different temperatures in the unaligned smectic phase. The dotted lines are intended as guides to the eye.

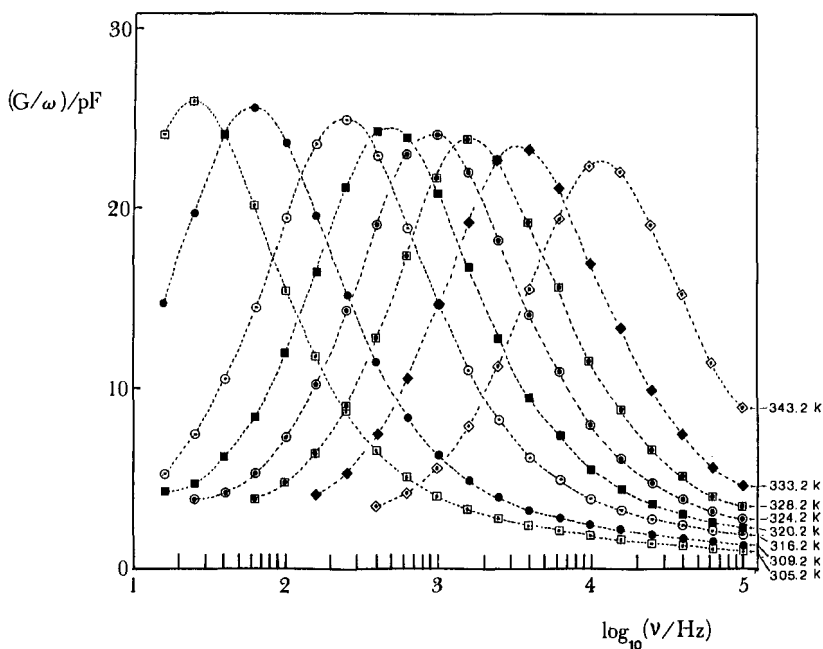


Figure 2.  $(G/\omega)$  shown as a function of  $\log_{10}$  (frequency) for different temperatures in the fully-aligned smectic phase produced by cooling the sample in the presence of an a.c. aligning field of 300 V (r.m.s.) at 3 kHz. The dotted lines are intended as guides to the eye.

and that the degree of homeotropic alignment obtained for a given voltage was independent of the frequency of the aligning voltage in the range 1 to 10 kHz [8, 10]. For brevity we show only a portion of our extensive data. Figure 2 shows plots of  $G/\omega$  against  $\log_{10} \nu$  at different temperatures for the material prepared by cooling with the directing voltage of 300 V (rms) maintained. An apparently single broad asymmetric loss peak is seen at each temperature. Note that these data were obtained for the same material in the dielectric cell as that in figure 1 only now the material has been homeotropically aligned. In confirmation of our preliminary study [8] we find that the dielectric properties of a partially or fully aligned sample at any temperature below the liquid crystal–isotropic transition temperature are quantitatively independent of time over periods of months. This shows that the aligned material, once formed, does not disalign appreciably by physical ageing or thermal ageing in the liquid-crystalline state irrespective of whether the material is above or below its apparent glass-transition temperature. This is an important result for the application of the new liquid-crystalline side-chain polymers as information storage media. It is also evident that dielectric relaxation spectroscopy provides a quantitative means of following alignment and disalignment processes in these materials.

The differences between the dielectric properties of unaligned (figure 1) and aligned (figure 2) samples are quite remarkable and these may be summarized as follows (compare the two sets of data at a common temperature, say 309.2 K):

- (i) The  $\delta$  process is increased in magnitude on going from unaligned (U) to aligned (A) material, but the frequency of maximum loss for this process appears to decrease slightly.
- (ii) The  $\alpha$  process diminishes considerably on going from U to A material.

