Molecular dynamics and macroscopic alignment properties of thermotropic liquid-crystalline side chain polymers as studied by dielectric relaxation spectroscopy

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Invited Article

Molecular dynamics and macroscopic alignment properties of thermotropic liquid-crystalline side chain polymers as studied by dielectric relaxation spectroscopy

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It is shown that dielectric relaxation spectroscopy provides a convenient means of studying the anisotropic reorientational dynamics of the mesogenic head groups in thermotropic liquid-crystalline side chain polymers. Their alignment behaviour in directing a.c. electric fields of different amplitudes and frequencies is examined, and samples having a macroscopic alignment which is fully homeotropic, fully planar or any desired intermediate alignment have been prepared. The nature and extent of alignment in such samples has been determined by dielectric spectroscopy. In addition both the temperature and pressure variations of the average dielectric relaxation times for certain relaxation processes have been determined and a bulk alignment phenomenon in the absence of a directing electric field is reported.

1. Introduction

Thermotropic liquid-crystalline polymers having the mesogenic groups in the side chains have been the subject of intense research activity since they were first synthesized in the late 1970s by Ringsdorf, Finkelmann and Wendorff and by Shibaev and Plate and their co-workers (for recent reviews see [1–3]). They are hybrid materials which have the advantageous properties of thermoplastic polymers and the electroactive and magnetoactive properties of thermotropic liquid crystals. They show promise as materials for optical information storage [1, 2, 4], for optical elements such as Fresnel lenses [5] and for non-linear optical processing such as second harmonic generation (SHG) of laser radiation [6]. In addition, photoactive groups may be incorporated into the chain or may be present as solute in a guest/host liquid-crystalline system, as described in [3] and [7], where pleochroic dye moeities allow dichroic films to be fabricated.

As with low molar mass liquid crystals, the liquid-crystalline side chain polymers find application as films 5–100 μm thick which are aligned macroscopically by applied electric or magnetic fields. In common with low molar mass smectics, but in contrast with low molar mass nematics, the polymer films retain their macroscopic alignment when the directing field is removed: hence their promise as materials for optical information storage and for optical elements. It is important, therefore, that the thermal/electrical treatments required to produce films of well-defined alignment

should be established experimentally and that a direct method for monitoring that alignment should be established. Also the fundamental processes involved in forming macroscopically-aligned films should be clarified at the macroscopic and molecular levels.

In the present paper we review researches we have conducted with liquid-crystalline side chain polymers having siloxane backbones, for which we have studied the anisotropic motions of dipolar groups and the alignment properties using dielectric relaxation spectroscopy. We show how the dielectric properties [8] of a partially-aligned film are related to the fundamental molecular properties, such as group dipole moment and the time-correlation functions for the anisotropic reorientational motions of 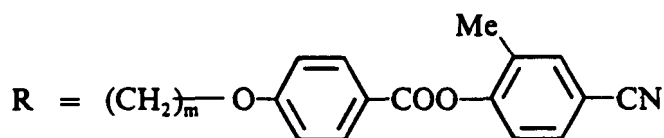the components of the group dipole moment, and to an operational quantity we term the 'director order parameter' S_d. We describe the thermal/electrical treatments required for the preparation of homeotropic, planarly- and intermediately-aligned films and how dielectric relaxation spectroscopy measurements allow S_d to be determined for our samples. In addition we show how a partially-aligned material increases its degree of alignment when cooled slowly from the biphasic range in the absence of an electric field.

2. Experimental

The liquid-crystalline side chain polymers were synthesized by G. W. Gray, D. Lacey and the Hull University Liquid Crystals Group. These materials were kindly made available to us by G. W. Gray. They had the following structures:

$$\text{Me}_3\!-\!\text{Si}\!-\!\text{O}\!\left[\begin{array}{c}\text{Me}\\|\\\text{Si}\!-\!\text{O}\\|\\\text{R}\end{array}\right]_n\!\text{Si}\!-\!\text{Me}_3$$

where $n \simeq 50$ and

$$\text{R} = (\text{CH}_2)_m\!-\!\text{O}\!-\!\langle\!\rangle\!-\!\text{COO}\!-\!\langle\!\rangle\!-\!\text{CN}$$
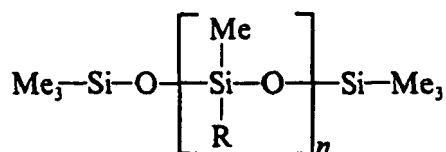
with $m = 5$, 6 or 8.

Their apparent glass transition temperatures (T_g) and clearing temperatures (T_c), as judged by d.s.c. measurements, were as follows [9]: $m = 5$, $T_g = 273\,\text{K}$, $T_c = 325\,\text{K}$; $m = 6$, $T_g = 275\,\text{K}$, $T_c = 314\,\text{K}$; $m = 8$, $T_g = 274\,\text{K}$, $T_c = 363\,\text{K}$. Optical microscopy indicated [9] that the polymers having $m = 5$ and $m = 6$ were nematic and that having $m = 8$ was smectic.

The dielectric measurements were made in the range 12 to $10^5\,\text{Hz}$ using a GenRad 1689 Precision RLC Digibridge which was computer controlled. For 10^{-1} to $10^2\,\text{Hz}$ a Scheiber bridge was employed [10], and for 4×10^{-4} to $10^{-1}\,\text{Hz}$ a transient method was used in which the charge–discharge currents following the step-application or withdrawal of small electric fields were determined and Fourier transformed to give loss data in the frequency domain [10]. For convenience we give loss data as $\varepsilon''C_0 = G/\omega$, where ε'' is the imaginary part of the complex dielectric permittivity

$\varepsilon = \varepsilon' - i\varepsilon''$, C_0 is the interelectrode capacitance of the space occupied by the sample, G is the measured equivalent parallel conductance of the sample measured at the angular frequency $\omega(= 2\pi v$ /Hz).

3. Results
3.1. *Unaligned material*

As one example, figure 1 shows the plot of loss against log (v/Hz) for the nematic polymer $m = 5$, as reported earlier [11]. The curves in the liquid crystalline state, up to 322·0 K, are broad with evidence of bimodal structure. At 325·4 and 326·5 K the loss curves increase in height and narrow, while those for 330·0–348·0 K retain an almost constant height and shape. These data show that the polymer goes from its nematic state to the isotropic state via a fairly narrow biphasic range, and that this change is readily monitored by the changes in the dielectric spectrum. The transformation is also seen conveniently in the plot of the frequency of maximum loss factor against reciprocal temperature for these data, as shown in figure 2. In the limited ranges of frequency covered in the isotropic range and in the nematic range the plots are approximately linear, giving apparent activation energies of 138 and 183 kJ mol^{-1} respectively. The transition range is observed and the rate
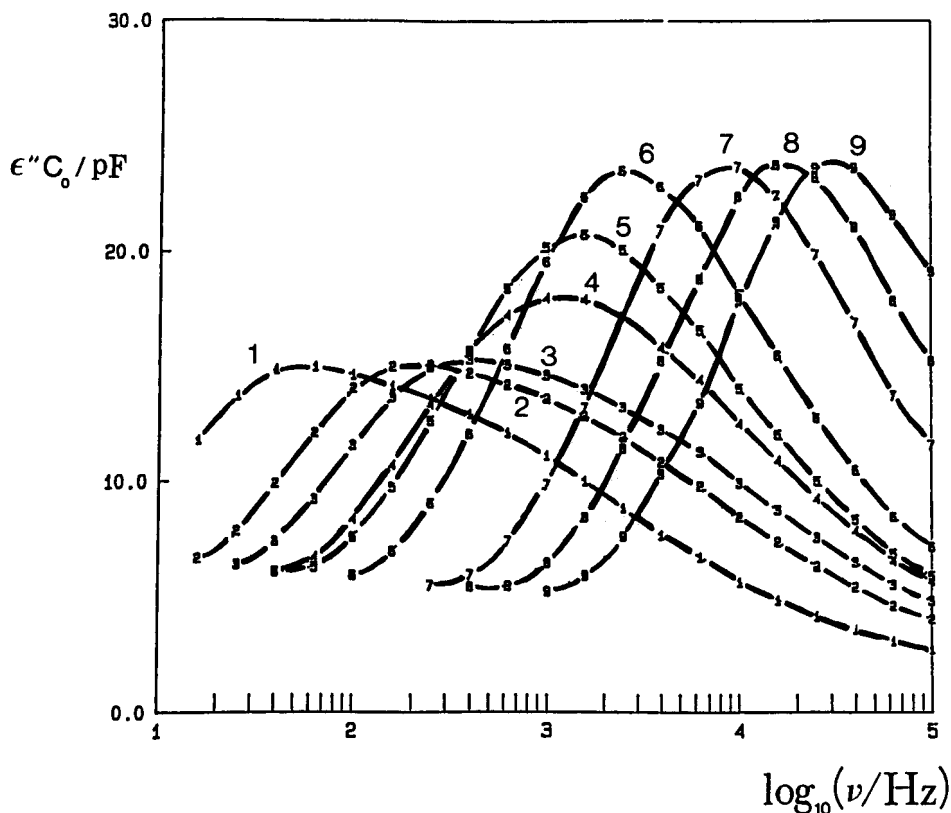

