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Electric Field Induced Phase Transitions and Colour Switching in the Blue Phases of Chiral Nematic Liquid Crystals†

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The phase behavior and electro-optic phenomena observed in a new system of blue phase mixtures have been determined. The mixtures, which include both cyanobiphenyl and chiral ester components, have relatively high pitch values (~0.3 μm) but nonetheless exhibit broad blue phase temperature ranges (~2.5°C total). On application of electric fields to samples of these materials, colour switches and phase transitions to both turbulent chiral nematic and homeotropic nematic states were induced in both BPI and BPII. Both of these electric field induced phenomena are described as functions of the applied voltage and frequency. The response times of these field effects were also determined with high accuracy and found in the case of the field transitions to be extremely fast (~100 μs). The mechanism associated with the field induced colour switch was found to have two distinct response times associated with it, one fast (~100 μs) and the second much slower (~1–10 ms). Finally, the relaxation phenomena observed for each of these field effects in BPI and BPII are described. These relaxation mechanisms give evidence supporting the belief that the structure of the fog phase (BPIII) is linked to that of BPII.

1. INTRODUCTION

Blue phases are mesophases which exist between the chiral nematic and isotropic phases of certain chiral materials. Usually they exist over a very small temperature range (<1°C) within which up to three thermodynamically distinct phases, BPI, BPII and the so called fog phase (BPIII), may occur. While the occurrence of blue phases was once regarded as something of a curiosity associated with the lower lying chiral nematic phase, over the past decade there has been increasing interest in characterising these mesophases as true liquid crystal phases and reviews of both the theoretical[1] and experimental[2,3] progress to date have been published. Through a combination of theoretical and experimental research, it is now widely accepted that certainly BPI and BPII, and possibly[4] also BPIII have specific cubic structures. Much of the experimental research into blue phase systems has included the examination of their structure through Bragg reflection spectra and electric field

†Presented in part at the 11th International Liquid Crystal Conference (1986).

phenomena.[5] In addition, the phase diagrams of blue phase mixtures[6] have been used to establish the dependence of their range of existence on the pitch of the systems as well as to predict and explain electric field induced phase transitions which have been observed in these mesophases.[1,7]

In this paper we extend our previous work on electric field effects in blue phase systems[8] to a new series of mixtures of chiral nematic liquid crystals. We consider the phase behavior of these broad range blue phase systems together with their optical and electro-optical properties. Particular emphasis is placed on the mechanisms associated with electric field induced effects and their relaxation.

We show that in these new mixtures a number of different electric field effects may be induced in both BPI and BPII, including distortions of the lattice structure and extremely fast transitions (~100 μs) from both of the lower lying blue phases to a homeotropic state. In addition, we consider the mechanisms associated with these phenomena. Finally, we consider the relaxation processes from the electric field induced states and discuss these results with respect to the liquid crystal structure of BPIII.

2. MATERIALS AND PHASE BEHAVIOR

Four chiral nematic liquid crystal mixtures denoted HGC1–4 were studied with compositions shown in Table I. The components of these mixtures were the BDH produced[9] chiral esters CE1, CE2, CE3 and small amounts of CB15, and up to 60% of eutectic nematic materials, to untwist the chiral base sufficiently to produce visible Bragg reflections. The chiral base had the composition CE1 (28.6%), CE2 (35.7%), CE3 (35.7%). Each mixture exhibited all three blue phases, BPI, BPII and BPIII as well as chiral nematic phases, and their transition temperatures, determined on heating at 0.1°C/min by optical microscopy, are given in Table II.

In the mixture HGC2, BPII was biphasic with the fog phase over approximately 0.3°C. These mixtures all exhibited extensive supercooling of BPI over a 6°C range, though the chiral nematic phase could always be restored from the supercooled BPI by application of an external stress or electric field to the sample.