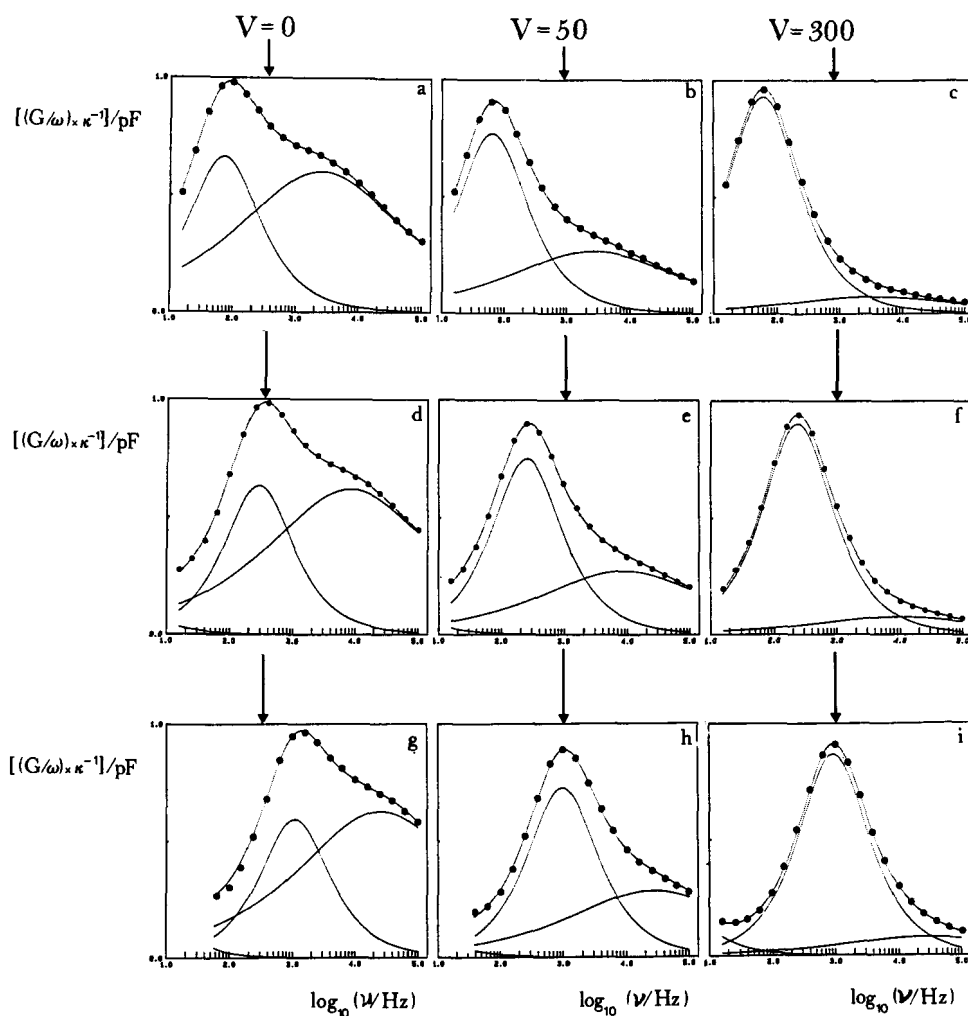


Figure 3. Representative examples of the fits to the experimental loss data at three temperatures in the smectic range for different degrees of alignment. (a), (d) and (g) unaligned sample ( $V = 0$ ), (b), (e) and (h) partially aligned sample ( $V = 50$  (r.m.s.)), (c), (f) and (i) fully aligned sample ( $V = 300$  (rms)), (a), (b) and (c)  $T = 311.2$  K, (d), (e) and (f)  $T = 316.2$  K, (g), (h) and (i)  $T = 324.2$  K. The curve parameters used to fit the experimental data are listed in the table.  $\kappa$  is a scaling factor which presents all loss curves on a comparable scale.

The variation in behaviour is conveniently seen in figure 3 where we show a portion of our results for the U and A materials together with data for the partially-aligned (PA) material prepared using  $V = 50$  V (rms). As  $V$  is increased the  $\delta$  process increases in magnitude relative to that of the  $\alpha$  process. Thus the dielectric properties of this (and other) liquid-crystalline side-chain polymer(s) may be varied in a systematic and predictable manner by prescribed thermal/electrical treatments. We do not show here, for the sake of brevity, the plots of sample capacitance against  $\log \nu$ , but note that these show the expected variations (as

predicted by the Krönig–Kramers relations) as the alignment is varied. The fact that these materials are dielectrically-variable suggests that they could be used as the electrical analogues of magnetic tape, capable of being addressed, erased and updated.

Figures 1 and 2 indicate strongly that the overall loss curve is made up of two broad components ( $\delta$  and  $\alpha$  processes). In accordance with our earlier interpretation of the dielectric properties of an unaligned nematic siloxane polymer [7] and unaligned and aligned smectic siloxane polymer (I) [8, 10] we consider that the  $\delta$  process is due to motions of the longitudinal component  $\mu_{\parallel}$  of the dipole moment of the mesogenic head group and that the  $\alpha$  process is due mainly to motions of the transverse component  $\mu_{\perp}$  of the dipole moment of the mesogenic head group. In earlier studies of acrylate and methacrylate liquid-crystalline side-chain polymers [12] Zentel and co-workers gave a similar assignment for the  $\delta$  process, but considered that the  $\alpha$  process was associated with the dynamic glass transition of the polymer. While there are many ways of deconvoluting the overall loss curves shown in figures 1 and 3 we have, in order to make progress, considered that two broad loss processes ( $\delta$  and  $\alpha$ ) are involved and that each is characterized by the Fuoss–Kirkwood empirical relaxation function [11] so that we may write

$$\frac{G}{\omega} = a_{\delta} \operatorname{sech} [\beta_{\delta} \ln (\omega/\omega_{m\delta})] + a_{\alpha} \operatorname{sech} [\beta_{\alpha} \ln (\omega/\omega_{m\alpha})], \quad (2)$$

where  $a_i$  is  $(G/\omega)_{\max}$  for process  $i$ , the angular frequency  $\omega_{mi} = 2\pi\nu_{mi}$  where  $\nu_{mi}$  is the frequency of maximum loss for process  $i$  and  $\beta_i$  is the linewidth parameter for process  $i$  ( $0 < \beta \leq 1$ ).

### 3.3. Relaxation parameters obtained using equation (2)

The loss data for unaligned, partially aligned and aligned samples were analysed using equation (2) by fitting, interactively, data displayed on the VDU of a computer using six adjustable parameters. The goodness of fit was judged visually and on hard-copy plots accompanied by print-outs of the residuals and minimum sum of squares. The table summarizes the values of  $a$ ,  $\log_{10} \nu_m$  and  $\beta$  determined for each process at each temperature studied. The quality of this representation was found to be extremely good in each case, as illustrated in figure 3 for the three materials at three temperatures. The  $\delta$  and  $\alpha$  processes combine to form the calculated overall loss curve which is in excellent agreement with the experimental data. While the loss curves determined experimentally do not span the entire relaxation region, it is possible to estimate the dielectric increment  $\Delta\epsilon$  for the entire relaxation using the Fuoss–Kirkwood fit parameters  $a$  and  $\beta$ . For a single function we have

$$\begin{aligned} \Delta\epsilon &= 2\epsilon_m''/\beta, \\ &= (2/C_a) (a/\beta), \end{aligned} \quad (3)$$

where  $\epsilon_m''$  is the maximum dielectric loss factor and  $a = (G/\omega)_{\max}$  for the single Fuoss–Kirkwood process. Thus the dielectric increment  $\Delta\epsilon_i$  for process  $i$  is proportional to  $a_i/\beta_i = \mathcal{A}_i$ , say, where  $i = \delta$  or  $\alpha$ . The table summarizes the values of  $\mathcal{A}_{\delta}$  and  $\mathcal{A}_{\alpha}$  and their sum for each loss curve.

