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## Liquid Crystals

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### Electric field induced AC alignment and realignment, a study of a liquid-crystalline copolymer having longitudinally and laterally attached mesogenic groups as side chains monitored through dielectric spectroscopy and optical thermomicroscopy

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**Electric field induced AC alignment and realignment, a study of a liquid-crystalline copolymer having longitudinally and laterally attached mesogenic groups as side chains monitored through dielectric spectroscopy and optical thermomicroscopy**

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A study of a liquid crystal side chain copolymer with a siloxane backbone has been carried out using dielectric relaxation spectroscopy and optical microscopy. We have found that this particular copolymer, a mixture of longitudinally and laterally attached mesogens, can be aligned both homeotropically and planarly between two electrodes using a directing AC field of specific frequency by cooling from the melt or more importantly at temperatures below the clearing point ( $T_c$ ). The switching of the material from homeotropic to planar and the reverse has been studied at temperatures below  $T_c$ . It is shown that the kinetics of realignment are strongly dependent on the electrical/thermal history of the sample. The dielectric data allows the state of alignment of the sample to be monitored and the molecular dynamics to be studied. The optical textures of the polymer which were subjected to different AC electric fields have been observed and provide complementary information to the dielectric work on the state of the aligned sample.

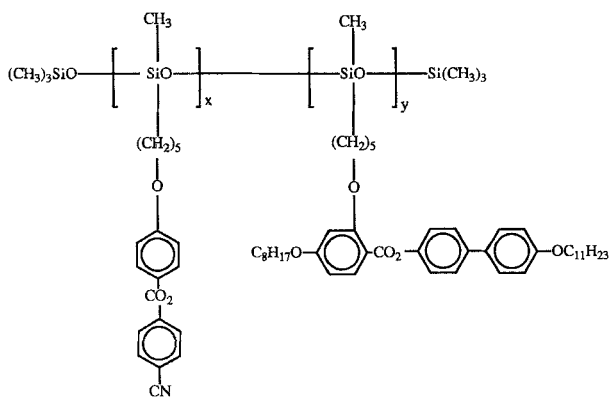
### 1. Introduction

Liquid-crystalline side-chain polymers are of current interest since they are electroactive, magnetoactive and show promise as materials for optical waveguides, second and third harmonic generation, optical data storage and processing [1-6]. An essential requirement for their physical study and for the different applications is that samples, usually in film form, should have been aligned macroscopically using electric or magnetic fields or surface forces. While the nature and extent of macroscopic alignment in such samples may be studied by different optical or spectroscopic methods [1] a particularly convenient method is that of dielectric relaxation spectroscopy, which also gives information on the molecular dynamics via the anisotropic motions of the dipolar mesogenic groups [1-4, 7-22].

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It has been found in our laboratories that the alignment behaviour of liquid-crystalline side-chain polymers varies with chemical structure and with the thermal and electrical (or magnetic) preparative treatments which are used. It was shown that siloxane-chain homopolymers could not be aligned using electric fields applied directly to a sample in its liquid crystal state [13–19] but alignment, usually homeotropic but sometimes anywhere in the range from homeotropic to planar, could be achieved by cooling from the melt in the presence of a strong AC electric field [13–19, 23, 24]. Partial alignment could be achieved by application of an AC electric field to a sample in its biphasic region [23, 25] but on subsequent cooling, either in the presence or absence of an external field, further alignment was obtained by a mechanism of template-induced alignment recovery [26, 27]. For siloxane-chain copolymers it was shown [28, 29] that homeotropic alignment could be achieved using an AC electric field applied to a sample in its liquid-crystalline state just below its clearing temperature  $T_c$ . The rate of alignment was shown to be strongly dependent on sample purity and its temperature [29].

Siloxane chain homopolymers and copolymers having mesogenic groups attached laterally to the backbone have been prepared recently [30–32]. The presence of small concentrations of laterally attached groups in a polymer containing longitudinally attached mesogenic groups gives a marked lowering of  $T_c$  and to a preference for the nematic over the smectic phase [32]. In the present work we present dielectric relaxation data and optical microscopy results for a *random* copolymer having the structure (I):



(I)

We have found that it is possible to align this material both by cooling from the melt and directly in its liquid-crystalline state using directing electric fields. It is shown that homeotropic (H), planar (P) or any intermediate degree of alignment may be achieved and that the nature and extent of alignment may be monitored by dielectric relaxation spectroscopy. The conditions required to obtain particular degrees of alignment have been studied and the optical textures of the resultant samples have been observed. In particular, we have followed the changes in optical texture of a sample during the conversions  $H \rightarrow P \rightarrow H$  caused by a directing electric field.