Figure 1. $\varepsilon'' C_0$ against log (v/Hz) for the nematic polymer $m = 5$ in its liquid-crystalline and isotropic states. Curves 1–9 correspond to 313·0, 319·0, 322·0, 325·4, 326·5, 330·0, 338·0, 343·0 and 348·0 K respectively [11].
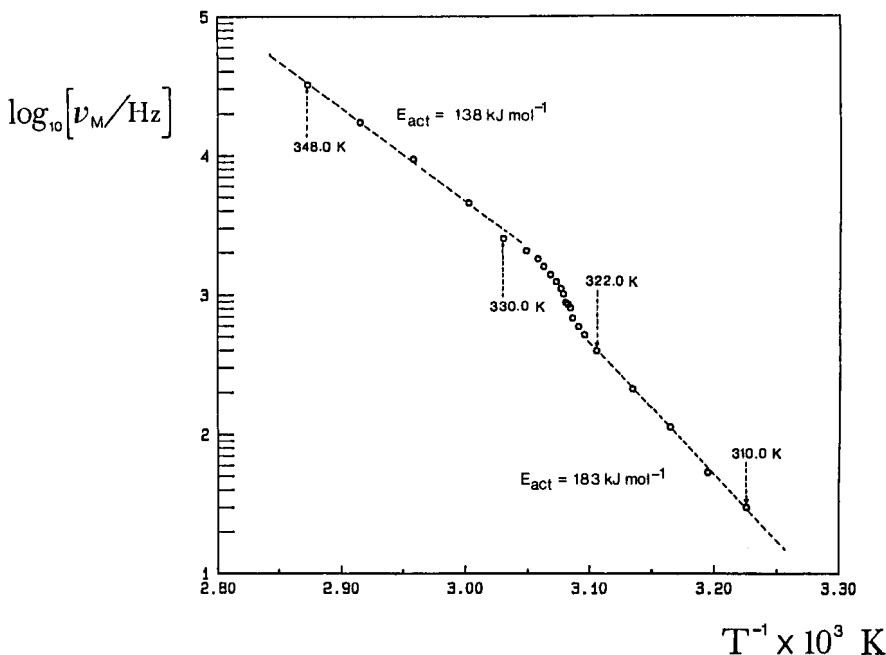
Figure 2. log (v_m/Hz) against $(T/\text{K})^{-1}$ for the data of figure 1 [11].

of motion in the liquid-crystalline state is slower and has a stronger temperature dependence than that which would be predicted for a hypothetical supercooled isotropic liquid.

While such data are important in characterizing the *average* rates of motion in the liquid-crystalline and isotropic states and in indicating the position and extent of the biphasic range, it is difficult to extract the essential information regarding the molecular processes which give rise to such broad loss features. A similar conclusion applies to the earlier work of Kresse and co-workers [12, 13] and of Zentel and co-workers [14] for acrylate liquid crystal polymers. A similar conclusion applies to N.M.R. studies of the molecular motions of liquid-crystalline side chain polymers [15, 16] where the frequency range is limited in comparison with that of dielectric studies. In order to assign the relaxation(s) observed in the dielectric and N.M.R. experiments, and to deduce their mechanisms, it is necessary to make assumptions regarding the reorientational modes of motion in the liquid crystal state or the isotropic state, which is often done in liquids [17] and crystalline solids [18] and solid polymers [10]. Notable exceptions are studies of glass-forming organic liquids using dielectric and dynamic Kerr-effect methods in a complementary manner over wide ranges of frequency and temperature [19, 20] where certain mechanisms for reorientational motions could be ruled out and others favoured. However, given data of the kind shown in figure 1 for the nematic polymer it is difficult to reach firm conclusions regarding the molecular origins of reorientational motions in the liquid-crystalline state. As we shall see, the ability to align, macroscopically, a liquid crystal polymer introduces a variation in loss spectrum which clarifies the origin and nature of the dielectric relaxation processes. We shall also see how this may be reversed, i.e. the dielectric properties may be used to determine the nature and extent of macroscopic alignment in the liquid crystal polymers.

3.2. *Alignment of a smectic liquid-crystalline polymer in directing electric fields*

In principle it should be possible to align, macroscopically, a liquid crystal polymer using d.c. or a.c. electric fields. In practice we have found that application of d.c. electric fields of up to ~ 200 V across a $100\,\mu$m sample in the liquid-crystalline state leads to irreversible dielectric breakdown before significant alignment effects are detectable. The application of a.c. electric fields of up to 3×10^6 V m^{-1} for frequencies in the range 500 Hz to 10 kHz to materials of structure **I** above *in their liquid-crystal states* did *not* lead to significant changes in macroscopic alignment. However we found that it was possible to achieve different extents of alignment between fully-homeotropic and fully-planar (homogeneous) by slow-cooling the isotropic materials back into the liquid-crystalline state in the presence of a.c. electric fields of given amplitude and frequency [21–25].