## 4. Discussion

### 4.1. General considerations

Our data (figures 1–3 and table) show that the smectic polymer (I) has variable dielectric properties determined by the thermal/electrical treatment. Two broad dielectric relaxations appear to be present, as was found for the nematic polymer studied earlier [7] and for acrylate liquid-crystalline polymers having aromatic ester mesogenic head groups, studied by Zentel and co-workers [12]. In contrast, Kresse and co-workers [13, 14] observed only one broad dielectric absorption for acrylate and methacrylate liquid-crystalline polymers having an alkyloxycyanobiphenyl mesogenic head group. In the latter case it is apparent that the mesogenic head group, which contains the dominant contribution to the mean square dipole moment of a chain repeat unit, has only a small transverse component  $\mu_{\perp}$  of the dipole moment  $\mu = (\mu_{\parallel}^2 + \mu_{\perp}^2)^{1/2}$  whereas the transverse component of the aromatic ester group in the polymers studied here and previously [7, 8, 10, 12] is substantial. As a result it seems reasonable to associate the  $\delta$  process with motions of the longitudinal component  $\mu_{\parallel}$  and the  $\alpha$  process with motions of the transverse component  $\mu_{\perp}$  of the dipole moment  $\mu$  of the mesogenic head group. This is supported by the observations that the strength of the  $\delta$  process increases and that for the  $\alpha$  process decreases as the sample is progressively aligned homeotropically, since the strengths are related to  $\mu_{\parallel} \cdot \mathbf{E}$  and  $\mu_{\perp} \cdot \mathbf{E}$  respectively where  $\mathbf{E}$  is the measuring electric field and  $\mathbf{E}$  is parallel to the director axis for the aligned material. The values of  $a_{\delta}$  and  $a_{\alpha}$  are internally consistent

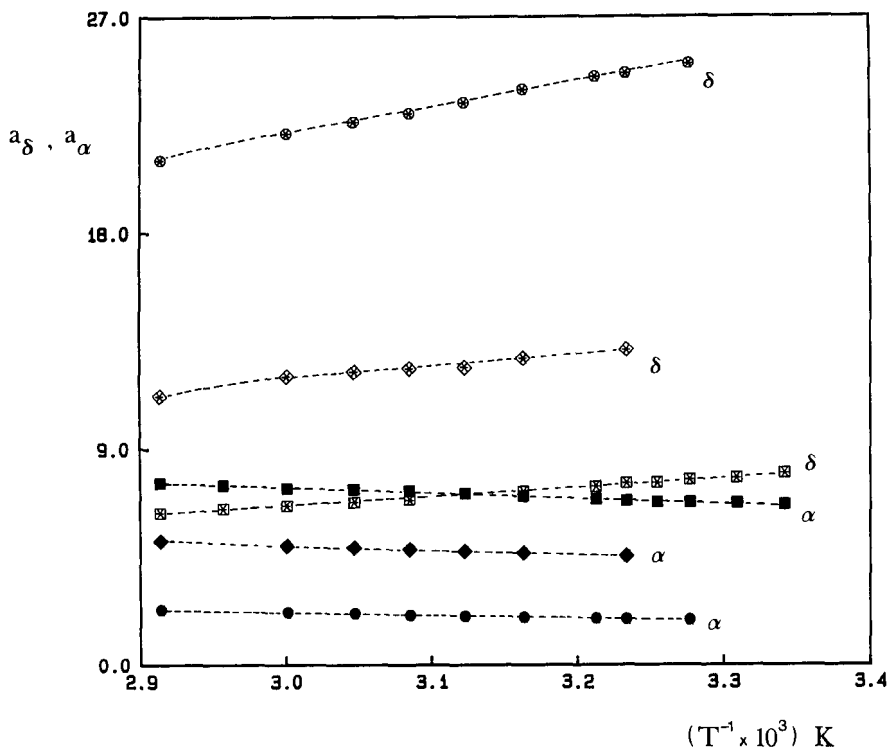


Figure 4. Amplitudes of maximum loss for the resolved components of the relaxation process as a function of  $T^{-1}$ . Open symbols are used to denote the  $\delta$  peak, while filled symbols are used to denote the  $\alpha$  peak; ( $\otimes$ ;  $\bullet$ ), fully aligned sample; ( $\diamond$ ;  $\blacklozenge$ ), partially aligned sample; ( $\square$ ;  $\blacksquare$ ), unaligned sample. Note that the dotted lines are intended as guides to the eye.



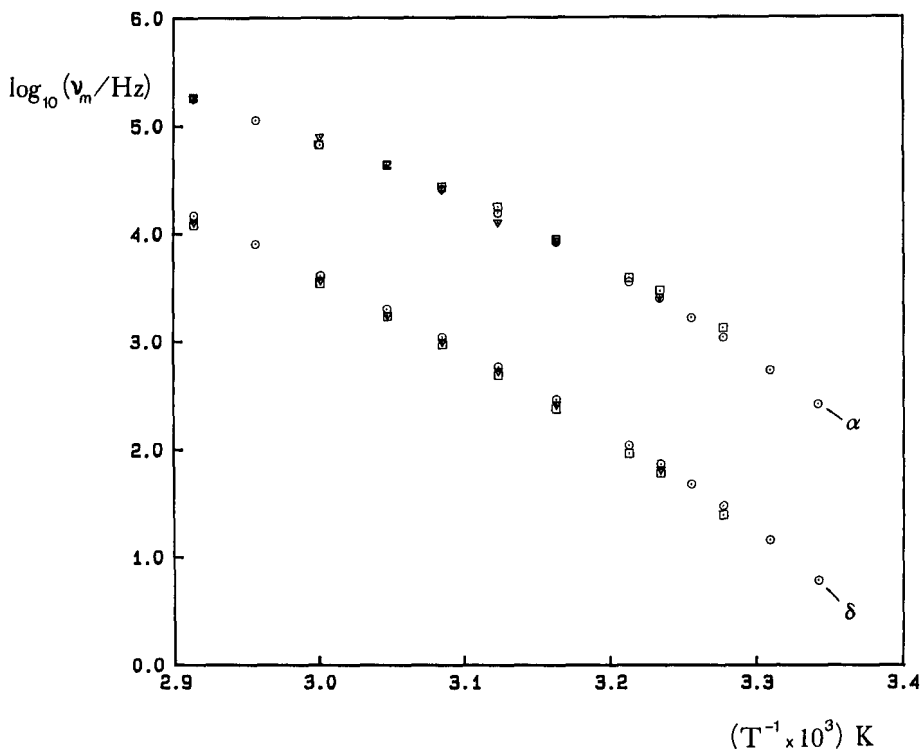


Figure 5.  $\log_{10}$  (frequency of maximum loss) for the two resolved components of the relaxation process as a function of  $T^{-1}$ ; (O), unaligned material; (▽), partially aligned material; (□), fully aligned material.

