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Dynamic properties of blue-phase mixtures

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The dynamics of electric-field-induced lattice distortions and phase transitions in the BPI, BPII and BPIII (fog) phases of blue-phase mixtures, which include low-molar-mass and/or polymeric components, have been studied. Several electric-field-induced effects have been observed in the blue phases, and the electro-optic characteristics of the driven and non-driven responses of each are considered. Anomalous behaviour in BPIII, where driven response times were measured to be slower than the relaxation responses, is described and considered with respect to relaxation processes previously observed in BPII. Finally, we present data for a mixture containing 40 per cent by weight of a side-chain-polymer liquid crystal. In this case only BPI was observed, and it appears that the increased viscosity had little effect on the response times of the system. These data are discussed.

1. Introduction

The application of electric fields to blue phases is widely used to probe both the structural properties and the phase behaviour of these mesophases. Several different electric-field effects have been reported in the lower-temperature blue phases (BPI and BPII), including field-induced phase transitions and distortions of the cubic lattices that form the mesophase structures. Not all of the field-induced phase transitions reported occur in every blue-phase system; transitions from BPI and BPII to chiral nematic or nematic phases appear to be universal [1–3], while BPII-to-BPI transitions [4] and changes from cubic to tetragonal lattices [5, 6] seem to occur only in certain materials. The distortion of the blue-phase lattices by electric fields is manifest as a shift in the Bragg-reflected light to longer wavelengths, and this effect has also been widely observed [1–7]. Although much work has been carried out regarding these different electric-field effects, very little has been aimed at studies of the dynamics of these effects. In this paper we extend our previous studies of the dynamic properties of BPI and BPII [8] to include electro-optic effects observed in the BPIII (fog phase), as well as in BPI of a blue-phase material containing 40 per cent by weight of a polymer liquid crystal.

2. Materials

The mixture used to study the electro-optic properties of BPIII included 60·8 per cent by weight of a chiral nematic base (comprising CE1 (28·6 per cent), CE2 (35·7 per cent) and CE3 (35·7 per cent)), and 39·2 per cent of the eutectic nematic E130. The nomenclature used is that of BDH Ltd, who supplied the pure liquid-crystal materials. This blue-phase mixture, denoted HGC4, has been described in detail previously [8], together with several related systems. The materials described exhibited all three blue phases—BPI, BPII and BPIII—and were unusual in that, although the pitches were relatively long (0·3 μm), the total blue-phase range was very broad (about 2·5°C).

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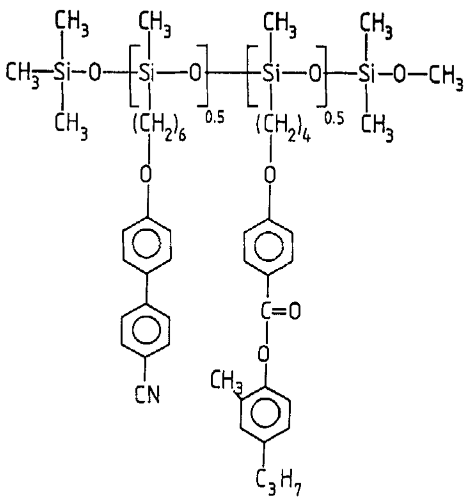


Figure 1. Structure of the smectic polysiloxane copolymer PG296, which had approximately 50 reacted sites.

In particular, HGC4 exhibited BPIII from 116·3 to 117·1°C, making it suitable for the study of electro-optic effects in the fog phase.

The polymer blue-phase mixture studied contained 60 per cent by weight of the chiral nematic base described previously, and 40% by weight of the smectic polysiloxane copolymer PG296. The structure of the polymer is shown in figure 1; its properties, and the properties of its solutions in the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl have been described in detail elsewhere [9]. Only BPI was observed in this mixture, but the phase occurred over a very wide temperature range, from 110·0°C to 114·6°C (measured on heating). The BPI supercooled by between 2°C and 5°C into the cholesteric phase on cooling the sample.

All of the measurements described for these blue-phase mixtures were carried out on 7·5 μm thick test cells. Uniform planar alignment was provided by a rubbed polyimide coating on the glass surfaces, and transparent indium tin oxide (ITO) electrodes allowed the application of electric fields. The electro-optic effects were studied using an adapted polarizing microscope [3] so that the sample could be viewed while simultaneously recording the electro-optic response on a Philips PM3315 storage oscilloscope. Voltages up to 100 V_{rms} at frequencies between 100 Hz and 5 kHz were applied to the blue phases and the sample temperature was maintained using a Mettler FP82 Hot Stage and FP80 Control Unit.