One of the most interesting features of this system of blue phase mixtures was the comparatively large temperature range over which the blue phases existed (~2.5°C) as shown in Table II. It is interesting to consider why this system of materials should exhibit such stable blue phases. It is well known that the chirality of a liquid crystal system strongly influences the occurrence of the blue phases (see

TABLE I

Weight Percentage Composition of the Blue Phase Mixtures

	Chiral Base	CB15	K18	E7	E49	E130
HGC1	42.8	10.9	24.6	21.6	—	—
HGC2	51.5	8.5	22.8	17.1	—	—
HGC3	57.1	—	31.6	1.1	10.1	—
HGC4	60.8	—	—	—	—	39.2

TABLE II

Transition Temperatures of the Mixtures HGC1–4

	Temperature (°C)				
	Ch → BPI	BPI → BPII	BPII → fog	fog → I	Total BP Range
HGC1	81.9	83.1	84.0	84.2	2.4
HGC2	97.8	98.3	98.9	100.5	2.7
HGC3	105.3	105.7	107.2	107.4	2.1
HGC4	114.7	115.6	116.3	117.1	2.4

Refs. 3, 6, 11 and references cited therein). The pitches of these mixtures were determined to be ~0.30 μm within their blue phases,[10] though this value varied slightly both from mixture to mixture and with temperature. In addition, there was no direct correlation between the pitch of a system and its blue phase range.

Clearly the stability of the blue phases is not determined solely by the temperature and chirality of the system, a result which agrees with the observations of Stegemeyer *et al.*[3] Nonetheless, the data presented here are distinct from any included in reference 3 in that the range of the blue phases (~2.5°C) is much larger than has been observed in systems of comparable pitch; average values quoted in reference 3 for $p \simeq 0.24$ μm are ~0.3°C and even smaller for longer pitches. This apparent anomaly is interpreted as being related to the fact that each of the mixtures HGC 1–4 has several components and characteristically broad phase transitions.[10]

3. EXPERIMENTAL DETAILS

The optical and electro-optical properties of the blue phases of these materials were examined as a function of temperature as well as the voltage and frequency of the applied electric field. The liquid crystal material was contained in sealed glass cells of 7.5 μm separation with Indium Tin Oxide (ITO) transparent electrodes and rubbed polyimide alignment layers in the twisted nematic configuration. The measurements were carried out using a specially constructed apparatus, outlined below, which has been described in detail elsewhere.[10] The apparatus was based on an Olympus BH2 polarising transmission/reflection microscope. A semi-silvered mirror placed in the tube of the microscope diverted half of the light reflected from or transmitted by the liquid crystal to a suitable detector. This detector was either a Rofin-Sinar RSO 6000 Optical Spectrum Analyser, when the spectral characteristics of the material were to be measured, or a storage oscilloscope (or a VELA Data Harvest System used as a transient recorder) for the electro-optic characterisation. These detectors were linked to a BBC microcomputer to allow signal averaging and accurate data analysis. The apparatus with these optical and electro-optical detectors had an accuracy of ±0.5 nm, in wavelength, and ±3 μs, in response time, respectively. Using this microscope/detector configuration, half of the light from the sample was detected, while the remainder passed through the microscope optics undeflected. This latter portion made it possible to photograph or observe the blue phases while simultaneously detecting their optical and electro-

optical properties. Electric fields were applied to the samples as described previously.[8] The temperature of the liquid crystal was regulated to ±0.05°C by a Mettler FP82 Hotstage and FP80 Control Unit.

The optical and electro-optical effects observed in the blue phases in these materials are presented in the sections below. Typical results for the mixtures are described since the phenomena recorded were found to be characteristic for all of the mixtures studied.

4. ORIENTATION EFFECTS IN BPI AND ELECTRO-OPTIC PHENOMENA

For each of the mixtures described, the wavelength of the Bragg reflected light from the blue phases was measured as a function of temperature using the apparatus outlined above. Because the glass cells containing the liquid crystal were relatively thin (7.5 μm) with good alignment layers, the blue phase textures observed were extremely homogeneous and only one Bragg peak corresponding to a specific orientation of the BPI body-centred cubic lattice was measured at each temperature.

It was found that the wavelength of light reflected from BPI was strongly dependent on whether the material had been heated into BPI from the chiral nematic phase or cooled from BPII. This hysteresis is shown in Fig. 1 which includes the temperature dependence of the Bragg-reflected wavelength from both BPI and BPII. It can be seen that the light reflected from BPI was always at shorter wavelengths on heating than on cooling and the measured ratio was $1/\sqrt{2}$ which is consistent with the BPI lattice adopting orientations resulting in the (200) and (110) reflections, on heating and on cooling, respectively.