for a given sample (see table) and show small but systematic variations with temperature, as we see in figure 4. As temperature increases  $a_\delta$  falls and  $a_\alpha$  increases. Note that for the unaligned material  $a_\delta \approx a_\alpha$  at 320 K. The frequency locations of the resolved  $\delta$  and  $\alpha$  processes are shown as a function of reciprocal temperature in figure 5. A striking feature of these results is that the values of  $\log_{10} v_m$  for each process are essentially independent of the degree of alignment of the material which suggests that the *same*  $\delta$  and  $\alpha$  processes occur at a given temperature in samples having different degrees of alignment. The values of  $\beta_\delta$  and  $\beta_\alpha$  at a given temperature are effectively unchanged on changing the alignment of the material, as is clear from the table. The quantities which change markedly on sample variation are  $a_\delta$  and  $a_\alpha$  and since  $\beta_\delta$  and  $\beta_\alpha$  are invariants at a given temperature, the relaxation strengths  $\mathcal{A}_\delta$  and  $\mathcal{A}_\alpha$  follow the variation of  $a_\delta$  and  $a_\alpha$ . These factors indicate that the observed loss curve at a given temperature is a weighted sum of  $\delta$  and  $\alpha$  processes, whose frequency locations and shapes are the same for U, PA and A samples, and where the weighting factors are to be determined by certain averages taken over the distribution function for the director axes which involve  $\mu_{\parallel}$  and  $\mu_{\perp}$ .

A surprising feature of the analysis of the overall loss curves in terms of two Fuoss-Kirkwood components is that the component  $\delta$  process is smaller than might have been supposed by inspection of the overall curve, for example, in figure 3 (a), it appears that there is a dominant  $\delta$  process and a small higher frequency shoulder ( $\alpha$

## (a) Unaligned material.

$T/K$	$a_\delta$	$a_\alpha$	$\log_{10}(v_m/\text{Hz})$	$\log_{10}(v_m/\text{Hz})$	$\beta_\delta$	$\beta_\alpha$	$\mathcal{A}_\delta$	$\mathcal{A}_\alpha$	$\mathcal{A}_\delta + \mathcal{A}_\alpha$
299.2	7.97	6.69	0.78	2.41	0.82	0.35	9.7	19.1	28.8
302.2	7.77	6.73	1.16	2.73	0.83	0.35	9.3	19.4	28.7
305.2	7.70	6.77	1.47	3.03	0.84	0.35	9.2	19.4	28.6
307.2	7.57	6.79	1.67	3.22	0.84	0.35	9.0	19.5	28.5
309.2	7.56	6.84	1.86	3.40	0.84	0.36	9.0	19.0	28.0
311.2	7.44	6.91	2.03	3.55	0.85	0.35	8.8	19.6	28.4
316.2	7.22	7.06	2.46	3.92	0.87	0.36	8.3	19.7	28.0
320.2	7.16	7.12	2.76	4.19	0.86	0.36	8.3	19.5	27.8
324.2	6.87	7.24	3.04	4.41	0.86	0.36	8.0	20.2	28.2
328.2	6.79	7.32	3.30	4.64	0.87	0.36	7.8	20.2	28.0
333.2	6.65	7.38	3.61	4.82	0.87	0.36	7.6	20.5	28.1
338.2	6.52	7.50	3.90	5.05	0.87 <sub>4</sub>	0.36	7.5	20.7	28.2
343.2	6.35	7.60	4.17	5.25	0.88	0.36	7.2	20.9	28.1

(b) Partially-aligned material  $V = 50$  V (rms).

$T/K$	$a_\delta$	$a_\alpha$	$\log_{10}(v_m/\text{Hz})$	$\log_{10}(v_m/\text{Hz})$	$\beta_\delta$	$\beta_\alpha$	$\mathcal{A}_\delta$	$\mathcal{A}_\alpha$	$\mathcal{A}_\delta + \mathcal{A}_\alpha$
309.2	13.1	4.54	1.81	3.41	0.84	0.35	15.6	13.0	28.6
316.2	12.8	4.66	2.41	3.93	0.85	0.35	15.0	13.2	28.2
320.2	12.4	4.74	2.72	4.10	0.86	0.36	14.5	13.3	27.8
324.2	12.3	4.83	2.99	4.41	0.85	0.36	14.5	13.5	28.0
328.2	12.2	4.90	3.25	4.64	0.86 <sub>4</sub>	0.36	14.1	13.7	27.8
333.2	12.0	4.98	3.57	4.90	0.87	0.36	13.9	13.9	27.8
343.2	11.2	5.17	4.11	5.25	0.88	0.36	12.7	14.4	27.1

(c) Aligned material  $V = 300$  V (rms).

$T/K$	$a_\delta$	$a_\alpha$	$\log_{10}(v_m/\text{Hz})$	$\log_{10}(v_m/\text{Hz})$	$\beta_\delta$	$\beta_\alpha$	$\mathcal{A}_\delta$	$\mathcal{A}_\alpha$	$\mathcal{A}_\delta + \mathcal{A}_\alpha$
305.2	25.0	1.86	1.39	3.12	0.83	0.34	28.2	5.4	33.6
309.2	24.6	1.91	1.78	3.47	0.84	0.35	29.3	5.4	34.7
311.2	24.5	1.94	1.96	3.59	0.85	0.35	28.8	5.5	34.3
316.2	23.9	2.00	2.38	3.95	0.85	0.35	28.2	5.6 <sub>5</sub>	33.9
320.2	23.4	2.04	2.69	4.25	0.86	0.35	27.2	5.8	33.0
324.2	23.0	2.09	2.97	4.43	0.87	0.36	26.4	5.9	32.3
328.2	22.6	2.15	3.24	4.64	0.87	0.36	26.0	6.1	32.1
333.2	22.1	2.20	3.54	4.83	0.87	0.36	25.5	6.1	31.6
343.2	21.0	2.31	4.08	5.26	0.88	0.36	24.0	6.4	30.4