## 2. Experimental

The copolymer (I) was synthesized by the method described previously [30, 32]; it had  $x = 34.5$ ,  $y = 11.5$ . Using GPC it was shown that  $\bar{M}_w = 2.38 \times 10^4$ ,  $\bar{M}_n = 7.11 \times 10^3$  (polydispersity index  $\gamma = 3.35$ ). From DSC measurements the apparent glass transition temperature,  $T_g$ , was  $5.8^\circ\text{C}$  (onset), to  $8.2^\circ\text{C}$  (mid-point) and  $T_{NI}$  was about  $110^\circ\text{C}$ . The sample was formed as a disc 1 cm diameter,  $100\ \mu\text{m}$  thickness, sandwiched between two brass electrodes in a three terminal dielectric cell. The dielectric properties were measured as described previously [18, 19] using a GenRad 1689 Precision Digibridge ( $12$  to  $10^5$  Hz) and with temperature control of  $0.05^\circ\text{C}$  achieved by use of a temperature controlled water bath. The dielectric results are presented as  $C_p$  and  $G_p/\omega$  where  $C_p$  and  $G_p$  are the equivalent parallel capacitance and conductance, respectively, of the sample at frequency  $f$  ( $\equiv \omega/2\pi$ ). These quantities are related to the real part,  $\epsilon'(\omega)$ , and the imaginary part,  $\epsilon''(\omega)$ , of the complex dielectric permittivity by  $C_p = \epsilon' C_0 + C_e$ ,  $G_p/\omega = \epsilon'' C_0$ , where  $C_0$  is the inter-electrode capacitance and  $C_e$  is the stray edge capacitance. Observations of the optical texture were made with a sample mounted in a sandwich glass cell with transparent conducting electrodes contained in a Linkam programmable hot-stage attachment to an Olympus BHSP polarizing microscope. It must be noted that the surfaces of all the electrodes (metal and glass) were not pretreated in any way whatsoever and so any memory effect observed was not deliberately induced by surface pretreatment.

## 3. Results

### 3.1. Dielectric data

The dielectric loss spectrum for an unaligned sample was obtained at  $70^\circ\text{C}$ . The sample was aligned homeotropically by cooling from the melt in the presence of 300 V applied at 1 kHz. The plots of  $C_p$  against frequency for both homeotropically aligned and unaligned samples at  $70^\circ\text{C}$  exhibit dispersion due to relaxation, and cross at the crossover frequency  $f_0(T)$  (an isosbestic point). It is well known (see, for example, [23, 33]) that if a directing AC electric field,  $f_D$  is applied to a sample at temperature  $T$  then, for  $f_D < f_0(T)$ , the liquid crystal polymer, which in this case has a positive dielectric anisotropy at low frequencies, will tend to align to form the homeotropic state. For  $f_D > f_0(T)$  then planar alignment is favoured. Knowing  $f_0(T)$  from the unaligned and homeotropically aligned samples at  $T = 70^\circ\text{C}$  allows us to choose  $f_D$  values which are sufficiently smaller than  $f_0(70^\circ)$  (for homeotropic alignment) or are sufficiently greater than  $f_0(70^\circ)$  (for planar alignment) but at the same time avoid the dielectric heating effects and electro-hydrodynamic instabilities which arise due to the dielectric loss peak and the low frequency conductivity regimes [33]. Proceeding in this way we found it was possible to align the sample at  $70^\circ\text{C}$  using 300 V at 200 Hz to obtain homeotropic alignment, and then to realign this sample at the same temperature using 300 V at 20 kHz to obtain planar alignment (approximately 1 hour required). The dielectric loss spectra were obtained for these aligned materials over a range of temperature.