The electric field effects which were observed in both BPI and BPII depended on the magnitude and frequency of the applied field, as has been found for other materials.[7,8] Fig. 2 shows typical results indicating which effect occurred within a particular voltage/frequency range in the BPI of HGC1. Essentially three different electric field induced phenomena were observed: 1) a small shift in the wavelength of the Bragg reflected light, 2) a transition to a chiral nematic focal conic texture (turbulent at lower frequencies), or 3) a switch to a nematic state in which the molecules adopted a homeotropic configuration. These effects are denoted "λ shift," "turbulent focal conic" and "BP → homeotropic" in Fig. 2 respectively.

1. The small shift in the Bragg-reflected wavelength induced at low voltages was entirely analogous to the small wavelength shifts observed in both BPI and BPII of other systems.[7,8] Such small shifts in the Bragg reflected wavelength were also observed in BPII, and in both cases this effect may be attributed to a distortion of the blue phase lattice in the direction of the electric field caused by a rotation of the molecules into the field direction, analogous to those reported by Pieranski and Cladis.[13]

2. At intermediate field strengths and frequencies a turbulent cholesteric fan texture was induced across the whole of the electrode area immediately the field had been applied. In contrast with other systems,[8] there was no gradual nucleation and growth of this texture, nor was it stored on removal of the field.

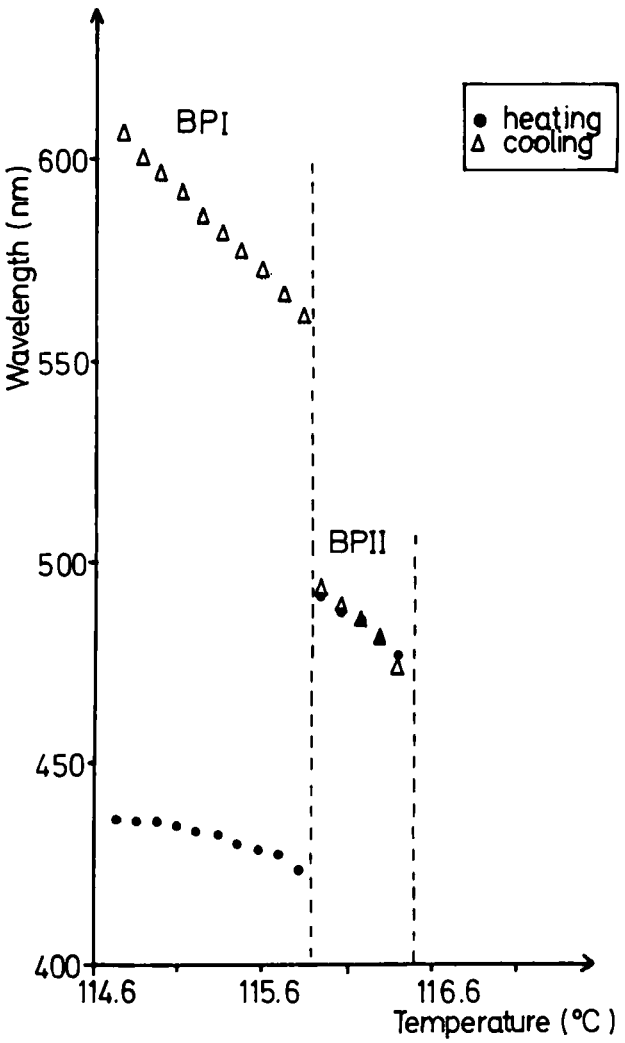


FIGURE 1 The temperature dependence of the Bragg reflections in BPI and BPII of HGC4 detected from a homogeneously aligned sample 7.5 μm thick. Note the differences observed in the orientation of BPI on heating and cooling the mixture.

3. At higher field strengths and frequencies, the BPI structure was completely unwound to a homeotropically aligned nematic phase as indicated by conoscopy. This realignment of BPI into the homeotropic state was found to be extremely fast, and together with the response times of the other two effects will be discussed further in the next section.