process, which does not actually give a separate maximum). However the high-frequency tail of the absorption is, in all cases, a slow function of frequency which implies that the  $\alpha$  process, if it is symmetrical in the  $\log_{10} \nu$  plot, extends to lower frequencies and strongly overlaps the  $\delta$  process. Also  $\beta_\delta \simeq 0.85\text{--}0.88$  while  $\beta_\alpha \simeq 0.34\text{--}0.36$ , and so the integrated intensity of the  $\alpha$  process is larger than might have been supposed from the overall loss curve. It is important at this stage to enquire if loss curves such as those shown in figure 3 could be treated in a different way. Phenomenologically we could have taken the data for the fully aligned sample (figures 3(c), (f), (i)) as representing a pure  $\delta$  process. These loss curves are asymmetric, with

respect to  $\log_{10} \nu_m$ , in the Davidson–Cole or Kohlrausch–Williams–Watts sense [15, 16] and would each be represented by three parameters  $a_\delta$ ,  $\log_{10} \nu_{m\delta}$  and  $\beta'_\delta$  where  $\beta'_\delta$  is now the Davidson–Cole or Kohlrausch–Williams–Watts spread parameter. If we had attempted to fit the overall curves to either form of  $\delta$  process, based on figures 3 (c), (f), (i) and to a Fuoss–Kirkwood form for the  $\alpha$  process, then poor fits would have been obtained since we have already shown that two Fuoss–Kirkwood components give an excellent representation of our data. If we had attempted to subtract an estimated Davidson–Cole or Kohlrausch–Williams–Watts function for the  $\delta$  process from the overall loss curve then the residual  $\alpha$  process would be found to be broad and asymmetrical, also in the same sense, since the  $\alpha$  process is now larger on its high-frequency side, giving a reduced net low-frequency tail to the  $\alpha$  process. The difficulties of resolving multiple processes are well known so in view of the excellent fits we have obtained using two Fuoss–Kirkwood functions we may use this approach as a practical working scheme which is able to give fairly precise estimates of  $a_\delta$ ,  $a_\alpha$ ,  $\log_{10} \nu_{m\delta}$ ,  $\log_{10} \nu_{m\alpha}$  but may incorporate small indeterminate uncertainties regarding the shapes of the loss curves and the effective magnitudes  $\mathcal{A}_\delta$  and  $\mathcal{A}_\alpha$ . However, we consider that the present approach gives a consistent analysis of our data and reasonable estimates of the total magnitude  $\mathcal{A}_\delta + \mathcal{A}_\alpha$  for the absorption.

We note that the component loss processes become narrower ( $\beta$  increasing) as the temperature is increased, which is in accord with experimental dielectric data for liquids and solids, including solid polymers [17]. The  $\delta$  process is a little broader than that for a single relaxation time process, but is far narrower than the dipole relaxations observed for amorphous or crystalline polymers [17]. For liquid crystals of low molar mass the dielectric relaxation due to the motions of  $\mu_{\parallel}$  is essentially that of a single relaxation time process [18] so the present  $\delta$  process resembles more this process than a typical  $\alpha$  or  $\beta$  process in a polymer [17]. However, the plots for the  $\delta$  process in figure 5 are curved at the lowest temperatures as are the loci of  $\alpha$  processes in amorphous polymers which show premonitory behaviour associated with the onset of an apparent glass transition. In addition the apparent activation energy  $E_{\text{app}}$  for the  $\delta$  process is much higher than that in the low molar mass materials (see, for example, [18]) and is strongly temperature dependent in the WLF [17] or Vogel sense. For example ( $E_{\text{app}}$ ) is about  $130 \text{ kJ mol}^{-1}$  at 327 K (see figure 5), which is comparable with the apparent activation energy for main chain motion ( $\alpha$  process) in amorphous polymers above  $T_g$ . Thus the values of  $E_{\text{app}}$  and its temperature variation suggest that the motions of the mesogenic head group responsible for the  $\delta$  process, i.e. the motions of  $\mu_{\parallel}$ , are strongly hindered and temperature dependent in a similar way to chain motions in polymers. Thus the  $\delta$  process has similarities with analogous motions in liquid crystals of low molar mass and in amorphous polymers. This behaviour implies that we should take care in impressing mechanisms of motion commonly used for either liquid crystals of low molar mass or amorphous/crystalline polymers. The present liquid-crystalline polymer materials are *hybrid* materials and the traditional interpretations may not apply.

In low molar mass liquid crystals (smectic or nematic) it is usually assumed that any individual molecule may reorientate through  $180^\circ$  with respect to the director axis, which reverses  $\mu_{\parallel}$  and gives rise to the dominant dielectric process in homeotropically-aligned materials. However for the present liquid-crystalline polymer (I) and those studied previously [6–8, 10, 12–14] the end of the alkyl tail of the mesogenic side group is bonded to the polymer chain so the diffusional motion of the mesogenic head group is topologically constrained. An immediate consequence is that

the backbone motions of the chain exerts an increasing hindrance to the motions of the head groups as  $T_g$  is approached and this is seen to be the case for both the  $\delta$  and  $\alpha$  processes (see figure 5).