In our earliest studies [21, 22] we found that a $100\,\mu$m thick film of the smectic material $m = 8$ when cooled from the melt in the presence of a.c. electric fields up to 200 V (r.m.s.)/$100\,\mu$m gave material aligned homeotropically and that the extent of homeotropic alignment was readily assessed from the changes in the dielectric relaxation spectrum. The height of the dielectric loss peak increased by a factor of $\sim 2\cdot 4$ and the loss curve narrowed as the homeotropic alignment was attained. These results were only obtained for samples cooled very slowly ($< 0\cdot 3$ K min^{-1}). If the rate of cooling was increased, the extent of alignment was decreased and samples cooled at states > 20 K min^{-1} in the presence of a very strong a.c. electric field did not align. Therefore it was evident that the formation of the aligned liquid-crystalline phase in the presence of an a.c. electric field was dependent on kinetic processes in this time scale. The form of the loss curves for unaligned and fully homeotropically-aligned smectic polymer are shown in figures 3 and 4. The bimodal nature of the loss peak for the unaligned material is evident and, following the notation first introduced by Zentel and co-workers [14], the low frequency peak is called the δ process and the high frequency peak (occurring as a shoulder in figure 3) is called the α process. As we shall see below, the dielectric relaxation curves may be thought to arise from *four* relaxation modes each weighted according to the extent of the director alignment with respect to the measuring electric field. However, the data of figures 3 and 4 suggest that resolution into *two* broad relaxations, δ and α, can be made. This was done by Attard and Williams [23] and figure 5 shows the results of fits to the experimental loss curves at a representative temperature of $316\cdot 2$ K by assuming that each overall loss curve has a Fuoss–Kirkwood line-shape function (characterized by the spread parameter β, $(0 < \beta < 1)$ and a strength factor, a, and a frequency of maximum loss. Details of the fitting method and the derived values of the relaxation parameters for δ and α processes are given in [23]. The relative values of a_δ and a_α and of log $v_{m\delta}$ and log $v_{m\delta}$ are seen by inspection of figure 5. The Fuoss–Kirkwood spread parameters were $\beta_\delta \simeq 0\cdot 85$, $\beta_\alpha \simeq 0\cdot 36$ showing that the δ process is close to that of a single relaxation time process and that the α process is unusually broad. Also it appears from this analysis that the α process has an integrated intensity approximately twice that of the δ process, so what appeared as a shoulder on the total loss curve is the more intense process of the two. Further, the fully-homeotropic material has a loss curve made up of a δ process, which dominates the spectrum, and a small-intensity α process. Clearly these conclusions are based on the assumption that the overall loss curve is composed of *two* component curves of a particular shape, so different conclusions may result if the basis set were changed. However the consistency of the values given in the table of [23] show that as the alignment is changed systematically only the relative
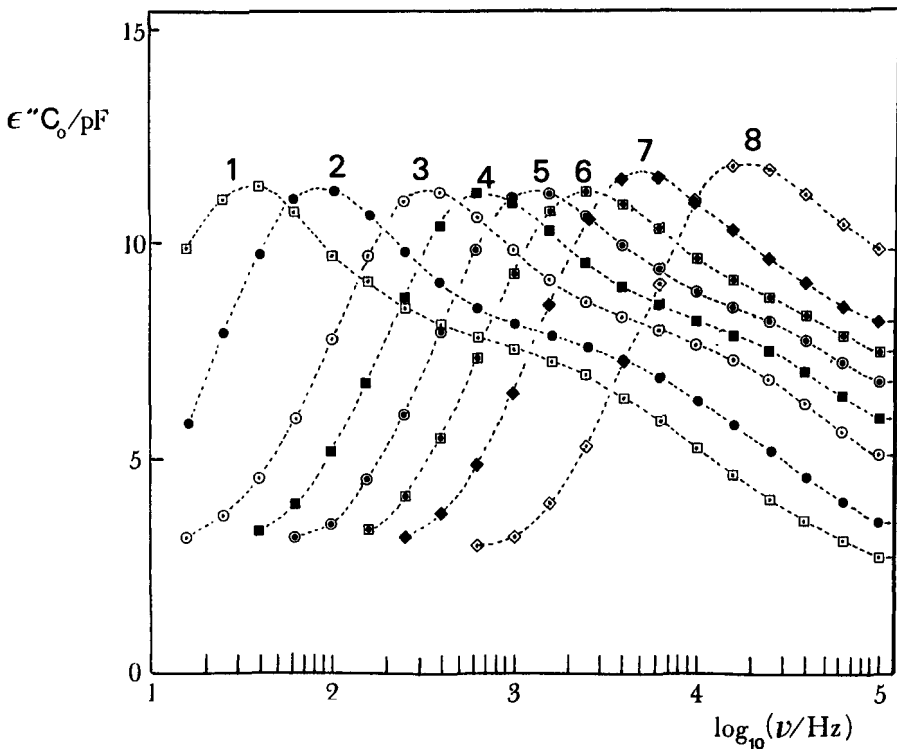
Figure 3. $\varepsilon''C_0$ against log (ν/Hz) for the unaligned smectic polymer, $m = 8$. Curves 1–8 correspond to 305·2, 309·2, 316·2, 320·2, 324·2, 328·2, 333·2 and 343·2 K respectively [23].

intensities a_δ and a_α change, all other parameters remaining unchanged. This implies that two components, δ and α, contribute to the loss curve at a fixed sample temperature, and that their relative magnitudes are a function of the nature and extent of the macroscopic alignment of the samples.

3.3. *Molecular theory for the dielectric permittivity of a partially-aligned liquid crystalline phase*

The theory of the static permittivity for a nematic liquid crystal is well known from the work of Maier and Meier [26] for a monodomain. The parallel and transverse static permittivities, $\varepsilon_{0\parallel}$ and $\varepsilon_{0\perp}$, were shown to be functions of a local order parameter S, and the dipole moment components μ_l and μ_t of the molecule with respect to the local director axis **n**. Theories of the dielectric relaxation of $\varepsilon_\parallel(\omega)$ and $\varepsilon_\perp(\omega)$ have been given by several workers [27–29] which consider the reorientational motions of the dipole moment μ in the nematic potential of the liquid-crystalline state. According to Nordio *et al.* [28] four relaxation modes are involved, as $\langle D_{ij}^1(0) \cdot D_{ij}^1(t) \rangle$ where ij are 00, 10, 01 and 11, and D indicates a Wigner rotation matrix element. It was shown that $\varepsilon_\parallel(\omega)$ was given by linear combinations of the 00 and 10 modes, expressed in the frequency domain, and that $\varepsilon_\perp(\omega)$ was given by linear combinations of the 01 and 11 modes. The explicit form for these modes was deduced [28] for the model of small-step rotational diffusion in a nematic potential.

As a development of the Nordio model, Attard [30] deduced the form of the permittivity $\varepsilon_Z(\omega)$ for an axially-symmetric, partially-aligned material measured
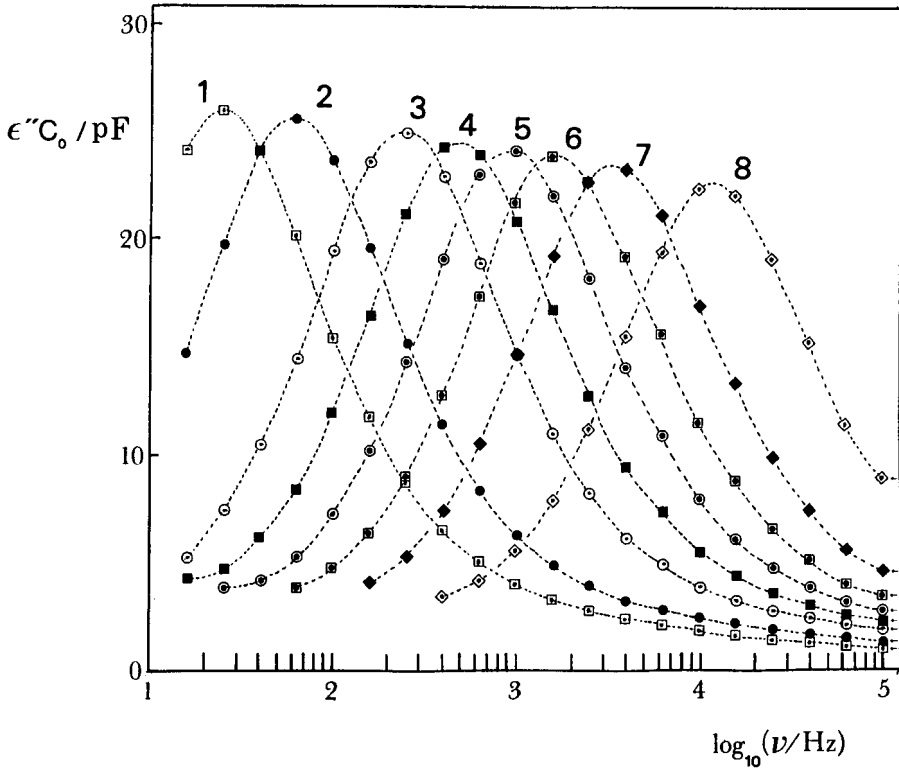
Figure 4. $\varepsilon'' C_0$ against log (ν/Hz) for the homeotropically-aligned smectic polymer, $m = 8$. Curves 1–8 correspond to the same temperatures as those given in figure 3 [23].