As examples of our results, figures 1 and 2 show plots of  $C_p(\omega)$  and  $G_p/\omega$  against  $\log(f/\text{Hz})$  for homeotropic and planar aligned and unaligned samples at  $70^\circ\text{C}$ . The crossover frequency is seen to be about 6 kHz at this temperature. From a simple macroscopic theory [25] it may be shown that

$$\epsilon'(\omega) = [(1 + 2S_a)/3]\epsilon'_{\parallel}(\omega) + 2[(1 - S_a)/3]\epsilon'_{\perp}(\omega), \quad (1)$$

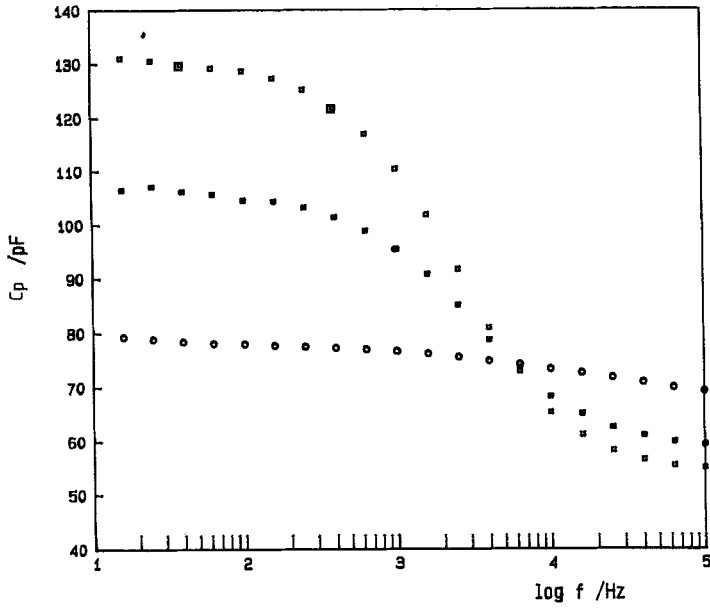


Figure 1.  $C_p(\omega)$  against  $\log_{10}(f/\text{Hz})$  for homeotropically aligned (□), unaligned (■) and planarly aligned (○) samples at 70°C. The crossover frequency  $f_0 \approx 6 \text{ kHz}$  at this temperature.

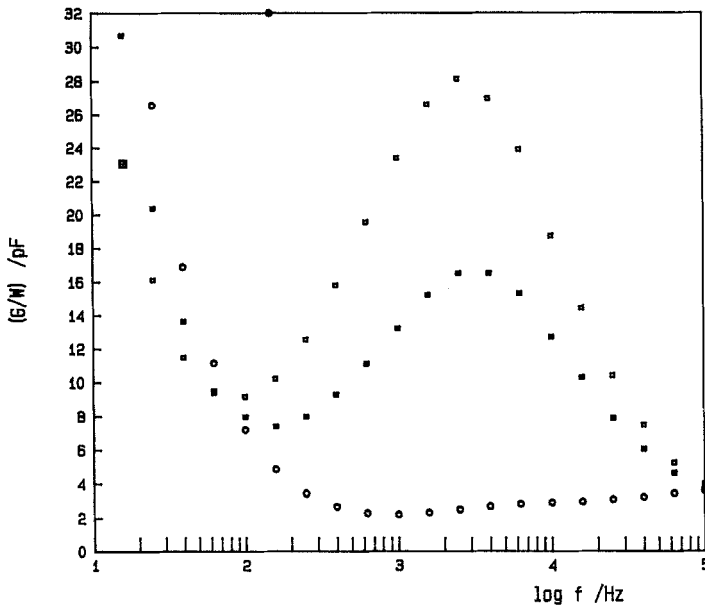


Figure 2.  $G_p/\omega = \epsilon''(\omega)C_0$  against  $\log_{10}(f/\text{Hz})$  for homeotropically aligned (□), unaligned (■) and planarly aligned (○) samples at 70°C. The isosbestic point  $\approx 100 \text{ kHz}$  at this temperature.