Both of the field-induced phase transitions, firstly to the turbulent chiral nematic state and secondly to the homeotropic nematic state, are effected as the free energy of the system is changed by the application of the electric field. Such phenomena have been reported by Yang and Crooker[6] and Onnuseit and Stegemeyer[12] in chiral

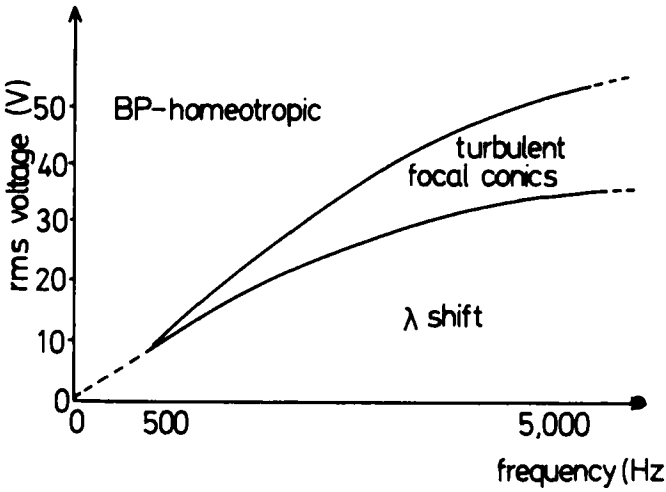


FIGURE 2 The voltage/frequency dependence of the electric-field induced phase transitions and lattice deformations in the BPI of the cyanobiphenyl/chiral ester material HGC1.

nematic/nematic mixtures as the concentration of the chiral component is reduced. It is apparent that each of the electric field effects induced in this system of materials is consistent with current understanding and experimental data consistent with these systems. It is worth noting, however, that no electric field induced phase transition was observed from BPII to BPI, such as has been reported by Heppke *et al.*,[14] nor was a transition to a tetragonal lattice detected, as reported by Pieranski and Cladis[13] and Chen and Ho.[15]

5. RESPONSE TIMES AND RELAXATION EFFECTS

Whilst carrying out the measurements described in the preceding section, particular emphasis was placed on the various response times associated with each of the different deformations. In all cases, the driven response (field on) was found to be fast (~ milliseconds or less) while the relaxation was considerably slower (~ seconds).

The electro-optic responses measured for the mixture HGC1 are shown in Fig. 3(a)–(c) which correspond to 1) an induced wavelength shift, 2) a BP → Ch phase transition, and 3) a BP → homeotropic nematic phase transition respectively. There was little variation in the driven response times between BPI and BPII and the small temperature dependence is not discussed further here.

The deformation of the blue phase lattice giving shifted Bragg peaks was the slowest one observed, occurring in typically 5 ms. Fig. 3(a) shows the electro-optic response of BPII of HGC1 on application of 25 Vrms at 5 kHz. The figure shows that there appear to be two mechanisms associated with this phenomenon, one rapid occurring in ~250 μs, and the second taking approximately 5 ms to be complete. Such two stage processes have been observed in other chiral liquid crystal

