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Pretransitional electro-optic response of 6CB liquid crystal in the isotropic phase

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In this work, the electro-optic response of a 6CB liquid crystal layer is studied using a sensitive differential technique. The layer is held at a temperature just above the nematic to isotropic phase transition. Transverse magnetic (p) polarized light incident on the cell is coupled to guided modes in the liquid crystal layer using prism coupling. The modes manifest themselves as sharp dips in the reflectivity as the angle of incidence is scanned. When a low frequency sinusoidal voltage is applied to the cell, the resonant mode shapes and excitation angles are altered at a frequency which is twice that of the applied field, resulting in a modulation of the reflectivity for a given angle of incidence. By synchronous observation of the modulated signal, a differential signal is recorded. Comparing the data with modelling generated from multilayer optics theory, two effects are then quantified. The first of these is an induced birefringence, varying quadratically with applied voltage, which is well understood and can be expressed in terms of Landau–de Gennes theory. The second is a field induced perturbation in the imaginary part of the optical permittivity, $\delta\varepsilon_i$, which implies a modification of the light scattering properties of the liquid crystal. The measurement of the latter effect is, as far as we know, a novel one, being only made possible by the remarkable sensitivity of the synchronous differential technique.

1. Introduction

Interest in the pretransitional effects which occur in the isotropic phase of liquid crystal materials at a temperature close to the nematic to isotropic (N–I) phase transition began in the early 1970s, when a number of workers [1–3] found that the field induced birefringence in liquid crystal material could be orders of magnitude larger than for standard 'Kerr' materials. The large effect was explained by the proximity of the nematic phase. Although the macroscopic order parameter for the isotropic phase is zero under no applied field, the microscopic picture is very different. Clearly, on a microscopic level, the liquid has an inhomogeneous distribution of free energy density, and in regions favoured by a low free energy density, nematic aggregates transiently condense from the isotropic melt. The average size of these aggregates is determined by the proximity of the N–I phase transition. Under an applied field, the isolated aggregates will tend to align along the field, and hence the comparatively large pre-transitional Kerr effect is orientational in origin. The linear variation of this induced

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birefringence, δn, with the square of the applied electric field E, characterizes the response of the cell and the Kerr coefficient is defined as

$$K = \frac{\delta n}{\lambda E^2}, \tag{1}$$

where λ is the wavelength of incident radiation.

De Gennes [4] extended the Landau theory of second order phase transitions and described this effect in terms of the macroscopic order parameter, S. The brief summary of the theory which follows is taken from Vertogen and de Jeu [5]. The expression for the Helmholtz free energy of a nematic liquid crystal is given by the Landau expansion

$$f = f_i + \frac{1}{3}AS^2 - \frac{2}{27}BS^3 + \frac{1}{9}CS^4, \tag{2}$$

where f_i is the Helmholtz free energy of the isotropic phase, S is the order parameter, and A, B, and C are the Landau expansion coefficients; all are functions of pressure and temperature. The additional free energy density f_E provided by an electric field is

$$f_E = -\frac{1}{3}\varepsilon_0 \delta\varepsilon_{ac} S E^2, \tag{3}$$

where $\delta\varepsilon_{ac}$ is the low frequency dielectric anisotropy in the perfectly aligned phase. In the isotropic phase with the field applied, $S \ll 1$ so the high order terms in S can be neglected and minimizing f with respect to S gives

$$S = \frac{\varepsilon_0 \delta\varepsilon_{ac} E^2}{2a(T - T_c^*)} \tag{4}$$

where $a = A/(T - T_c^*)$ is the temperature independent Landau coefficient, and T_c^* is a temperature just below the N/I phase transition. The induced birefringence is given by

$$\delta n = \frac{\delta\varepsilon_{max} S}{2\sqrt{\bar{\varepsilon}}} \tag{5}$$

where $\bar{\varepsilon}$ is the optical permittivity of the isotropic liquid crystal and $\delta\varepsilon_{max}$ is the optical dielectric anisotropy in the perfectly aligned phase. Hence we have

$$\frac{E^2}{\delta n} = \frac{4a\sqrt{\bar{\varepsilon}}(T - T_c^*)}{\varepsilon_0 \delta\varepsilon_{max} \delta\varepsilon_{ac}}, \tag{6}$$

the theory predicting that δn should be quadratic in applied field, and in addition, that the reciprocal Kerr coefficient be linear in temperature. Both these results have been shown to be true for a number of materials [3, 6, 7].