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where  $S_a$  is the macroscopic director order parameter and  $\epsilon'_{\parallel}$  and  $\epsilon'_{\perp}$  are the permittivities measured parallel and perpendicular to the director  $n$ , respectively, at frequency  $\omega$ . For  $\epsilon'_{\parallel}(\omega) = \epsilon'_{\perp}(\omega)$ , i.e. for  $\omega = \omega_0 = 2\pi f_0(T)$ , then  $\epsilon'(\omega)$  is independent of  $S_a$ , and all dispersion curves cross at  $\omega_0$ . The corresponding loss data at 70°C are shown in figure 2. Note that the loss peak at 3 kHz for the homeotropically aligned sample is nearly eliminated on going to the planar aligned sample. This peak corresponds to the  $\delta$  peak observed previously for siloxane chain homopolymers and copolymers in which the mesogenic side chain, terminally attached to the polymer backbone, contains an aromatic ester group and a cyano group positioned terminally in the end benzene ring [13–21]. This process is associated with the motions of the longitudinal component  $\mu_l$  of the dipole moment of the mesogenic side chain with respect to the director and is also known as the 00 relaxation mode [17, 19]. Since the aromatic cyano ester group has a very large dipole moment in comparison with that for the transversely attached mesogenic side-chain (see structure (I)), and since such side chains dominate ( $x/y = 3$ ), it follows that our dielectric studies probe mainly the motions of the aromatic cyano ester side chains, as before [13–21, 29]. The anisotropic motions of these side chains lead to the  $\delta$  process seen for the homeotropic sample and to further processes (termed 01, 10, 11 processes or modes [15, 17]). The loss curves of figure 2 cross at about  $10^5$  Hz, which is an isobestic point predicted by the analogue of equation (1) for the real permittivity [15]. The rising loss at higher frequencies for the planar aligned sample indicates that the loss maxima for the 10 and 11 processes occur at still higher frequencies at this temperature. Since  $\epsilon_{\infty\parallel} \approx \epsilon_{\infty\perp}$  it follows from inspection of the data for the homeotropically and planar aligned samples that  $\Delta\epsilon_{\parallel}/\Delta\epsilon_{\perp}$ , the relative relaxation strengths, are in the ratio 2.7:1. The rising loss at low frequencies for the data of figure 2 indicates the presence of a DC conductivity process.

We have determined the frequency of maximum loss ( $f_m$ ) and the crossover frequency ( $f_0$ ) for the permittivity for the sample at different temperatures using data similar to those of figures 1 and 2. The resulting loci are shown in figure 3. Both plots are curved downwards in anticipation of the apparent glass transition ( $1/T_g \approx 3.6 \times 10^{-3} \text{ K}^{-1}$ ). The temperature variation of  $f_m$  was studied for a siloxane homopolymer to very low frequencies when the curvature of the plot  $\log f_m$  versus  $T^{-1}$  was shown to conform to the Williams–Landel–Ferry equation [16]. We note that  $f_m$  and  $f_0$  are approximately parallel in this range and differ by about 0.2 units of  $\log f$ . These data indicate the frequency temperature conditions required for the alignment of the material by strong AC electric fields applied during cooling from the melt or directly in the liquid crystal state. In order to avoid dielectric heating effects which may destroy the alignment, it is necessary to use directing fields whose frequencies are sufficiently removed from  $f_m(T)$  at the given sample temperature, when alignment is induced in a liquid crystal sample. Figure 3 gives the required information. Also on cooling a sample from the melt in the presence of a directing field, the alignment behaviour is complex but is understood in terms of figure 3. Consider the case where a strong electric field at  $10^4$  Hz, say is applied to the polymer melt. On subsequent cooling into the liquid crystal state ( $1/T_c \approx 2.6 \times 10^{-3} \text{ K}^{-1}$ ), since  $f_D(T) < f_0(T)$  for  $2.6 \times 10^{-3} \leq 1/T \leq 2.80 \times 10^{-3}$ , homeotropic alignment is favoured initially and the aligned material forms by a kinetic process. As  $f_m(T)$  of  $10^4$  Hz is approached, dielectric heating may destroy the homeotropic alignment achieved previously. On further cooling, the sample temperature is reached for which  $f_0(T) = 10^4$  Hz (i.e. for  $1/T \approx 2.86 \times 10^{-3} \text{ K}^{-1}$ ) so at still lower temperatures planar alignment is favoured and the sample will attempt to realign to this macroscopic orientation. It is important to note also that