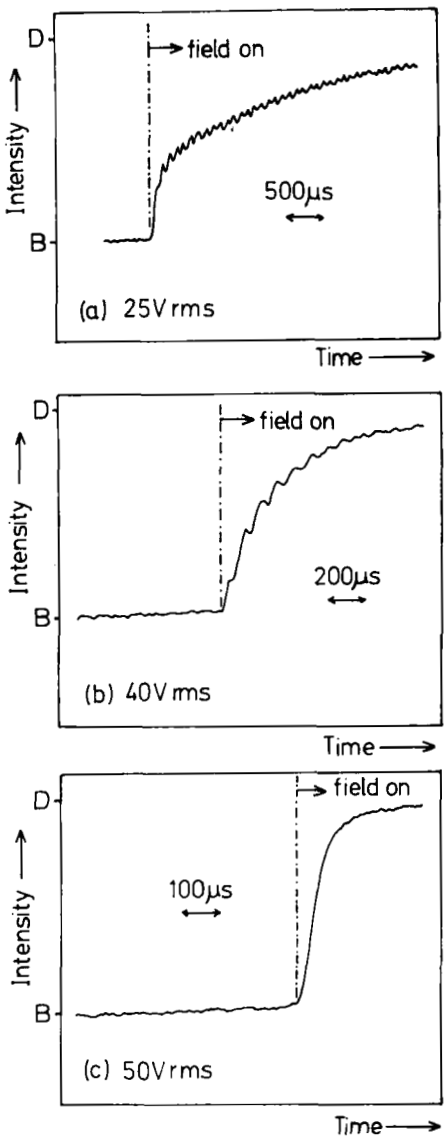


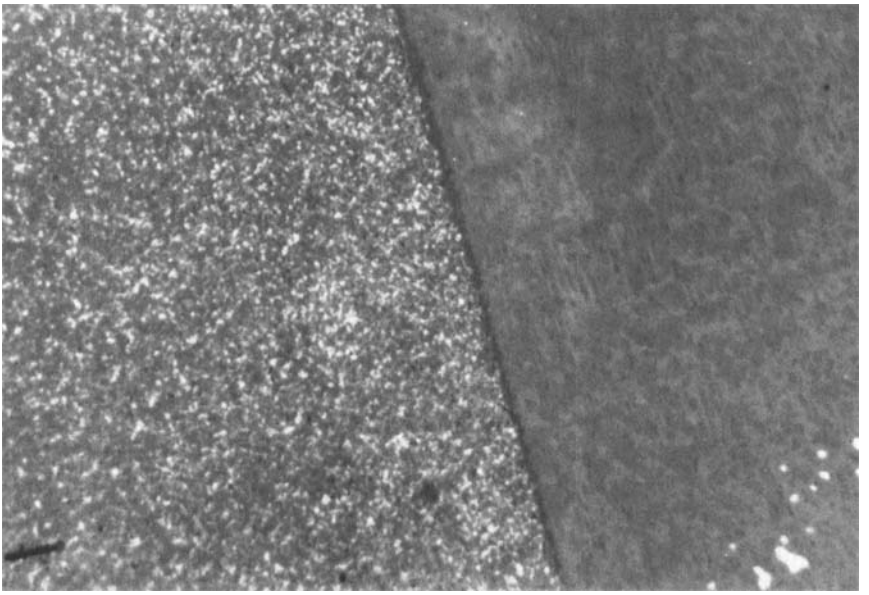
FIGURE 3 The electro-optic responses for the BPII of HGC1 in a 7.5 μm cell for voltages of (*a*) 25 Vrms at 5 kHz, (*b*) 40 Vrms at 5 kHz, and (*c*) 50 Vrms at 5 kHz. These electro-optic transients were detected in reflection between crossed polars as indicated. The letters D and B refer to the bright and dark states. It should be noted that although the electric field had certainly been applied to the sample before the broken line shown, this was not necessarily the point of application. Thus there was possibly a delay in the electro-optic response of the sample following the application of the field which was not measured or depicted in these figures.

systems, particularly supertwist devices, and may easily be observed in polymer systems.[10] Although this two-step process has previously been suggested for such deformations in blue phase systems,[8,16] it is the first time that the fast component in this process has been measured with sufficient resolution to determine the rapid (~250 μs) response time. In both of these previous reports, the fast component was measured to be of the order of ms. In addition, the measurements reported here have demonstrated that the fast response for the lattice deformation is essentially the same as that determined for the switch to the homeotropic state.