Clearly the simple phenomenological theory presented above cannot model the effect of aggregation within the liquid. The theory merely considered macroscopic effects. In order to model the light scattering properties of the isotropic fluid in the pretransitional regime, de Gennes extended the theory making the order parameter a function of spatial position, and introducing gradient terms to the free energy expansion. By applying the equi-partition theorem to the Fourier transform of the free energy expansion, it can be shown that the correlation length of the aggregates which form the scattering centres varies with temperature in the following fashion

$$\xi = \left[\frac{L}{a(T - T_c^*)}\right]^2, \tag{7}$$

where L is related simply to the elastic constants of the material. In addition, since the light scattered by the aggregates is proportional to the square of the fluctuation correlation length, the macroscopic light scattering effect was predicted to vary as the inverse of the reduced temperature $(T - T_c^*)$. This result was also found experimentally by a number of workers [8–10], indeed Stinson and Lister [8] were able to deduce the correlation length of the aggregates in MBBA which varied with temperature in the following way:

$$\xi = \frac{(6{\cdot}8 \pm 1{\cdot}0)}{(T/T_c^* - 1)^{1/2}} \text{ Å}. \tag{8}$$

It must be noted however, that despite the close agreement between theory and experiment which was generally observed, as the isotropic liquid crystal layer approaches the phase transition temperature, significant deviations from a simple Landau–de Gennes type behaviour are seen.

Despite the interest in this subject, there have been few reported studies of the effects of a field on the light scattering properties of liquid crystal materials in the pretransitional regime, although Dunmur refers to unpublished work on the field induced quenching of orientational fluctuations in his review paper [11]. In the present study, prism coupling to optical guided modes in a thin layer of 6CB liquid crystal is used to examine both the induced birefringence and the change in light scattering, which manifests itself as a change in the imaginary part of the optical permittivity, $\delta\varepsilon_i$ as a function of field and temperature.

2. Experimental

In this series of experiments, prism coupling to guided modes excited in the liquid crystal layer was used to determine both the voltage induced birefringence, and the light scattering properties of the liquid crystal. The cell geometry is shown in figure 1; it consists of a ≈ 4 μm layer of 6CB liquid crystal confined between two high refractive index ($n = 1{\cdot}8$) 60° pyramids. The square pyramid faces were coated with ≈ 50 nm of silver, after which half of each silver surface was coated with 20 nm of 60° evaporated silicon oxide (SiOx). The SiOx gives good homogeneous alignment of the liquid crystal in the nematic phase and coating half the cell with this aligning agent enabled a comparison of the response to the electric field in the two halves. It was conjectured that there would be some evidence for the persistence of the surface alignment in the isotropic phase as compared with the uncoated part of the cell. This effect has been reported by Hsiung *et al.* [12], for 5CB liquid crystal material when the cell walls were treated with a homeotropic surfactant.

The cell was mounted in a thermally insulated box, and the temperature inside the box controlled to $\pm 0{\cdot}1$°C. p polarized light (transverse magnetic) of wavelength 632·8 nm incident on the cell's uppermost silver surface is mostly reflected but a small percentage of it tunnels through the thin silver film and propagates in the liquid crystal layer. At certain angles of incidence, corresponding to the guided mode excitation momenta, the system is resonant, and a large proportion of the incident energy tunnels through the silver layer and may propagate for substantial distances in the liquid crystal layer. This results in a sharp dip in the reflected signal.

An AC electric field of 900 Hz was applied to the cell using the silver layers as electrodes and the isotropic liquid crystal responded by developing both an induced birefringence and a smaller change in the light scattering properties of the liquid crystal in phase with the applied field. The degree of birefringence induced by a given field

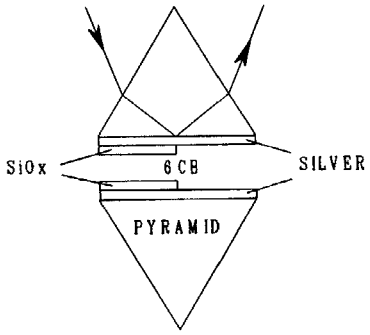
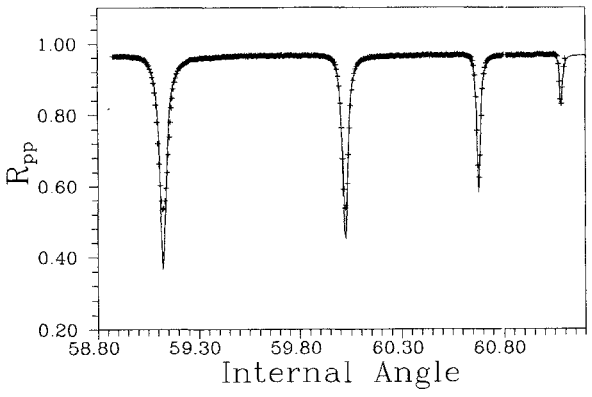