along the symmetry axis Z and showed that the relaxation modes ij contributed according to the following intensities:

$$A_{00}^1 = (\mu_l^2/9)(1 + 2S_d)(1 + 2S), \qquad (1\,a)$$

$$A_{10}^1 = (\mu_t^2/9)(1 + 2S_d)(1 - S), \qquad (1\,b)$$

$$A_{01}^1 = (2\mu_l^2/9)(1 - S_d)(1 - S), \qquad (1\,c)$$

$$A_{11}^1 = (2\mu_t^2/9)(1 - S_d)(1 + S/2), \qquad (1\,d)$$

where

$$S_d = \frac{\langle 3\cos^2\theta_{Zn} - 1 \rangle}{2}. \qquad (2)$$

S_d is the 'director order parameter' which gives an estimate of the average alignment of the local directors $\mathbf{n}$ with respect to the laboratory axis Z. For a monodomain with $\mathbf{n}\|Z$, $S_d = 1$ (fully homeotropic) while for the monodomain with $\mathbf{n}\perp Z$, $S_d = -1/2$. An unaligned material has $S_d = 0$. According to the theory of Attard [30], four relaxation modes, $ij = 00, 10, 01, 11$, contribute to the overall dielectric loss spectrum for a partially-aligned sample. For $S_d = 1$ (homeotropic sample) only the 00 and 10 modes contribute, having strength factors A_{00}^1 and A_{10}^1, and $\varepsilon_\|(\omega)$ is measured. Similarly for $S_d = -1/2$ (planar sample) only the 01 and 11 modes contribute,

(*a*)

(*b*)

(c)
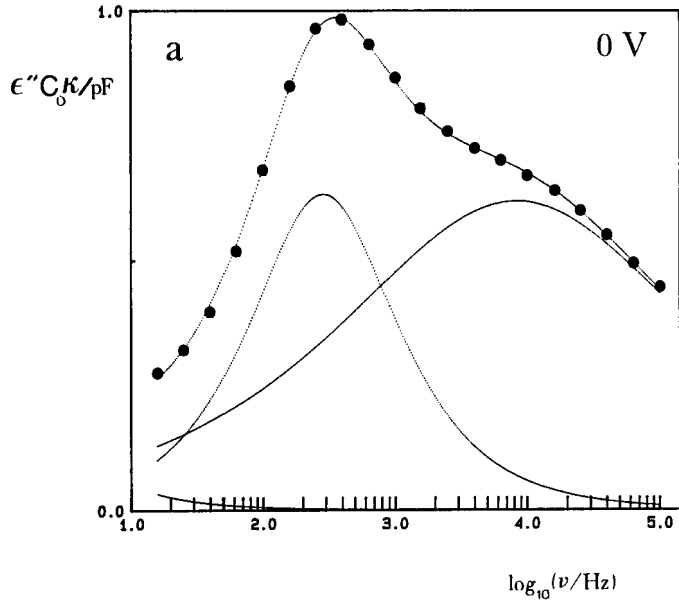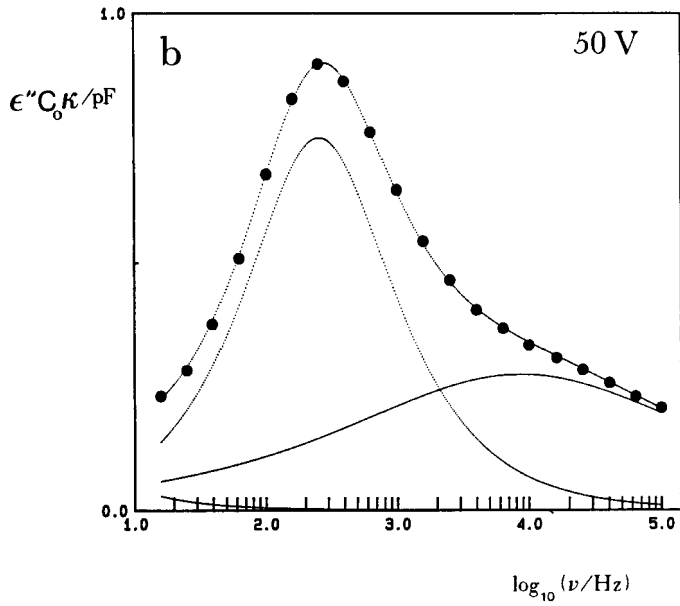
Figure 5. Representative examples of the fits of two component Fuoss–Kirkwood loss curves to the overall loss curves for the smectic polyme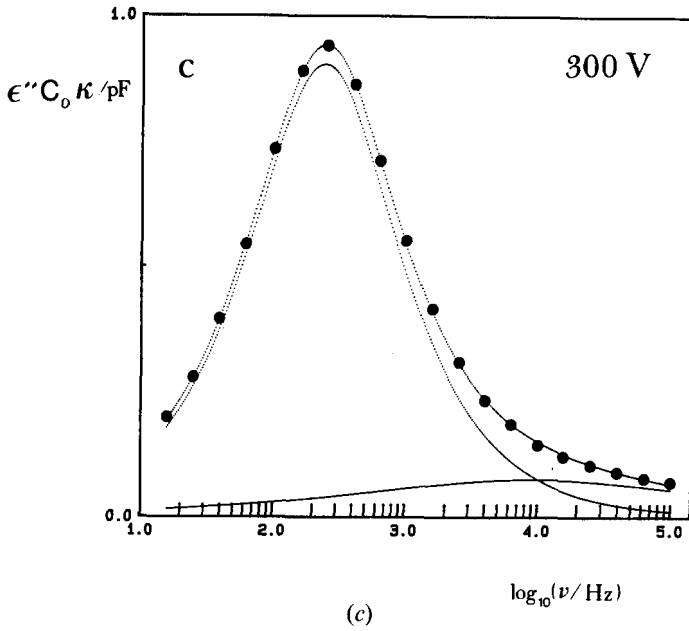r, $m = 8$, in different states of alignment. Curves (a), (b) and (c) are for unaligned, partially-aligned (homeotropically) and fully aligned (homeotropically) materials at $T = 316 \cdot 2$ K. κ is a scaling factor which presents all loss curves on a comparable scale.

with strength factors A_{01}^1 and A_{11}^1, and $\varepsilon_\perp (\omega)$ is measured. The four modes of motion have been illustrated schematically in [30].

The question arises, if experimental data appear to indicate *two* broad component relaxations, δ and α, as discussed above for the smectic polymer figures 3 and 4), how can this be reconciled with the theoretical prediction of Nordio *et al.* [28] and Attard [30] that four relaxation modes are present? Calculations of the average relaxation times τ_{ij} for small-step diffusion in the nematic potential suggest that [28, 31]

$$\tau_{00} > \tau_{01} \gtrsim \tau_{11} \gtrsim \tau_{10}. \qquad (3)$$

Therefore the δ process can be assigned to the 00 relaxation mode and, in addition, it seems reasonable to suppose that the three remaining modes comprise the broad α process observed experimentally. This was the basis of the analysis of the data [23] for the smectic polymer (figures 3 and 4 above) which yielded reasonable values for S_d, S and (μ_t/μ_l), following the resolution of the overall loss curves into component δ and α processes.