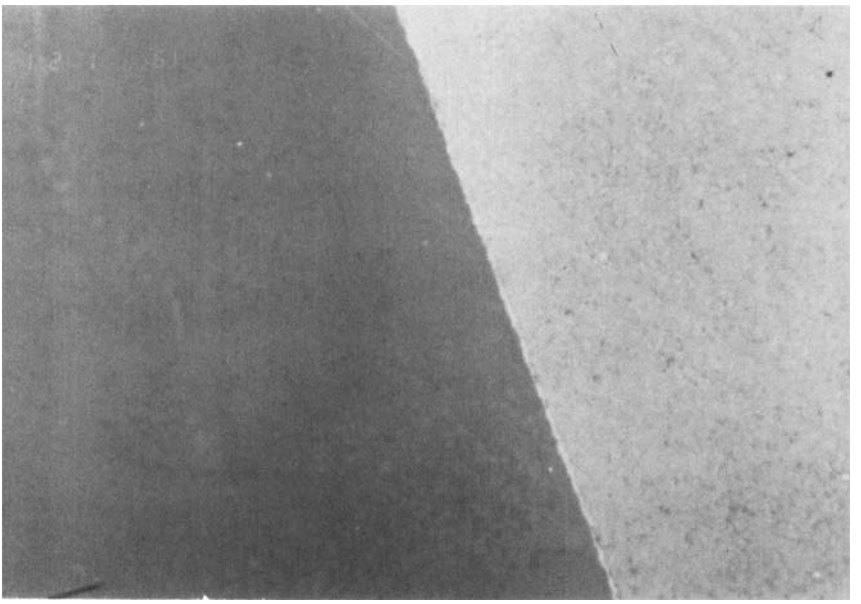
The two electric field induced phase transitions observed in the blue phases of these mixtures occurred much more rapidly than the shift in the Bragg reflected wavelength. These transitions occurred typically in ~100 μs, and the electro-optic response curves of the BPII in HGC1, which was switched to a turbulent focal conic texture by 40 Vrms and to a homeotropic alignment by 50 V (rms) at 5 kHz, are shown in Fig. 3(b) and (c). In the second case, Fig. 3(c), it can be seen that the sample switched from a Bragg reflecting texture (high intensity) to a homeotropic state (dark between crossed polarisers) very rapidly. Fig. 3(b) shows the same rapid switching, but the "field on" state is not completely dark because of the varying birefringence of the turbulent focal conics. The observed response time to the homeotropic state showed a small dependence on the frequency of the applied field (above the threshold for this effect) and decreased from ~400 μs at 100 Hz to ~100 μs at 5 kHz. There was no measured dependence of the response time on the applied voltage above the threshold for this effect. In both cases, only one reorientation mechanism was resolved in the electro-optic response curves. Whilst it is clear from the data presented in Fig. 2, as well as from other reported electric field effects in blue phases, that there is a voltage and frequency dependent threshold associated with these phenomena, it appears from these response time measurements that the "fast" distortion is associated with all three phenomena, but that the wavelength shift also has a much slower mechanism involved.

The relaxation of BPI from the electric-field distorted state depended on which initial effect had been induced. Where a simple wavelength shift had been observed, the blue phase relaxed to its original appearance over several ms following removal of the field. Relaxation from the cholesteric fan texture resulted in the randomly oriented BPI platelets shown in Plate 1(a). In this plate, the electrode area is on the left and the original appearance of BPI is shown on the right. Here, the material had been cooled into BPI from BPII before these measurements were carried out and the orange area on the left therefore corresponds to the (110) Bragg reflection observed in these systems on cooling (c.f. Fig. 1).

Relaxation of BPI from the electric field induced homeotropic state always resulted in a lattice orientation giving the (110) Bragg reflection, independent of the initial lattice orientation of BPI. This is shown in Plate 1(b) in which the electrode area is on the left and the unaffected region on the right side of the plate. It should be noted that the wavelengths of each of the Bragg peaks detected from the sample shown in Plate 1(b) were measured to be 437 nm and 642 nm corresponding exactly to those measured at the same temperature in BPI on heating and cooling the sample. Thus we concluded that there was no phase change connected with this phenomenon, simply a reorientation of the BPI lattice.



(a) See Color Plate I.

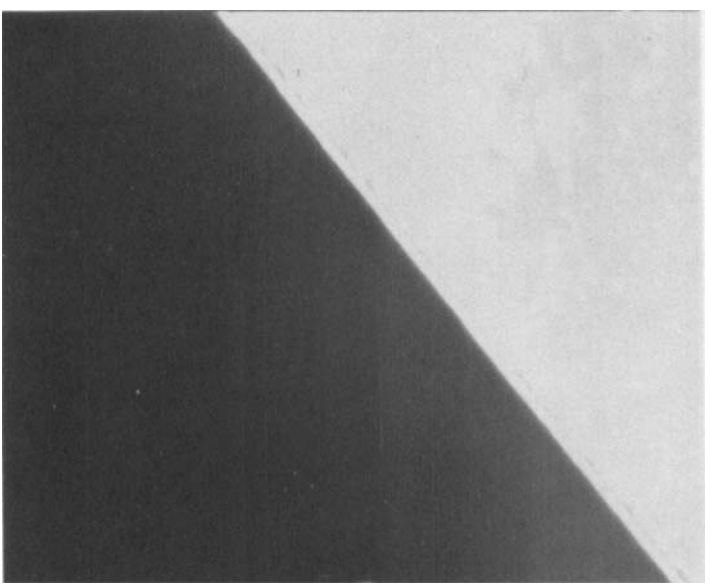


(b) See Color Plate II.