Figure 1. Cell geometry.

depends on the temperature of the sample, so to help quantify this, the experiment was performed at three different temperatures in the region of the cell which had the aligning layers, and at one temperature in the other region. It should be appreciated that the induced birefringence affects the angular positions of the modes, whilst the induced change in light scattering affects the sharpness and depth of the reflectivity minimum. Therefore at any given angle, a modulation of the reflectivity signal, R_{pp}, is recorded which reflects the changes in the width and position of the modes. This modulation is at a frequency of 2ω, where ω is the frequency of the applied field, because the liquid crystal material under investigation has no effective permanent dipole moment and therefore responds to the magnitude of the field applied, but is insensitive to its direction. Using a lock-in amplifier to detect the 2ω signal, it was possible to obtain measurements of the angular dependent differential reflectivity for RMS fields up to 0·9 V μm^{-1}. All data were taken using the TM_3 mode, since this was the sharpest and deepest mode which had been observed giving the largest differential optical response. In addition, the frequency of the applied field was chosen to be low enough for the liquid crystal to respond in phase with it. If the frequency is too high then the liquid crystal responds to the RMS field by developing a constant, unmodulated birefringence which is not detectable differentially. Note that the data obtained must be scaled appropriately to account for the response of the lock-in amplifier to the input waveform. In addition to the differential data, undifferentiated data were recorded for the angular dependent zero field reflectivity at each new temperature in order that the absolute values of the optical permittivity and the cell thickness could be found.

3. Results

It was expected that the changes which took place as a result of the applied field would be a combination of the induced birefringence, which gives a shift in the mode excitation angle, and a change in the scattering properties of the material, which would appear as changes in the mode depth and width. This microscopic scattering effect is well modelled by changing the macroscopic value of ε_i for the material. However, before these effects could be modelled, it was necessary to know the values for the optical permittivity of the isotropic liquid crystal layer in the absence of an applied field in order to predict reflectivity curves which are compared with data. This was done using multilayer-optical modelling [13]. Figure 2 (*a*) shows the best agreement which could be found between the theory (solid line) and the data (crosses), when the thickness and optical permittivity of the liquid crystal were varied. There is quite obviously a problem



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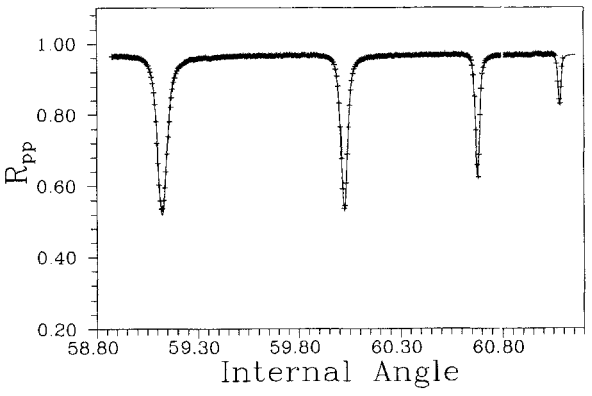
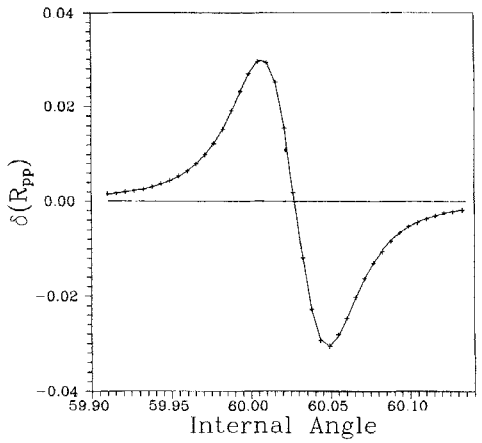


(*b*)

Figure 2. (*a*) Comparison between theoretical modelling and the data without allowing for thickness spread or laser beam divergence. (*b*) Comparison between theory and data allowing for a small thickness spread of $\pm$ 0·048 μm across the beam and a laser beam divergence of 0·9 mrad.