The data for the smectic polymer ($m = 8$) allowed of such an analysis since the frequency location of the δ and α processes were sufficiently different ($\Delta \log v_m \simeq 1 \cdot 6$). However the loss curves shown for the nematic polymer ($m = 5$) in figure 1 are not easily resolved. Attard [30] has carried out a resolution of the data for this nematic polymer [30] (figures 1 and 3), and finds $\Delta \log v_m \simeq 0 \cdot 9$. He has obtained satisfactory fits to the observed line shape for the unaligned nematic material using two component relaxation (δ and α) and has determined the relaxation parameters (magnitude, frequency location, line-shape parameter) for each process over a range of temperature and has further deduced values of S, S_d and μ_t/μ_l.

Given the experimental fact that in certain liquid crystal side chain polymers the δ and α processes were not sufficiently well resolved, it seemed desirable to obtain expressions for the observed dielectric permittivity for a partially-aligned material in a form which would allow S_d to be determined without the need to resolve the component relaxation modes. This was done recently by Attard *et al.* [32]. They used a simple matrix method for the projection of dielectric displacement, induced by a measuring electric field, of a local liquid crystal region into the coordinates of the measuring electric field. Using the assumption that the local electric field is uniform within the material they obtained the following result, that the measured permittivity was given simply by

$$\varepsilon = \varepsilon_\parallel (1 + 2S_d)/3 + \varepsilon_\perp 2(1 - S_d)/3. \tag{4}$$

Here $\varepsilon = \varepsilon' - i\varepsilon''$, and is a function of frequency, and $\varepsilon_\parallel$ and $\varepsilon_\perp$ have their usual significance. They also showed, quite generally, that

$$\varepsilon_\parallel(\omega) = \varepsilon_\parallel^\infty + \frac{G}{3kT}[\mu_l^2(1 + 2S)F_\parallel^l(\omega) + \mu_t^2(1 - S)F_\parallel^t(\omega)], \tag{5a}$$

$$\varepsilon_\perp(\omega) = \varepsilon_\perp^\infty + \frac{G}{3kT}[\mu_l^2(1 - S)F_\perp^l(\omega) + \mu_t^2(1 + S/2)F_\perp^t(\omega)]. \tag{5b}$$

$\varepsilon_\parallel^\infty$ and $\varepsilon_\perp^\infty$ are limiting high frequency permittivities and S is the local order parameter of the liquid crystal. The different $F_B^A(\omega)$, where $A = l, t, B = \parallel, \perp$, are given by

$$F_B^A(\omega) = 1 - i\omega\mathscr{F}[f_B^A(t)] \tag{6}$$

where each $f_B^A(t)$ is a normalized relaxation function in the time domain. Equations (5) are obtained as generalizations of the equilibrium theory of Maier and Meier to the frequency domain and, as such, give the molecular origins of the four relaxation modes. Equation (4) shows that the measured dielectric permittivity for a partially-aligned material is simply a linear combination of $\varepsilon(\omega)$ and $\varepsilon(\omega)$ where the weighting factors are simple functions of the macroscopic director order parameter S_d. Therefore we may obtain S_d values for an unknown material if $\varepsilon_\parallel(\omega)$, $\varepsilon_\perp(\omega)$ and $\langle\varepsilon(\omega)\rangle = [\varepsilon_\parallel(\omega) + 2\varepsilon_\perp(\omega)]/3$ (any two of these three) are known. According to equation (4) $\varepsilon \equiv \varepsilon_\parallel$ if $S_d = 1$ (homeotropic sample), $\varepsilon \equiv \varepsilon_\perp$ if $S_d = -1/2$ (planar sample) and $\varepsilon = \langle\varepsilon\rangle = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ if $S_d = 0$ (unaligned sample) We shall describe below the applications of equation (4) to our experimental results.

3.4. *Preparation of homeotropic and planarly-aligned nematic samples*

Araki and Attard [25] aligned the nematic siloxane polymer having $m = 6$ by cooling slowly from the melt with saturating electric fields of different audio-frequencies. Figure 6 shows the dielectric loss spectra for the homeotropic and planar materials prepared using 600 Hz and 10 kHz respectively, and the difference between these spectra, and that for the unaligned material, are striking. Note that all three loss curves appear to be unstructured, showing that all four relaxation modes have frequencies of maximum loss which are similar (~ 1 unit of log ν spans all four).

The ability to prepare both homeotropic and planar materials has its origins in the two-frequency addressing principle, well known for low molar mass liquid crystals [33, 34], in which if $\Delta\varepsilon'(\omega) > 0$, homeotropic alignment results, and if $\Delta\varepsilon'(\omega) < 0$, planar alignment results. Here ω is the angular frequency of the directing electric field.
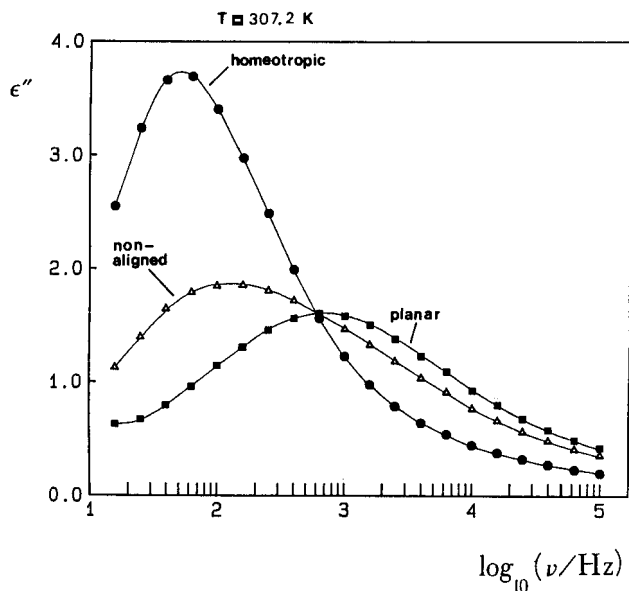
Figure 6. ε'' against log (ν/Hz) for the nematic polymer $m = 6$ in its homeotropically-aligned (●), unaligned (△) and planarly-aligned (■) states [25] at 307·2 K.