We consider that the  $\delta$  and  $\alpha$  processes correspond mainly to motions of  $\mu_{\parallel}$  and  $\mu_{\perp}$  respectively, i.e. motions of the mesogenic head group about axes perpendicular and parallel to the local director axis. A striking feature of figure 5 is that the locus for the  $\alpha$  process parallels, almost exactly, that for the  $\delta$  process in the range where both plots are strongly curved as  $T_g$  is approached (i.e. for  $T < 312$  K). This suggests that the progressive slowing-down of the main chain retards the motions of  $\mu_{\parallel}$  and  $\mu_{\perp}$  in a similar way. For liquid crystals of low molar mass the motions of  $\mu_{\parallel}$  and  $\mu_{\perp}$  occur via cooperative rearrangements of the neighbouring molecules. For liquid-crystalline side-chain polymers such motions also involve the cooperative motions of the main chain. This is a further constraint which leads to (i) a general decrease in relaxation rate for  $\delta$  ( $\mu_{\parallel}$ ) and  $\alpha$  ( $\mu_{\perp}$ ) processes when compared with the low molar mass analogues, and (ii) to premonitory behaviour as  $T_g$  is approached. The values of  $\beta_{\alpha}$  ( $\sim 0.34$ – $0.36$ ) are small and resemble values obtained for the secondary relaxations in amorphous polymers [17]. This means that the  $\alpha$  process is extremely broad, having a half-width approximately 3.2 units of  $\log_{10}$  (frequency). As is the case for polymers [17] it seems difficult to devise a simple reorientational mechanism which would give such a broad loss curve and it is usual in polymer science to assume that the distribution is due to a range of local environments [17, 19].

#### 4.2. Dielectric properties and molecular dynamics

As we have shown, the same  $\delta$  and  $\alpha$  processes are observed for each sample but their magnitudes are dependent on the degree of alignment. Molecular models for the dielectric relaxation of nematic liquid crystals of low molar mass have been described by several workers [20–23] who have assumed that a molecule undergoes small step rotational diffusion in an effective nematic potential. The earliest treatment was due to Maier and Meier [21] who derived expressions for the static permittivities  $\epsilon_{\parallel}^0$  and  $\epsilon_{\perp}^0$  measured parallel to and perpendicular to the director axis in a fully-aligned material. It was shown that these permittivities were functions of  $\mu_{\parallel}$ ,  $\mu_{\perp}$  and the order parameter  $S$  for the molecules in the uniaxial material. Subsequently Martin and co-workers [22] and Nordio and co-workers [23] derived expressions for the complex dielectric permittivities  $\epsilon_{\parallel}(\omega)$  and  $\epsilon_{\perp}(\omega)$  for the fully-aligned material in which it was assumed that individual molecules undergo small-step rotational diffusion leading to relaxation of  $\mu_{\parallel}$  and  $\mu_{\perp}$ . These model theories have been applied to experimental dielectric data for fully-aligned liquid crystals of low molar mass (for example, for an alkylcyanobiphenyl [24] and for mono and diester nematogens [25]). It is a feature of the present liquid-crystalline polymers that the materials may be prepared having different degrees of homeotropic alignment. The intermediate degree of alignment may be conveniently expressed in terms of an order parameter  $S_d$  for the local director axes with respect to the symmetry axis of the partially-aligned material. Thus  $S_d = 0$  and  $S_d = 1$  for unaligned and fully-aligned materials respectively. Attard [26] has extended the Nordio theory [23] for anisotropic rotational diffusion in the nematic potential to include the case where the director axes are partially aligned along an axis which is perpendicular to the plane of the film of liquid-crystalline material. In this theory [23, 26] the components of the dipole moment  $\mu$  of the mesogenic head group are expressed in the spherical representation in the usual way [27, 28] and the irreducible components  $\mu^{(1,m)}$  are related to the laboratory components  $\mu^{(1,p)}$  via Wigner

rotation matrices as has been described previously [29, 30]. The resultant dipole moment correlation for dielectric measurements made with the measuring electric field parallel to the symmetry axis ( $z$  axis) of a partially aligned material is given by [23, 26]

$$\langle \mu_z(0) \mu_z(t) \rangle = \sum_{m,n} g_{mn}^1 \psi_{mn}^1(t), \quad (4)$$

where the superscript 1 indicates that dielectric relaxation involves spherical harmonics of rank one and the  $m, n$  combinations are 00, 10, 01 and 11. The  $g_{mn}^1$  factors are the strength factors of the individual relaxation modes and the  $\psi_{mn}^1(t)$  are the normalized relaxation functions.  $g_{mn}^1$  depends upon the order parameters  $S_d$  and  $S$  where the latter quantity is the order parameter for the molecules with respect to the local director axis, as defined by Maier and Meier [21]. Attard [26] obtains the following results for small step rotational diffusion:

$$g_{00}^1 = c(1 + 2S_d)(1 + 2S)\mu_{\parallel}^2, \quad (5a)$$

$$g_{10}^1 = c(1 + 2S_d)(1 - S)\mu_{\perp}^2, \quad (5b)$$

$$g_{01}^1 = 2c(1 - S_d)(1 - S)\mu_{\parallel}^2, \quad (5c)$$

$$g_{11}^1 = c(1 - S_d) \left( 1 + \frac{S}{2} \right) \mu_{\perp}^2, \quad (5d)$$

where  $c$  is a factor involving the number density of dipoles. The relaxation functions are given by [23]

$$\psi_{mn}^1(t) = \exp(-t/\tau_{mn}^1), \quad (6)$$

where the relaxation times  $\tau_{mn}^1$  are complicated functions of the nematic potential and of  $D_{\parallel}$  and  $D_{\perp}$ , the rotational diffusion coefficients for anisotropic motion. In general Nordio [23] shows that

$$\tau_{00}^1 > \tau_{01}^1 \gtrsim \tau_{11}^1 \gtrsim \tau_{10}^1. \quad (7)$$

The normalized complex dielectric permittivity in the frequency domain is obtained by Fourier transformation of the correlation function in equation (4) (see, for example, [31]) and four single relaxation time processes are obtained. These are characterized by a strength factor  $\Delta\epsilon_{mn}$ , which is proportional to  $g_{mn}^1/9kT$ , and a relaxation time  $\tau_{mn}^1$ . (Explicit relations for the quantities  $\Delta\epsilon_{\parallel}$  and  $\Delta\epsilon_{\perp}$  are given by Bone *et al.* [25] in terms of  $\mu_{\parallel}$ ,  $\mu_{\perp}$  and  $S$  for a fully-aligned material.) As the degree of alignment is varied (via  $S_d$ ) the relative magnitudes of these four relaxation modes will vary in accord with equations (5), but the relaxation times are unaffected.