here with the relative depths of the modes—if the TM_1 guided mode's depth is modelled so that it agrees well with the data by adjusting the value of ε_i then the other guided mode depths become progressively too deep to agree well with the data. This problem is mainly caused by a small thickness spread in the cell which affects the lower momentum guided modes more than the higher ones, since the former are much more sensitive to the thickness of the liquid crystal layer. The other factor which must be taken into account is the small divergence of the laser beam. Clearly, for guided modes which have a half width of only 0·08°, the divergence of the laser beam will give a noticeable shallowing in the mode depth. Once these two factors are also incorporated in the model, then a very good fit to the data is obtained (see figure 2 (*b*)). The zero field parameters of the liquid crystal layer found from such a fit are then substituted into the differential modelling program. This program first evaluates the reflectivity curve for the zero applied field case using the parameters obtained from the previous fit, then introduces a small birefringence and an even smaller change in ε_i to produce a second reflectivity curve. Finally, this new curve is subtracted from the original one to give the



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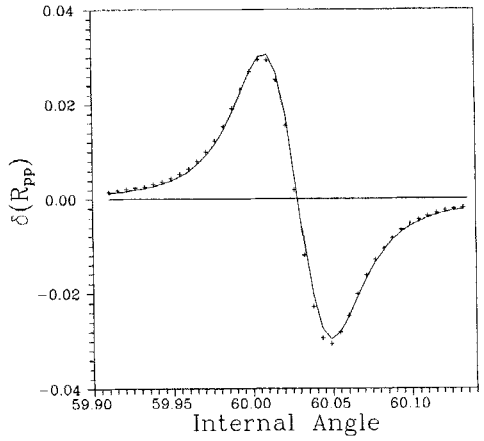

(*b*)

Figure 3. (*a*) The best theoretical fit (solid line) to the data (crosses) taken at 2·539 volts and 30·8°C. (*b*) The fit obtained if the small change in ε_i is not included.

'differential' trace. This is then compared with the experimental data and the fitting parameters, that is the birefringence and the change in ε_i are adjusted until the agreement between theory and data is acceptable. Figure 3 (*a*) shows the data taken at 30·8°C and the best theoretical fit obtained. In figure 3 (*b*) the comparison of theory with data is shown if the changes in ε_i are not included and it is quite clear from this that the changes in scattering are a necessary part of the model. Figure 4 shows the variation of $\delta\varepsilon_r$ with E^2 for all four different temperatures; the relation is clearly linear. In addition, if the reciprocal Kerr coefficient is plotted as a function of temperature for the data taken from the region of the cell with surface aligning layers then again the relation is found to be linear. This is shown in figure 5. It is however noticeable that the data taken from the region of the cell with no surface aligning layers, seem to have a larger induced birefringence, at a given temperature, than for the SiOx coated region of the cell. The variation of $\delta\varepsilon_i$ with E^2, shown in figure 6, is the most startling result, since it clearly shows that as the temperature is reduced towards T_c for a given applied field, the

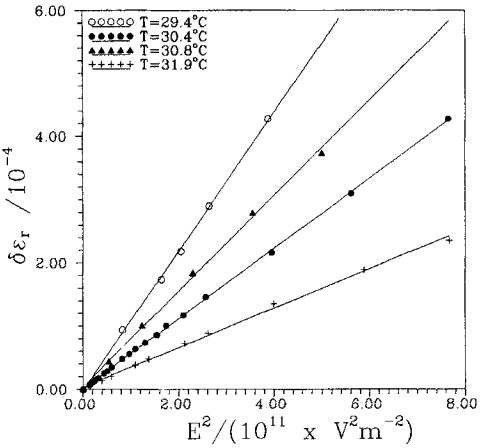

Figure 4. Variation of $\delta\varepsilon_r$ with E^2 Note that the solid triangles are results obtained in the region of the cell with no surface aligning layers.

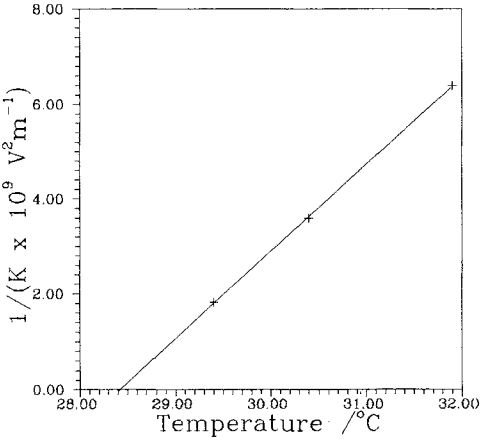

Figure 5. Variation of the reciprocal Kerr coefficient with temperature for the region of the cell with surface aligning layers.