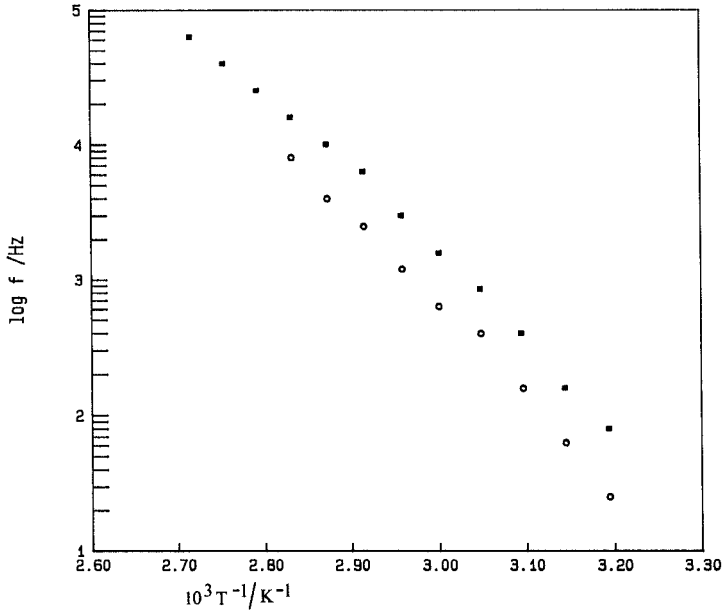


Figure 3. The variation of the crossover frequency  $f_0$  (■) and also the frequency of maximum loss,  $f_m$  (for the homeotropically aligned sample) (○) with sample temperature.

the rate of realignment for a siloxane polymer subject to a directing electric field in its liquid crystal state is strongly dependent on the sample temperature [29]; thus realignment from homeotropic to planar alignment may be slow at lower temperatures as the viscosity of the sample increases. This also means that the nature and extent of the alignment achieved during cooling from the melt to  $1/T \approx 3.1 \times 10^{-3} \text{ K}^{-1}$ , say, in the presence of the strong field applied at  $10^4 \text{ Hz}$  will depend upon the cooling rate. For samples cooled fairly quickly from the melt, homeotropic alignment may be retained at the lowest temperature due to the increasingly high viscosity of the polymer as  $T_g$  is approached. However very slow cooling is anticipated to lead to disalignment (by dielectric heating) of the homeotropically aligned material formed initially, followed by realignment to partially planar aligned materials at lower temperatures as the crossover frequency domain is traversed. For metal electrodes the energy from dielectric heating is quickly dissipated through the electrodes into the metal body of the cell and we do not anticipate any significant rise in the temperature. For glass electrodes some heating is anticipated, the consequences of which are discussed in the next section.

### 3.2. Optical microscopy

A sample,  $30 \mu\text{m}$  thickness, was contained between conducting glass electrodes (indium–tin oxide) and was mounted in a temperature controlled hot stage on the polarizing microscope. The sample was subjected to different thermal/electrical treatments in order to align it both homeotropically and planarly and to observe the resultant changes in optical properties. As we shall explain, the response of the sample is complicated; also the optical texture achieved is dependent upon the thermal-

/electrical history. Since it is not possible to present all of our optical results here, we summarize them, illustrating them with representative data.

In one experiment a voltage of 150 V at 10 kHz was applied to the molten sample and the sample was cooled into its liquid-crystalline state with the voltage maintained. Viewed through crossed polarizers the onset of liquid-crystal formation was observed in the voltage free region adjacent to the active electrode region. For a sample cooled to 105°C, figure 4(a) shows the unaligned and homeotropically aligned (optically extinct) regions, and demonstrates the good optical quality of the latter region. According to figure 3, homeotropic alignment is favoured on cooling with a strong voltage at 10<sup>4</sup> Hz. Also under these conditions the loss peak and the conductivity tail should not interfere appreciably with the alignment process. Annealing the sample at this temperature leads to an overall enhancement of the scattering from the unaligned region and to no change in the appearance of the homeotropically aligned region (see figure 4(b)). Further cooling to 95°C with the voltage maintained gave a further increase in scattering from the unaligned region and the appearance of a mottled texture (or graininess) in the homeotropically aligned region (see figure 4(c)). Annealing, with the voltage maintained, at this temperature produced marked changes in both regions, with the homeotropically aligned region developing a definite texture (see figure 4(d)). On cooling to 90°C, with this voltage maintained, the texture seen in figure 4(d) develops further and after 45 min has the appearance shown in figure 4(e). It is noticeable that the homeotropically aligned region has a globular texture and the unaligned region appears to contain droplets. The use of glass electrodes in these experiments enhances dielectric heating effects since the thermal conductivity of the glass is low (when compared with that of the metal electrodes used for the determination of the dielectric relaxation properties). These observations might be thought to be consistent with local melting in both regions produced via dielectric heating. However  $T_c$  is 110°C and it seems unlikely that dielectric heating to this extent could occur because the whole specimen would have to become isotropic. Also the configuration of the glass cell is such that a 20–30°C rise in temperature is highly unlikely. Therefore the development of the globular texture is likely to be associated with electrohydrodynamic instabilities arising from the fact that the applied field ( $f_p = 10$  kHz) is close to the crossover frequency ( $f_0 = 16.2$  kHz) at 82°C. Although the homeotropic alignment is disturbed (see figure 4(e)) the conoscopic image of the region is surprisingly good (see figure 4(f)).