Consider first the case of an unaligned sample, i.e.  $S_d = 0$ . From equations (5) we have

$$(\Delta\epsilon_{00})_{\text{U}} = \frac{c'}{9kT} (1 + 2S)\mu_{\parallel}^2; \quad (\Delta\epsilon_{10})_{\text{U}} = \frac{c}{9kT} (1 - S)\mu_{\perp}^2, \quad (7a, b)$$

$$(\Delta\epsilon_{01})_{\text{U}} = \frac{2c'}{9kT} (1 - S)\mu_{\parallel}^2; \quad (\Delta\epsilon_{11})_{\text{U}} = \frac{2c}{9kT} \left( 1 + \frac{S}{2} \right) \mu_{\perp}^2 \quad (7c, d)$$

from which we deduce

$$\sum_{m,n} (\Delta\epsilon_{mn})_{\text{U}} = \frac{c'}{3kT} (\mu_{\parallel}^2 + \mu_{\perp}^2). \quad (8)$$

Since  $\mu^2 = \mu_{\parallel}^2 + \mu_{\perp}^2$ , equation (8) shows that all of  $\mu^2$  is relaxed for the unaligned sample.

Next consider the case of a fully-aligned sample, i.e.  $S_d = 1$ . From equation (5) we obtain

$$(\Delta\varepsilon_{00})_A = \frac{c'}{3kT}(1 + 2S)\mu_{\parallel}^2; \quad (\Delta\varepsilon_{10})_A = \frac{c'}{3kT}(1 - S)\mu_{\perp}^2; \quad (9a, b)$$

$$(\Delta\varepsilon_{01})_A = (\Delta\varepsilon_{11})_A = 0.$$

Thus for this sample only a portion of  $\mu_{\parallel}^2$  and  $\mu_{\perp}^2$  is relaxed by the dielectric experiment in which  $\mathbf{E}$  (the measuring field) is parallel to the director axis.

Denoting an individual process by the combination of indexes ( $lmn$ ), it seems reasonable to relate the (100) process to the observed  $\delta$  process since both are lowest frequency processes in the model and in experiment. Only a part of  $\mu_{\parallel}^2$  is relaxed by the  $\delta$  process for an aligned sample. Equations (7) and (8) predict the ratio of strengths for the  $\delta$  process in aligned and unaligned samples to be  $(\Delta\varepsilon_{00})_A/(\Delta\varepsilon_{00})_U = 3$ . The table shows that  $(\mathcal{A}_{\delta})_A/(\mathcal{A}_{\delta})_U$  lies in the range 3.06 to 3.33 as temperature is increased from 305 to 343 K. Thus there is fair agreement between experiment and the prediction of the theory. The experimental ratio exceeds the theoretical value of 3 and this may be attributed to a number of causes. Clearly any systematic error in decomposing the overall loss curve into two Fuoss-Kirkwood components will affect our values of  $\mathcal{A}_{\delta}$  and hence of the ratio. If we had assumed two components of Cole-Cole type (see [17]) slightly different values of  $\mathcal{A}_{\delta}$  and  $\mathcal{A}_{\alpha}$  would have been obtained. If we had assumed that each component was of Davidson-Cole or Kohlrausch-Williams-Watts type then the  $\delta$  process would have been enhanced in all curves and the  $\alpha$  process diminished relatively. However, it is not possible to say how this would have affected  $(\mathcal{A}_{\delta})_A/(\mathcal{A}_{\delta})_U$ .

The resolved  $\alpha$  process was extremely broad ( $\Delta \log_{10} \nu \sim 3.2$ ,  $\beta \sim 0.35$ ) compared with a single relaxation time process ( $\Delta \log_{10} \nu = 1.14$ ). We may speculate that the (110), (101) and (111) processes all contribute to the overall  $\alpha$  process for a partially-aligned or unaligned sample. The relative strength of  $\delta$  and  $\alpha$  processes for a partially-aligned sample is determined by  $\mu_{\perp}^2/\mu_{\parallel}^2$  ( $=y$  say), by  $S_d$  and by  $S$ , all of which are unknown quantities. From equations (7) and (9) and from the definitions of  $\mathcal{A}_{\delta}$  and  $\mathcal{A}_{\alpha}$  we have

$$\begin{aligned} r_1 &= \frac{(\mathcal{A}_{\delta} + \mathcal{A}_{\alpha})_A}{(\mathcal{A}_{\delta} + \mathcal{A}_{\alpha})_U}, \\ &= \frac{(1 + 2S) + (1 - S)y}{1 + y}, \end{aligned} \quad (10)$$

$$\begin{aligned} r_2 &= \frac{(\mathcal{A}_{\alpha})_U}{(\mathcal{A}_{\delta})_U}, \\ &= \frac{2(1 - S) + 3y}{1 + 2S}. \end{aligned} \quad (11)$$

From the table we have  $r_1 = 1.15 \pm 0.05$  and  $r_2 = 2.25 \pm 0.10$ . Using  $r_1 = 1.15$  and  $r_2 = 2.25 \pm 0.10$  we calculate  $(S, y)$  pairs in the range to (0.68, 1.48) to (0.56,

1.40), with an average (0.63, 1.43). Equation (9) predicts that

$$\begin{aligned} r_3 &= \frac{(\mathcal{A}_\alpha)_A}{(\mathcal{A}_\delta)_A}, \\ &= \frac{(1 - S)y}{1 + 2S} \end{aligned} \quad (12)$$

and insertion of the median values (0.63, 1.43) into this equation predicts a ratio  $r_3 = 0.23$  which is to be compared with the experimental value of 0.21 (see data of the table (c)). This apparently satisfactory result is subject to systematic errors in our analysis. We have already noted that  $(\mathcal{A}_\delta)_A/(\mathcal{A}_\delta)_U$  is greater than the theoretical value of 3. This may arise if the 'unaligned' sample is planar-aligned to some extent, giving  $S_d$  negative and not zero. Pursuing this possibility, equations (10) and (11) are modified to

$$\begin{aligned} r'_1 &= \frac{(\mathcal{A}_\delta + \mathcal{A}_\alpha)_A}{(\mathcal{A}_\delta + \mathcal{A}_\alpha)_{PA}}, \\ &= \frac{(1 + 2S) + (1 - S)y}{(1 + 2S_d S) + (1 - S_d S)y}, \end{aligned} \quad (13)$$

$$\begin{aligned} r'_2 &= \frac{(\mathcal{A}_\alpha)_{PA}}{(\mathcal{A}_\delta)_{PA}}, \\ &= \frac{3(1 - S_d S)y + 2(1 - S_d)(1 - S)}{(1 + 2S_d)(1 + 2S)}, \end{aligned} \quad (14)$$

where  $S_d$  refers to the partially-aligned sample; also

$$\begin{aligned} r_4 &= \frac{(\mathcal{A}_\delta)_A}{(\mathcal{A}_\delta)_{PA}}, \\ &= \frac{3}{1 + 2S_d}. \end{aligned} \quad (15)$$