PLATES 1(a) & (b) The texture of BPI observed following relaxation from (a) the field-induced turbulent focal conic texture and (b) the field-induced re-orientation to the homeotropic nematic state. In both cases the electrode area is on the left and magnification is 100x.

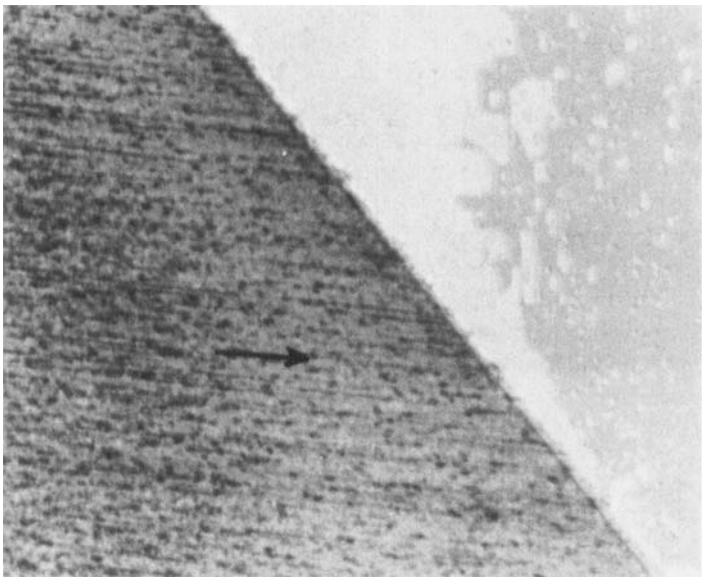
The relaxation of BPII from this electric field induced homeotropic (or totally unwound) state was much slower than relaxation from the slightly distorted lattice, taking several seconds rather than ms for the original texture to be reinstated. This very long relaxation time was not observed for the same distortion in BPI, where the systems relaxed to the (110) Bragg reflecting lattice orientation in several hundred μs. The relaxation process of BPII from its totally unwound state is shown in Plates 2(a)–(c). The BPII lattice appeared to re-form as if the sample was cooling from the isotropic or fog phase. This phenomenon was also observed in electro-optic cells with low quality polyvinyl alcohol (PVA) alignment layers, though in this case the relaxation process took longer and the state intermediate to those shown in plates 2(a) and (b) was entirely analogous to the fog phase. This phenomenon may be explained as follows.

In the homeotropic state, the bulk structure of the BPII lattice is destroyed and only the surface molecules anchored by the aligning agent retain their planar orientation. On removal of the field, the blue phase lattice must reform, and this process is initiated at the surfaces where "crystallites" are formed. Co-operative alignment is then propagated through the bulk of the material as a seeding process until all of the molecules are aligned in the BPII lattice which represents the lowest free energy of the system. The efficiency of this seeding process would seem to be

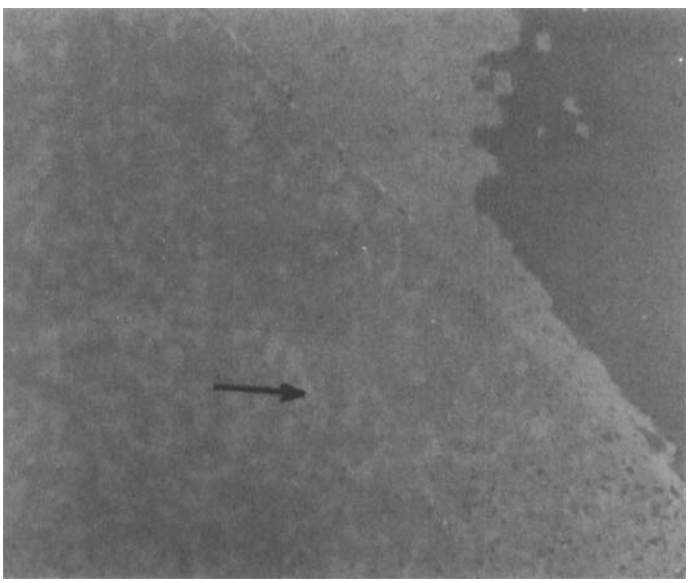


(a) See Color Plate III.