The fact that the loss spectra for homeotropic and planar materials give maxima at very different frequencies means that $\Delta\varepsilon > 0$ below a certain frequency and $\Delta\varepsilon < 0$ above a certain frequency for the nematic material *at the given temperature*. In principle it should therefore be possible to two-frequency address the nematic material in its liquid crystal state, but we have already stated that we find that this is *not* possible for this material. The H and P aligned materials of figure 6 were obtained by cooling from the melt. Therefore the cross-over frequency involved when H or P materials are prepared is that at the temperature at which the liquid-crystalline phase first forms in the cooling experiment; but its value is not easily defined since the material forms aligned in the whole of the biphasic range. We have made a careful study [35] of the effect of the frequency and amplitude of the aligning field on the macroscopic alignment behaviour for the nematic polymer $m = 6$. Figure 7 shows a small part of our data where the degree of homeotropic alignment is monitored as the ratio R/R_0 of the height of the observed loss peak for the treated material to that of the unaligned material at a fixed temperature (307·2 K) in the nematic state. The electrical field is sufficient to cause full alignment (H or P) below and above critical frequency. In all experiments the cooling rate was $\sim 0·05\,\mathrm{K\,min^{-1}}$. Figure 7 shows that for ν(aligning) $> \sim 1·6\,\mathrm{kHz}$ that planarly aligned material is obtained, while for ν(aligning) $< 1·2\,\mathrm{kHz}$ that homeotropically-aligned material is obtained. The transition is sharp and the two-frequency condition under these experimental conditions is well defined. Interestingly, the values of the cross-over frequency were determined at fixed temperatures in the liquid-crystalline state from the observed permittivity data [35] and we find that $\nu_c \sim 1·6\,\mathrm{kHz}$ at 319 K from an *extrapolation* of these data into the biphasic range to the temperature at which the isotropic phase begins to become biphasic. Thus on cooling the material from the isotropic melt the material forms homeotropic or planarly-aligned, dependent on the frequency of the aligning field with respect to ν_c at the onset of the transition temperature $T_\mathrm{isotropic} \rightarrow T_\mathrm{biphasic} = 322\,\mathrm{K}$.
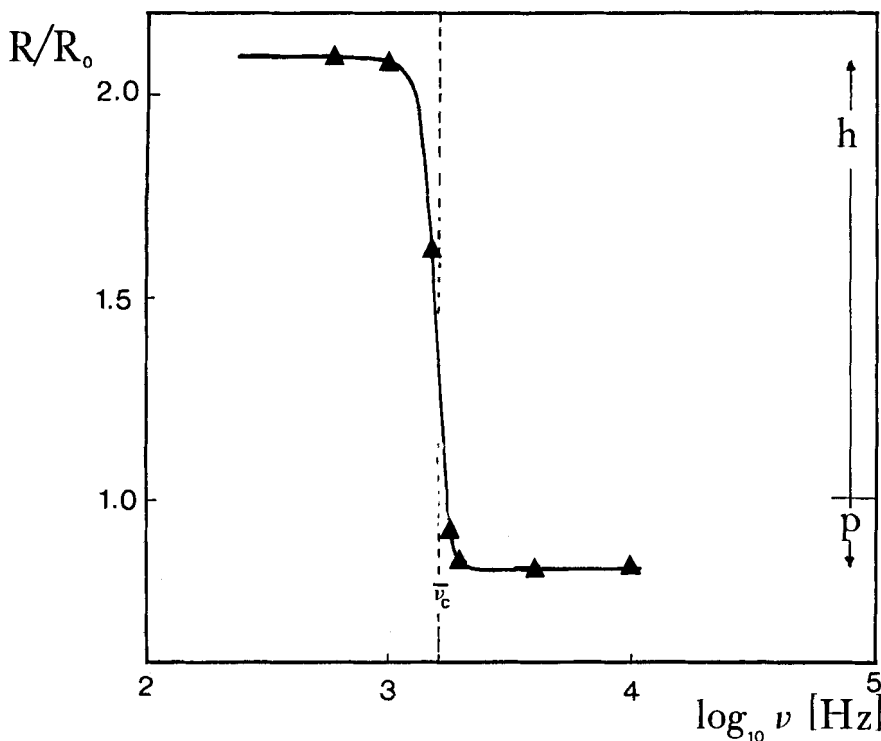
Figure 7. R/R_0 against the frequency of the aligning electric field for the nematic material $m = 6$ cooled from the melt [35]. The amplitude of the applied field was 300 V (r.m.s.)/120 μm, and was of a chosen frequency. For $R/R_0 \simeq 2.1$ or ~ 0.70 the material prepared is fully homeotropic or planarly-aligned respectively.

Note that the loss data of figure 6 and the permittivity data shown in [35] exhibit isobestic points in a frequency at which the loss or permittivity is independent of the director order parameter S_d. For the permittivity data, the isobestic point occurs at the cross-over frequency and its value is different from that of the loss factor for a given sample temperature. Inspection of equation (4) shows that if $\varepsilon''_\parallel = \varepsilon''_\perp$ in the frequency plot then ε'' is independent of S_d, i.e. the isobestic condition. Similarly the frequency at which $\varepsilon'_\parallel = \varepsilon'_\perp$ also gives (a different) isobestic point. Isobestic points are well known in physical chemistry in connection with equilibria of absorbing species [36].

3.5. Alignment processes studied by dielectric relaxation spectroscopy

The changes in macroscopic alignment of the liquid-crystalline side chain polymers occurring as a result of different thermal/electrical treatments can be monitored by dielectric relaxation spectroscopy because of the marked changes which occur in the permittivity and loss spectra.

In one experiment we prepared a planarly-aligned material by cooling the nematic polymer, $m = 6$, into the liquid crystal state with a saturating high frequency a.c. field applied. We found that this material would not change its alignment (as judged by the dielectric loss spectrum) when a.c. fields of a frequency higher than the cross-over frequency were applied to the material at a fixed temperature in its liquid crystal state. However, by going to sample temperatures in the biphasic range we found that the
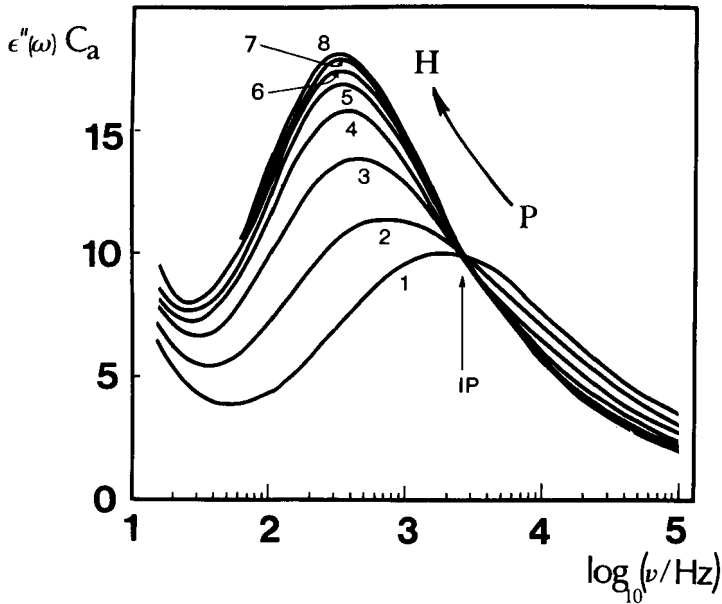
Figure 8. $\varepsilon''C_0$ against log (v/Hz) for the nematic polymer, $m = 6$, in its biphasic range ($T = 315\cdot7$ K) which is realigning in the presence of a saturating electric field of 300 V (r.m.s.) applied at 600 Hz. Curves 1–8 correspond to times of application of the aligning field of 0, 20, 40, 60, 80, 100, 120 and 140 min. respectively. As time proceeds, the sample transforms from planar to homeotropic alignment at this temperature.

material could be realigned to form a homeotropic material using low frequency a.c. fields. Figure 8 shows data obtained as follows. A fully planar sample was heated to 315·7 K in the biphasic range. At this temperature this partially-homeotropic material was subjected to 300 V (r.m.s.) at 600 Hz which forced the material to realign slowly from the planar to homeotropic condition. The process was followed by removing the aligning field at set times, scanning the dielectric spectrum, then reapplying the field for a further period, followed by further dielectric measurements. No changes in spectrum were observed when the scans were made. Under these conditions it appears that the sample realigns deterministically when the field is applied, and does not change its alignment when that field is removed. The isobestic point is apparent in the data of figure 8. The time scale for the transformation is very long. We have reported [35] extensive data for the transformations homeotropic → planar and planar → homeotropic, using high and low frequency directing fields for different temperatures in the biphasic range. In all cases the time for realignment are at least tens of minutes. We have shown [32] that the director order parameter $S_d(t)$ may be determined from such data and it follows an exponential dependence in on time. Moore and Stupp [37] have studied the realignment of certain main-chain liquid crystal polymers in a strong magnetic field B and have monitored the transformation from a random 'polydomain' to a fully-homeotropic domain using N.M.R. (^1H) spectroscopy. They derive the following relations for the transformation:

$$\tan \theta(t) = \tan \theta(0) \exp (-t/\tau), \tag{7}$$

where $\theta(t)$ is the orientation of a local director at t following application of the directing field at $t = 0$. $\tau = \gamma/(\Delta\chi B^2)$, where γ is an effective rotational viscosity

coefficient for the element and $\Delta\chi$ is the anisotropy of magnetic susceptibility. In their case $\langle S_d^2 \rangle$ is measured by their experiment, and they write

$$\langle S_d^2(t) \rangle = \int \varrho(\theta_d,\, t) \frac{[3\cos^2\theta_d(t) - 1]^2}{2} \sin\theta_d(t)d\theta_d(t)$$

$$\times \left[\int \varrho(\theta_d t) \sin\theta_d(t)d\theta_d(t) \right]^{-1}. \tag{8}$$