From the table and equation (15) we have  $S_d = -0.045$ . Solving equations (13) and (14) as before, using the experimental value of  $r_1 = 1.15$  and  $r_2 = 2.25 \pm 0.10$  and now with  $S_d = -0.045$  we obtain  $(S, y)$  pairs in the range (0.78, 1.53) to (0.68, 1.47) with an average of (0.73, 1.50). Insertion of these values into equation (12) gives a calculated value of  $r_3 = 0.165$ , in poorer agreement with experiment, but it must be remembered that the extraction of the  $\alpha$  process from the overall process for an aligned sample is the most stringent test of our analysis. We note that an increase in the ratio  $r_1$  (experimental) leads to a substantial decrease in the derived values of both  $S$  and  $y$ . For example, taking  $r_1 = 1.25$  and  $r_2 = 2.25$  with  $S_d = -0.045$  we calculate the pair ( $S = 0.50$ ,  $y = 1.04$ ) and  $r_3 = 0.26$ .

From equations (5) and (7) we may write

$$\frac{(\mathcal{A}_\delta)_{PA}}{(\mathcal{A}_\delta)_U} = 1 + 2S_d. \quad (16)$$

Hence the order parameter for the director in a partially-aligned sample can be deduced using the dielectric data for the resolved  $\delta$  process. From the data of the table we calculate  $S_d = 0.38 \pm 0.02$  in the temperature range studied for the partially aligned sample assuming that the 'unaligned' material had  $S_d = 0$ . If planar alignment is present in the latter material, and we use  $S_d = -0.045$  in calculating  $S_d = 0.30 \pm 0.02$ , a substantial decrease on the former value. Alternatively, we may use the ratio

$$\begin{aligned} r_5 &= \frac{(\mathcal{A}_\delta)_{PA}}{(\mathcal{A}_\delta)_A}, \\ &= \frac{1 + 2S_d}{3}, \end{aligned} \quad (17)$$

which, using the data of the table, yields the value  $S_d = 0.30 \pm 0.01$  over the range of temperature studied. This value is more reliable than that calculated from equation (16) and since it agrees with the earlier value calculated on the basis that the 'unaligned' sample has slight planar alignment, confirms that possibility. Thus our dielectric data provide a new and convenient method for estimating  $S_d$  for a partially-aligned material, as we had indicated earlier [8].

Note that  $\mu_{\parallel}^2$  is partially relaxed by the (101) fast process and the remainder by the (100) slow process for an unaligned sample. The relaxation of a given dipole vector in stages by fast and slow processes is a well-known phenomenon for group motions in solid polymers [19] and for small flexible molecules. In the present case the (101) process involves motion of  $\mu_{\parallel}$  with respect to both  $\theta$  and  $\phi$  polar coordinates defined with respect to the local ( $z$ ) director while the (100) process involves motions of  $\mu_{\parallel}$  with respect to  $\theta$  only. The smaller  $S$  becomes the larger is the (101) process and the smaller is the (100) process, so that the total strength  $\Delta\epsilon_{00} + \Delta\epsilon_{01}$  is conserved.

While we have found that the small-step rotational-diffusion model gives a reasonable account of our data for unaligned, partially-aligned and aligned samples, it should be emphasized that the breadth of the  $\delta$  process and the overall  $\alpha$  process imply relaxation processes which are more co-operative than are envisaged in a small-step diffusional model. Also, alternative models for motion can be envisaged. For example, the mesogenic head group might undergo limited angular motions leading to partial relaxation of  $\mu_{\parallel}$  and possibly total relaxation of  $\mu_{\perp}$  in one broad  $\alpha$  process and the remainder of  $\mu_{\parallel}$  might be relaxed by occasional local fluctuations of the ensemble surrounding a reference molecular group, leading to a process which might be described by a strong collision or fluctuation-relaxation model (see, for example, [32] and references therein). The alkyloxycyanobiphenyl mesogens studied by Kresse [13, 14] appear from their structure to have only a small transverse dipole moment for the mesogenic head group. Their dielectric data show no indication of an  $\alpha$  process, and this may be taken as evidence that the  $\alpha$  process in the present polymer [7, 8, 10] is due to motions to  $\mu_{\parallel}$  and  $\mu_{\perp}$  and not simply by partial relaxation of  $\mu_{\parallel}$ .

## 5. Conclusions

The present work has shown that the dielectric properties of a liquid-crystalline side-chain polymer can be varied systematically by varying the thermal/electrical



treatment used to prepare a given material. The  $\delta$  process is enhanced by a factor of 3 and the  $\alpha$  process is diminished remarkably on going from unaligned to aligned material, but the frequency of maximum loss and the relaxation spread parameter are unchanged, at a given temperature, as the sample condition is changed. Molecular theory suggests that the  $\delta$  process is due to motions of  $\mu_{\parallel}$  and that the  $\alpha$  process contains contributions from both  $\mu_{\parallel}$  and  $\mu_{\perp}$ . It is shown that the dielectric data for unaligned and aligned material may be used to estimate  $\mu_{\perp}/\mu_{\parallel}$  and the order parameter  $S$  and that the dielectric data for the unaligned and partially-aligned material may be used to estimate the order parameter  $S_d$  for director alignment in the latter material.

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