3. Electric-field effects in BPIII

Our previous work [8] described the static and dynamic electro-optic properties of BPI and BPII of these broad blue-phase mixtures. Three different electro-optic effects were observed in both blue phases; (i) a small shift in the Bragg-reflected wavelength at low voltages; (ii) a switch to turbulent chiral nematic or nematic textures at intermediate voltages and frequences; and (iii) a complete unwinding of the blue-phase structure to a homeotropic state allowing observation of a conoscopic figure at high voltages and frequencies. The driven response times of effects (ii) and (iii) were found to be extremely fast (typically of order 100 μs), while the lattice distortion (i) occurred with two distinct contributions to the response time, one fast (of order 100 μs), and the other much slower (1–10 ms).

The electro-optic effects that were observed in the BPIII were similar to (i)–(iii), but with a further electric-field-induced phase transition from BPIII to BPII. The voltage dependence of these effects and their optical appearance, is summarized here and in figures 2(*a*)–(*d*).

(*a*) $V < 25\,\mathrm{V_{rms}}$, 1 kHz, sine wave. There was a slight shift in the colour of the fog phase from blue-grey to green-grey.

(*b*) $25\,\mathrm{V} \leqslant V \leqslant 50\,\mathrm{V}$, 1 kHz, sine wave. There was a field-induced phase transition from BPIII to BPII. At lower voltages the BPII appeared bright blue (figure 2(*b*)), but, as the voltage was increased, the color shifted to longer wavelengths (figure 2(*c*)), becoming less distinct at the same time.

(*c*) $V \geqslant 50\,\mathrm{V_{rms}}$, 1 kHz, sine wave. The system became homeotropically aligned and a conoscopic cross could be observed. The voltage threshold between this and the lower voltage switch to BPII was far from sharp; some homeotropic alignment was evident between 50 V and 60 V, but the conoscopic figure was sharp only at voltages greater than $60\,\mathrm{V_{rms}}$. In all cases the sample appeared uniform and there was no evidence of different field effects in different areas of the cell.

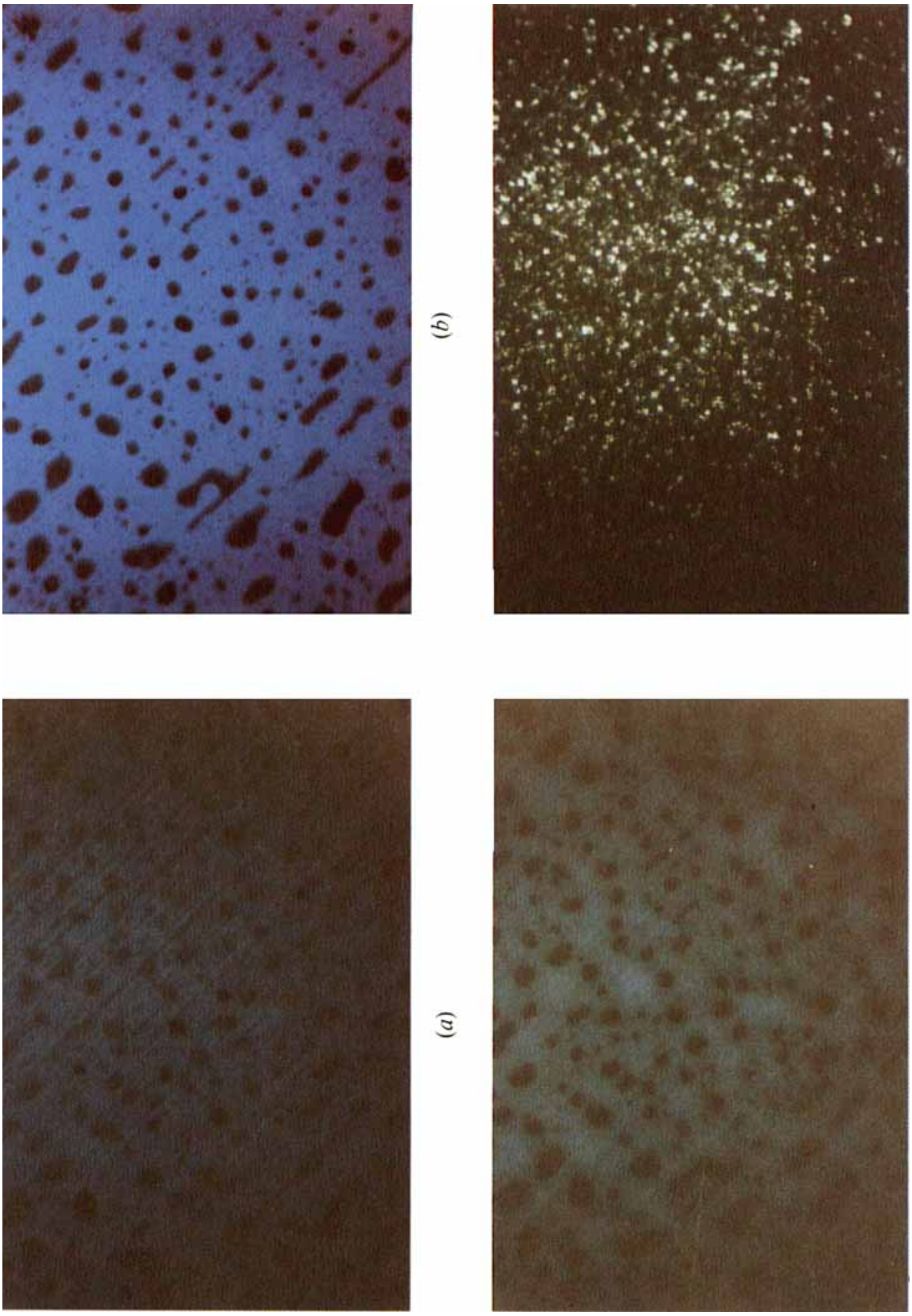
(*d*) Approx. $55\,\mathrm{V} \leqslant V \leqslant 80\,\mathrm{V_{rms}}$, square wave. A nematic texture was observed only on application of a square waveform to the cell. At high frequencies (of order 1 kHz) this was turbulent, but at low frequencies (of order 100 Hz) there was little motion of the nematic threads.