Here $\varrho(\theta_d,\, t) \sin\theta_d(t)d\theta_d(t)$ is the probability of obtaining the local directors in the solid angle around $\theta_d(t)$ given the initial distribution at $t = 0$. For the special case of a random polydomain transforming into a homeotropic monodomain in the presence of B they show that

$$\varrho(\theta_d,\, t) = \left[\frac{\sin[\tan^{-1}(\exp(t_r))\tan\theta_d(t)]}{\sin\theta_d(t)} \right],$$

$$\times \left[\frac{\exp(t_r)}{\cos^2\theta_d(t) + (\sin^2\theta_d(t))\exp(2t_r)} \right] \tag{9}$$

where $t_r = t/\tau$. Moore and Stupp [37] have fitted their data for the aromatic polyester liquid-crystalline polymer using equations (8) and (9) and find good agreement between theory and experiment for a low molar mass sample where the transformation goes to completion, but obtain poor fits for samples of intermediate and high molecular weights where the transformation is incomplete (i.e. $\langle S_d^2(t \rightarrow \infty) \rangle < 1$).

The extension of the approach of Moore and Stupp [37] to our dielectric data is possible if, instead of $\langle S_d^2(t) \rangle$ in equation (8), we determine $\langle S_d(t) \rangle$ and also write $\tau = \gamma/(\Delta\varepsilon(\omega)E^2(\omega))$. The form of $\varrho(\theta_d,\, t)$ given by equation (9), is true only for an initial distribution which is random. We are currently investigating the extension to cases of different initial distributions, as we have experimentally in our dielectrics experiments with the side-chain polymers.

It is important to emphasize that we found that both the smectic ($m = 8$) and nematic ($m = 5$, $m = 6$) liquid crystalline siloxane polymers would *not* realign in their liquid crystal states, but would realign, very slowly, in their biphasic ranges. However, it has been found [4, 38] that a smectic copolymer PG 296, whose structure has been described [4], realigns in the liquid crystal state at temperatures up to 20°C below the clearing temperature.

3.6. *Determination of the director order parameter S_d*

Using the expression derived by Attard *et al.* [32], equation (4) above, we may write

$$S_d = \frac{\varepsilon_z - \bar{\varepsilon}}{\varepsilon_\| - \bar{\varepsilon}} = \frac{1}{2}\frac{(\varepsilon_z - \bar{\varepsilon})}{(\bar{\varepsilon} - \varepsilon_\perp)},$$

$$= \frac{3\varepsilon_z - (\varepsilon_\| + 2\varepsilon_\perp)}{2(\varepsilon_\| - \varepsilon_\perp)}. \tag{10}$$

If the permittivity (ε') or loss factor (ε'') are determined for any two of the three reference materials homeotropic ($S_d = 1$), planar ($S_d = -1/2$) or unaligned ($S_d = 0$) and for the unknown material at the given frequency ω, then S_d follows from equation (10). Since the loss curves have been determined over the entire relaxation

range, it is possible to determine S_d for the unknown sample using all measured frequencies. For the data of figure 6 Attard *et al.* [32] have calculated S_d for the 'unaligned' material at each of the 19 frequencies using the data for homeotropic and planar materials as the two references. They find [32] S_d values all lie in the range -0.054 to $+0.036$ and the consistency of these values supports the method used. Similar determinations of S_d using the capacitance data [32] again give S_d close to zero, consistently, for the unaligned material. Further calculations of S_d for samples of intermediate alignments give values of S_d approximately constant for all frequencies used. Therefore we consider that equation (4) and the derived equations (10) provide a convenient means for determining the semi-empirical quantity S_d from experimental data for samples treated in this way. We note that equation (4) is not appropriate for a twisted-nematic monodomain and other regular structures. The model which leads to equation (4), as described by Attard [30] and Attard *et al.* [32], assumes that the electric field is continuous in the Z direction through the sample. This is one bound.

The other bound would be to assume that the dielectric displacement is uniform in the Z direction, and this leads to a different working equation for $\varepsilon(\omega)$, which is given in [32]. For systems having $\varepsilon_\parallel(\omega) \simeq \varepsilon_\perp(\omega)$ at all frequencies then S_d values determined by both representations will be close numerically. For the present liquid crystal systems this is not the case and the values of S_d determined using the different equations will be different. It seems likely that the 'true' value of S_d will lie between the two bounds. However, given the simplicity of a linear equation (equations (4) and (10)) and the fact that consistent values of S_d have been obtained from our data using equations (4) and (10), we consider that this is a useful method for the determination of S_d and will give all the qualitative features of its variation as the thermal/electrical treatment of a material is changed.

3.7. *Temperature variation of the dielectric relaxations*

As we have seen in figure 2, the shape of the plot log v_m against reciprocal temperature is approximately constant for data obtained over a limited range. This behaviour resembles that for low molar mass nematics and smectics, i.e. they appear to give Arrhenius behaviour with a constant apparent activation energy. However, the liquid-crystalline polymers exhibit an apparent glass transition (as judged by d.s.c.) and therefore, in common with other polymers [10, 39], we expect strong deviations from Arrhenius behaviour as T_g is approached from above. In order to study this behaviour we carried out dielectric measurements on the smectic polymer ($m = 8$) in its unaligned and homeotropically-aligned states [40] and have determined the plots of log v_m against temperature for both the resolved δ and α processes. Figure 9 shows the plot log v_m versus $(T/K)^{-1}$ which covers the frequency range 10^5 to $10^{-3.5}$ Hz. The expected curvature, being premonitory behaviour in relation to the apparent T_g, is clearly seen. Both loci fit the Vogel equation

$$\log v_m = A - \left(\frac{B}{T - T_\infty}\right), \tag{11}$$

and we find $B_\delta = 1800\,\mathrm{K}^{-1}$, $T_{\infty\delta} = 218.2\,\mathrm{K}$, $B_\alpha = 946\,\mathrm{K}^{-1}$, $T_{\infty\alpha} = 238.2\,\mathrm{K}$. The differences between the two values of T_∞ simply reflects the different curvatures of the plots for the δ and α processes. It is important to stress that δ and α processes tend to coalesce as T_g is approached and that a crossing of the two processes, predicted by the Vogel fits, will not occur in practice. In physical terms the reorientational motions
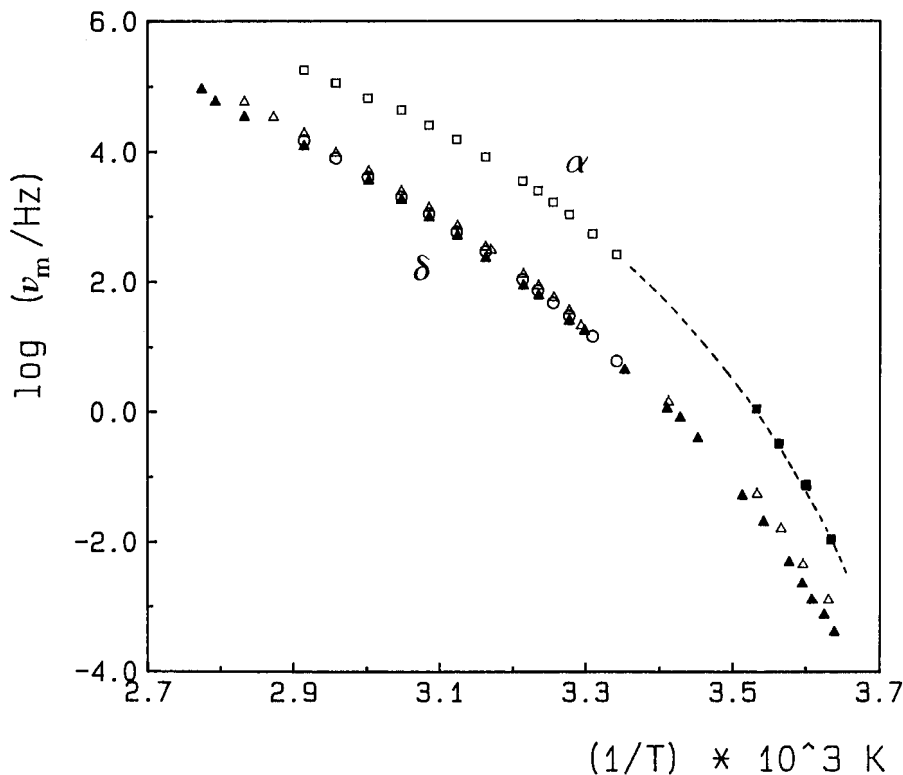
Figure 9.   log (v_m/Hz) against $(T/\text{K})^{-1}$ for the resolved δ and α processes in the smectic polymer, $m = 8$ [40].