PLATES 2(a)–(c) (a) The electric field-induced transition to a homeotropic nematic state in BPII on application of 50 Vrms at 5 kHz. Plates 2(b) and (c) show the relaxation from this state 2 and 4 s after removal of the field respectively. The rubbing direction of the polyimide alignment layer is shown. Magnification was 100x.



(b) See Color Plate IV.



(c) See Color Plate V.

strongly dependent on the coupling of the surface layers of the molecules to the aligning layers since, where a low quality PVA alignment layer was used, it occurred even more slowly.

There are two points to note from these observations. Firstly, the fact that during the relaxation from a homeotropic state to BPII, an intermediate fog-like phase is

clearly seen supports the findings of Collings,[4] *i.e.*, the structure of the fog phase is locally the same as that of BPII (*i.e.*, simple cubic), but lacks any long-range order. Exactly this situation is observed where BPII first starts to re-form from the homeotropic state. The second interesting point is that while BPII relaxed very slowly, relaxation of BPI from the same distorted homeotropic state was extremely rapid (~ 100 μs). This may be interpreted as due to the large difference in the elastic constants between BPI and BPII; this postulation is not unreasonable since the elastic forces must fall rapidly from some finite value in the chiral nematic phase to essentially zero in the isotropic phase over an extremely narrow temperature range. Clearly direct measurement of the elastic constants within the blue phases would allow more detailed interpretation of all of the electro-optic responses of the systems, and such measurements are currently being carried out by electric field light scattering.

CONCLUSIONS

In this paper we have described a new system of mixtures based on chiral esters and cyanobiphenyls and reported their blue phase properties. The phase behavior of these materials showed relatively broad blue phase ranges (~2.5°C), considerably broader than may have been expected for such long pitch materials. The extensive blue phase ranges observed in these mixtures were interpreted as resulting from the influence of the broad phase transitions associated with these systems.

Three different electric field phenomena were induced in the blue phases of these materials: a transition to a chiral nematic phase, a shift to a homeotropic nematic phase, and a switch in the Bragg reflected wavelength. All of these effects are consistent with other blue phase systems reported, and may be interpreted by considering the chirality dependence of the phase behavior of blue phases or their cubic lattice description. The driven response times associated with these electric field induced phenomena have been measured accurately. The response times associated with the induced phase transitions were found to be extremely fast, ~100 μs, with little difference in response time between the two transitions. Clearly, the mechanism associated with both is essentially the same, since, although there were small differences observed in τ_R for these deformations (BP → Ch:τ_R ~ 200 μs and BP → N:τ_R ~ 100 μs), these could be attributed entirely to differences in voltage (~40 Vrms and ~50 Vrms respectively). Above the threshold observed, at a given frequency, within each of these effects there was no voltage dependence observed in τ_R. The electro-optic response measured for the shift in Bragg reflected wavelength showed two distinct mechanisms, one fast, on a similar timescale to the other induced phenomena (~100 μs), and the second much slower (~ms). This is the first time that the processes have been measured with sufficient resolution to allow a comparison between the lattice deformation response time and that determined for the field induced phase transitions.

A study of the relaxation phenomena observed in these blue phase systems has also yielded some further useful information. The first was that observation of BPII from the field-induced homeotropic state confirmed the findings of Collings[4];

i.e., the structure of the fog phase (BPIII) is locally the same as that of BPII, but lacks any long range order. The second interesting feature related to relaxation times; that of BPI was rapid whilst the BPII relaxed extremely slowly. This was interpreted as being due to a rapid divergence of the elastic constants close to the isotropic phase transition and measurements to confirm this postulation are currently being carried out.

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