In another experiment the sample was cooled slowly from the melt to 70°C in the absence of a field; then 150 V at 200 Hz was applied. Under these conditions homeotropic alignment is favoured giving a well-aligned region (see figure 5(a)) with a slight texture. The sample was subjected to 150 V at 20 kHz in order to induce homeotropic to planar realignment. As time progressed, the texture of the region slowly changed, as shown in figures 5(b), (c), as planar alignment was achieved at this sample temperature over a period of 60 min. A low frequency voltage, 200 V at 200 Hz, was applied at this sample temperature in order to realign the sample from P→H alignment; figures 5(d)–(g) show the response. There is a marked change after only 15 s and homeotropic alignment is deemed complete within 5 min as no further change is observed in the interval from 5 to 30 min. It is evident that the P→H transformation is much faster than the H→P transformation under these conditions. The conoscopic image (see figure 5(h)) shows that the homeotropic alignment is recovered within 11 min of application of the low frequency voltage. The sample was cooled from 70°C to room temperature in the absence of the applied voltage and had the appearance shown in figure 5(i) showing that a texture develops which reduces the optical quality of the



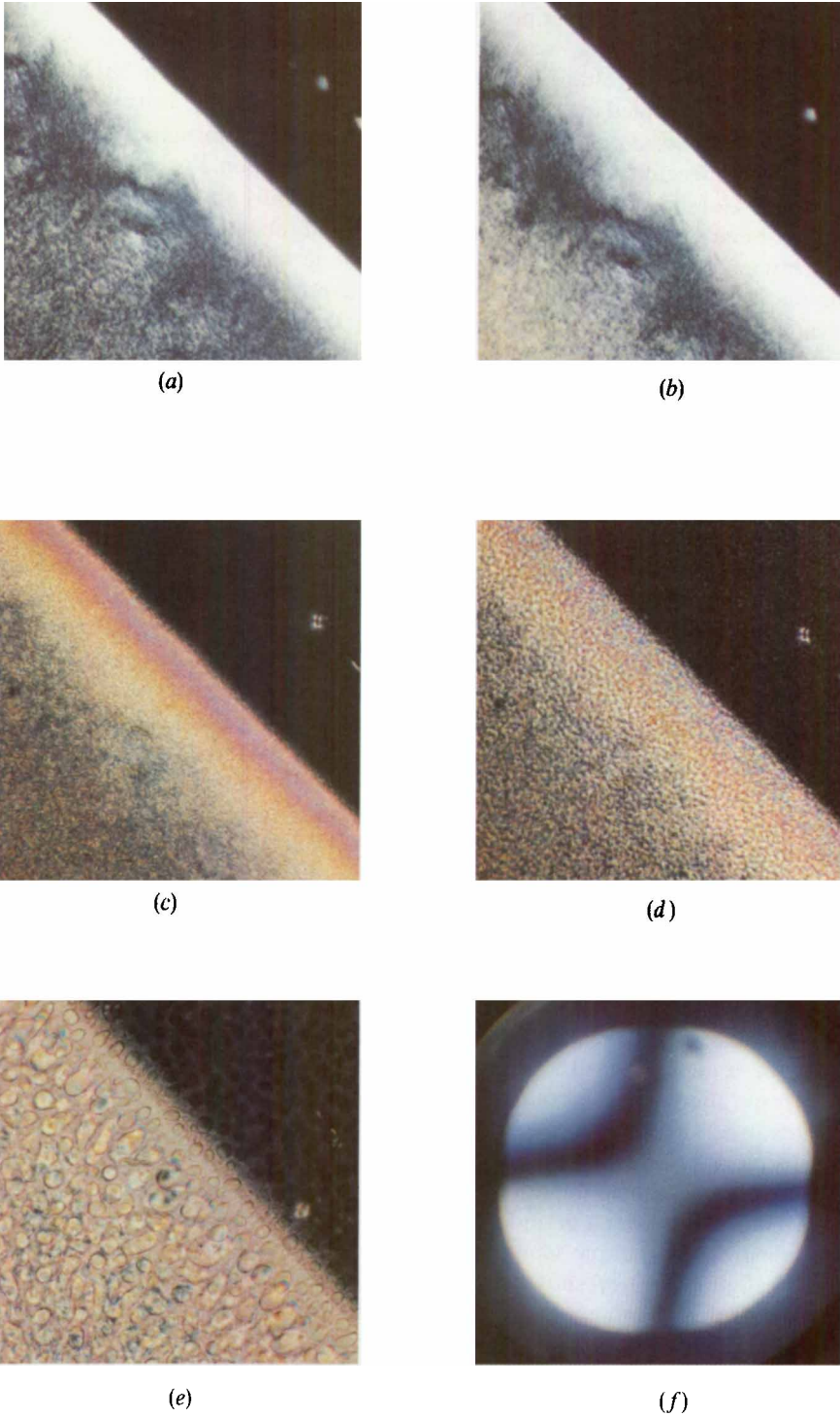


Figure 4. The optical texture of a sample cooled from the melt in the presence of 150 V applied at 10 kHz. Magnification  $200\times$ ; polarizer and analyser crossed. (a)  $T = 105^{\circ}\text{C}$ , held for 3 min; (b)  $T = 105^{\circ}\text{C}$ , after 15 min; (c)  $T = 95^{\circ}\text{C}$ , after 5 min; (d)  $T = 95^{\circ}\text{C}$ , after 15 min; (e)  $T = 90^{\circ}\text{C}$ , after 45 min; (f)  $T = 90^{\circ}\text{C}$ , after 50 min: the conoscopic image.

Figure 5.



(a)



(b)



(c)



(d)



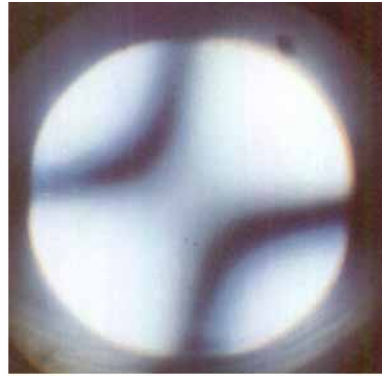
(f)



(e)



(g)



(h)

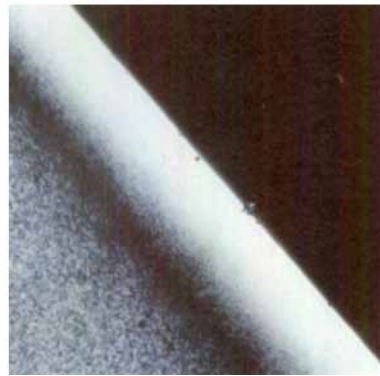


(i)

Figure 6.



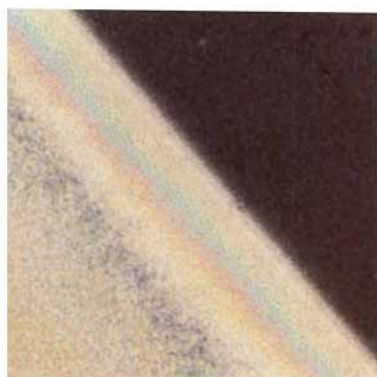
(a)



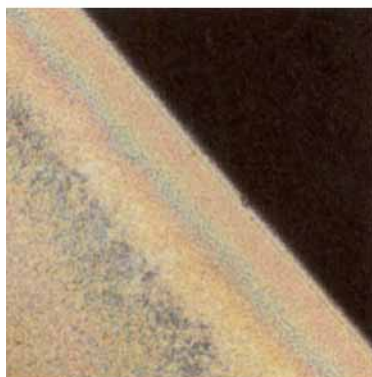
(b)



(c)



(d)



(e)



(f)



(g)



(h)

homeotropically aligned region. It is important to note that the stability of homeotropic alignment with no field is very good in the liquid crystal domain and so removal of the field at 70°C would not cause any noticeable disalignment.