involved in the δ and α processes becomes more and more cooperative as temperature is decreased, as for other glass-forming systems, so log v_m for both processes exhibits a critical slowing-down as T_g is approached.

3.8. *Effect of pressure on the dielectric relaxations*

We have studied the effect of pressure on the dielectric relaxation for unaligned and homeotropically-aligned samples of the smectic polymer, $m = 8$. As one example of our data figure 10 shows the behaviour of the loss for the homeotropic material as the applied pressure is increased to 1·52 kbar. There is a rapid movement of the peak to lower frequencies, without a significant change in its shape, and the peak height increases more than is predicted on the basis of changes of polymer density. The observed loss peak is mainly due to the δ process, in this case, and the increase in the height of the peak arises from an increase in the mesophase order parameter S with increasing pressure. The plot of log v_m versus p was linear and gave $(\partial \log v_m / \partial p)_T = 1·52 \text{ kb}^{-1}$. This value is comparable with those for the effect of pressure on the α relaxation in amorphous solid polymers (see [4] for a review) and the solid-state rotational process in rotator-phase substituted benzenes [42]. While $(\partial \log v_m / \partial p)_T$ can be related to an apparent activation volume ΔV from transition state theory [41, 44], its meaning is unclear for such cooperative relaxation processes.
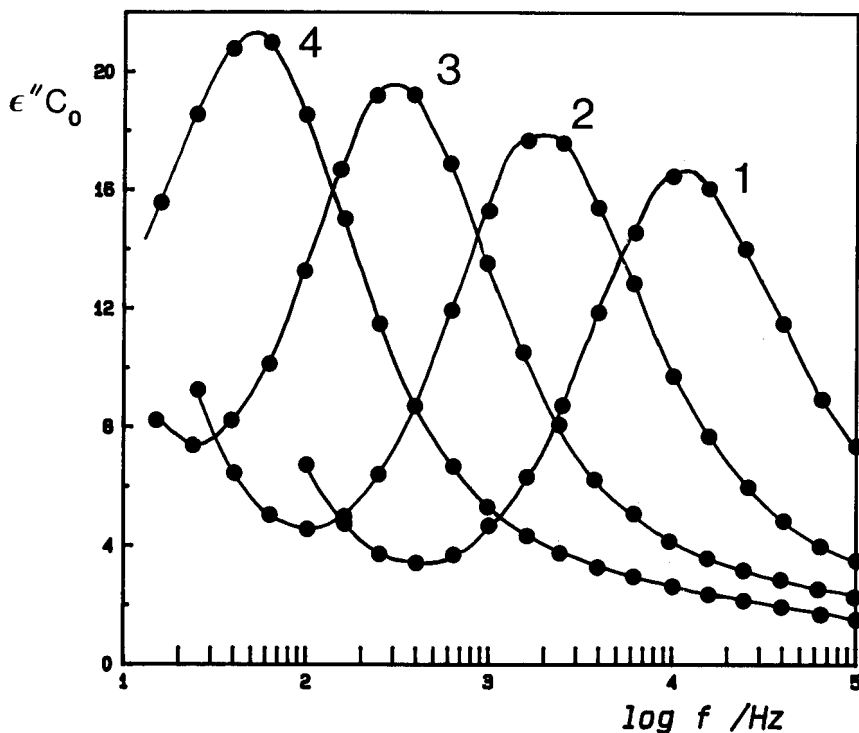
Figure 10. $\varepsilon''C_0$ against log (v/Hz) for the smectic liquid-crystalline polymer, $m = 8$, in its homeotropically-aligned state, showing the effect of applied pressure on the location of the δ process. Curves 1–4 correspond to 0, 0·51, 1·02 and 1·52 kbar applied pressure for a sample at 343·2 K.

We note that Heinrich and Stoll [43] have studied the effect of pressure on the dielectric properties of two liquid-crystalline polyacrylates (called P/H/2/CN and P/H/6/CN) in their unaligned states. They resolved the overall loss curves into δ and α processes and find that $(\partial \log v_m/\partial p)_T$ varies from 3·47 to 2·05 kb^{-1} as temperature is increased for P/H/2/CN from 373 to 410 K while for P/H/6/CN this quantity varies from 2·06 to 1·31 kb^{-1} as the temperature is increased from 350 to 390 K.

3.9. *Alignment phenomena in the absence of directing electric fields*

If a homeotropic sample of the nematic polymer, $m = 6$, is prepared by cooling from the melt in the presence of a directing electric field, and the material subsequently heated in the absence of an applied field to a temperature T_i in the biphasic range of this material (314–316 K), then a partially-homeotropically aligned sample will be prepared at T_i. We have found [45] that if the material is cooled slowly back into the liquid crystal state ($T < 314$ K) in the absence of an applied electric field then the 'recrystallization' of the isotropic component occurs with a strong correlation in orientation with the aligned liquid crystal phase present in the biphasic material. In other words, the material tries to reform the homeotropic monodomain on cooling back into the liquid-crystalline state. The closer T_i to the $T_{N\rightarrow\text{biphasic}}$, the greater is the extent of alignment-recovery. We have detected this phenomenon and we have quantified the extent of recovery using the dielectric loss curves measured during the cooling process and in the liquid crystal state. Apart from its intrinsic interest, this

observation is important since it makes clear the nature of the alignment processes which occur when a material is cooled from the melt through the biphasic range to the liquid crystal state in the *presence* of a directing field. As the material is cooled, *aligned* liquid crystal phase nucleates and propagation in these regions occurs by 'template recrystallization' (analogous to epitaxial growth in molecular crystals), and further regions nucleate with further lowering cᶠ temperature so that the formation of aligned mesophase results from both processes occurring in parallel. If the directing field is removed at any stage in the cooling process, alignment is still possible by the template recrystallization process, if the cooling rate is small. If the cooling rate is increased then nucleation of randomly aligned liquid crystal regions dominates the formation of the liquid crystal phase and the resultant liquid-crystalline material is effectively a mixture of aligned and unaligned mesophases. A full account of our experimental work is in preparation [45] and a theoretical model has been developed [46] which rationalizes the experimentally-observed recovery of alignment in the absence of a directing electric field.

4. Conclusions

We have shown that studies of the dielectric relaxation behaviour of certain liquid-crystalline side chain polymers give information on the anisotropic motions of the mesogenic groups attached to the main chain and also provide a direct and quantitative method for determining the nature and extent of macroscopic alignment of the material prepared by different thermal/electrical treatments. It is evident that dielectric relaxation spectroscopy will provide a useful experimental method for assessing the properties of guest/host liquid-crystalline polymer systems, especially those which show promise as media for optical processing (e.g. for second harmonic generation of laser radiation).

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