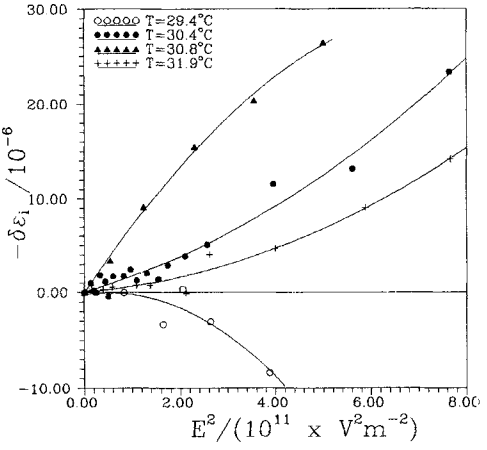

Figure 6. Variation of $\delta\varepsilon_i$ with E^2. Once again the solid triangles are obtained in the region of the cell with no surface aligning layers.

suppression of fluctuations first grows to a maximum and then rapidly diminishes, until close to T_c there seems to be an increase in the scattering properties when a field is applied. Note that the solid lines drawn through the data points are not theoretical fits but are merely to guide the eye.

4. Discussion

It is clear from the results obtained that the changes in ε_r with both field and temperature follow closely the Landau–de Gennes type behaviour. Moreover, using the gradient of the graph in figure 5, together with equation (6), the Landau expansion coefficient a may be deduced. This coefficient is essentially a measure of the magnitude of the effect and here $a = (23{\cdot}3 \pm 0{\cdot}4) \times 10^3\,\mathrm{J\,m^{-3}\,K^{-1}}$. This value is of the same order as that found for MBBA.

The changes observed in the ε_i however are more complex. Clearly there are two physical processes occurring, with one dominating close to the phase transition temperature and the other having a larger effect at higher temperatures. These results may be explained by examining the free energy of the nematic-like aggregates. There are two effects which need to be considered when discussing the field induced change in scattering. The first is the index mismatch between the aggregate and the isotropic melt, with and without an applied field. The second and probably more dominant is the size change of the aggregates under an applied field. We also need to consider both bulk and surface regions of the nematic-like aggregates. If a field is applied to a system made up of isotropic fluid together with nematic-like aggregates, then the total free energy of the system is reduced. This leads to the slight increase in T_c^* which has been measured indirectly through observations of the small increase in the first order phase transition temperature, T_c [14]. So an aggregate which aligns in the direction of the field will have its bulk free energy reduced, since it is the bulk of the aggregate which aligns along the field. Clearly one cannot say the same for the surface region. The effect of an applied field here is to set up some anisotropic elastic strain within the surface region, therefore increasing its free energy. These two effects compete with each other and it is clear that in the high temperature regime, where the aggregates are smallest and the surface to volume ratio of the aggregate is largest, the effect of an applied field may well be to increase the aggregate free energy which will both diminish the dimensions of existing aggregates and make the formation of others less likely. As the temperature is reduced towards T_c and the surface to volume ratio is diminished with increasing aggregate dimensions, the bulk effect begins to dominate, and close to the phase transition a growth in aggregate size may result from the application of a field. Since the scattered intensity is proportional to the square of the fluctuation correlation length, we expect the measured variations in $\delta\varepsilon_i$ to vary with temperature accordingly.

The larger changes in $\delta\varepsilon_r$ at a given temperature for the region of the sample without the SiOx aligning layers may also be explained using a free energy argument. Consider an aggregate which has transiently condensed out of the isotropic phase and is situated close to the surface. Such an entity will be affected by the homogeneous surface alignment and it is to be expected that on average there will exist a small spontaneous birefringence in the alignment direction. If a field is now applied perpendicular to the alignment direction (as in this experiment), the aggregate cannot minimize its free energy as effectively as it would in the absence of the surface aligning layers. The bulk of the fluid is of course unaffected by the surface layers and hence a birefringence is induced in the direction of this field; however because of the conflicting energy considerations at the surfaces, there will be a smaller contribution to the total

birefringence induced from the surface regions. Hence, the total birefringence is reduced in the area of the cell with surface aligning layers as compared with the area of the cell with no surface alignment layer.

5. Conclusions

A differential detection technique with optical excitation of guided modes has been used to probe the pretransitional effects in the isotropic phase of 6CB. The experiments confirm the relation predicted by de Gennes' theory of a linear variation of the reciprocal Kerr coefficient with temperature. In addition, field induced changes in light scattering have been observed and the variation with temperature has been explained by considering the surface and bulk free energies of nematic-like aggregates in response to an applied field. There is also evidence for the suppression of the induced birefringence when surface aligning layers are present in the cell, and this effect is also explained using a free energy argument for this material with positive dielectric anisotropy.

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