In an attempt to obtain an improved homeotropically aligned film at room temperature, we cooled the sample from the melt in the presence of a strong AC voltage whose frequency was continuously reduced so that dielectric heating effects, and reverse realignment (H→P) could be avoided, using figure 3 as the guide. Starting at 150 V, 10 kHz at the clearing temperature, the frequency was reduced continuously in order to retain a difference of  $\log f_m - \log f_D \approx 1.0$  as the temperature was decreased. Figures 6(a)–(e) show our results for the initial part of the cooling experiment. The excellent contrast observed at high temperatures gives way to a good contrast at 82°C, where a slight texture in the homeotropically aligned region is detectable. Figures 6(f), (g) show the result at 72°C and 58°C. Although there is some texture in the homeotropically aligned region the contrast is good. Cooling from 58°C to room temperature in the absence of the field, a grainy texture appears in the homeotropically aligned region (see figure 6(h)) which is similar to that seen previously (see figure 5(i)) for a sample cooled to room temperature. It appears from figures 5 and 6 that it is possible to obtain homeotropically aligned material of good optical quality at higher temperatures, but on cooling to room temperature a scattering texture develops which reduces the optical quality of the film. It seems likely that this texture arises due to strain induced between the polymer and the glass substrate on cooling. The expansion coefficient of the polymer exceeds that of the glass and so the optically anisotropic liquid crystal film, which adheres to the glass, develops strains which manifest themselves as a residual birefringent, scattering texture.

#### 4. Conclusions

We have shown that films of the copolymer (I) may be aligned macroscopically either by cooling from the melt in the presence of a strong AC voltage or by application of an AC voltage to the film in its liquid-crystalline state. Both homeotropic and planar alignments may be achieved and the frequency, temperature conditions required have been established through the dielectric relaxation data. The dielectric spectra of

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Figure 5. (a) Sample aligned homeotropically at 70°C using 150 V at 200 Hz. Magnification 200 ×, polarizer and analyser crossed; (b) sample initially as in (a) but subjected to 150 V at 20 kHz at 70°C for 30 min, showing partial realignment to the planar orientation; (c) sample initially as in (a) but subjected to 150 V at 20 kHz at 70°C for 60 min, showing realignment to the planar orientation; (d) sample initially as in (c) but subjected to 200 V at 200 Hz at 70°C for 15 s, showing partial realignment to the homeotropic orientation; (e) sample initially as in (c) but subjected to 200 V at 200 Hz at 70°C for 1 min, showing partial realignment to the homeotropic orientation; (f) sample initially as in (c) but subjected to 200 V at 200 Hz for 5 min, showing realignment to the homeotropic orientation; (g) sample initially as in (c) but subjected to 200 V at 200 Hz for 30 min, showing full realignment to the homeotropic orientation; (h) the conoscopic image of the aligned region of a sample initially as in (c) but subjected to 200 V at 200 Hz for 11 min; (i) the sample initially as in (g) but cooled to room temperature, showing texture in the homeotropically aligned region.

Figure 6. Optical textures of a sample cooled from the melt in the presence of an AC voltage. Magnification 200 ×; polarizer and analyser crossed. (a) 110°C, 150 V, 10 kHz; (b) 102°C, 150 V, 5 kHz; (c) 96°C, 150 V, 3 kHz; (d) 87°C, 150 V, 1 kHz; (e) 82°C, 100 V, 500 Hz; (f) 72°C, 100 V, 200 Hz; (g) 58°C, 100 V, 70 Hz; (h) sample initially as in figure 5(f) but cooled to room temperature.

homeotropically and planarly aligned samples are very different and may be understood in terms of the anisotropic motions of the dipolar mesogenic head groups [15, 17]. It is shown that the rate of realignment from planar to homeotropic states is far faster than that from homeotropic to planar states for a sample, in the liquid crystal state, which is subjected to a high frequency (for H→P) or low frequency (for P→H) directing AC voltage. This asymmetry of time response is likely to be due to undetermined surface factors which favour the homeotropically aligned state and therefore give the material an apparent memory when aligned from H→P→H conditions in the liquid crystal state. We note that we observed a memory effect [26, 27] when cooling a partially-aligned sample from the bi-phasic region to the liquid crystal state, but in that case it is assigned to a template-induced recrystallization in the bulk material. We are currently studying this new memory effect for the copolymer (I) and are attempting to obtain quantitative data for the kinetics of the realignment processes H→P and P→H at different sample temperatures and for different applied fields of low and high frequencies.

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