In general, the electric-field effects were less distinct at low frequencies (of order 100 Hz), and enhanced at frequencies greater than 1 kHz. The voltage thresholds appeared to be independent of frequency.

It should be noted that, although the effects corresponding to (*a*) and (*c*) were relatively easy to observe by optical microscopy, they were extremely difficult to quantify since the resulting changes in light level were too small to be detected on our apparatus. For example, although by eye we saw the slight shift in the wavelength of light reflected by BPIII from blue-grey at zero field to green-grey on application of approximately $20\,\mathrm{V_{rms}}$ at 1 kHz, we have so far made no spectral measurements that quantify our observation.

Similarly, electro-optic response times were recorded only for the field effects that showed a significant optical contrast to the fog phase, i.e. (*b*) BPIII → BPII and (*d*) BPIII → N. For the BPIII → BPII field-induced transition we measured $\tau_{\mathrm{on}} = 40\,\mathrm{ms}$ and $\tau_{\mathrm{off}} \approx 5\,\mathrm{ms}$ at $30\,\mathrm{V_{rms}}$, and for the BPIII → N phase transition $\tau_{\mathrm{on}} \approx 20\,\mathrm{ms}$ and $\tau_{\mathrm{off}} \approx 800\,\mu\mathrm{s}$ at $70\,\mathrm{V_{rms}}$ (1 kHz). The comparison of these response times with those measured for electric-field effects in BPI and BPII is extremely interesting. We should note first that both of the field effects measured in BPIII have faster relaxation times than the driven response times. Furthermore, τ_{on} for the BPIII → N transition is 20 ms, an order of magnitude slower than BPI/II → N transitions, although τ_{off} is comparable in all of the systems. No really suitable comparison exists for the BPIII → BPII phase transition. On application of the field, the BPII texture appeared to form gradually from the fog phase, and τ_{on} was always greater than 40 ms.

We can attempt to explain these results in two different ways. First, we may assume that the electric-field-induced blue-phase transitions may be treated analogously



(*a*)

(*b*)

(*c*)

(*d*)

Figure 2. Appearance of BPIII in HGC4 on application of (*a*) 0 V_{rms}, (*b*) 30 V_{rms} and (*c*) 40 V_{rms} at 1 kHz a.c. and (*d*) 72 V_{rms} square wave at 100 Hz.

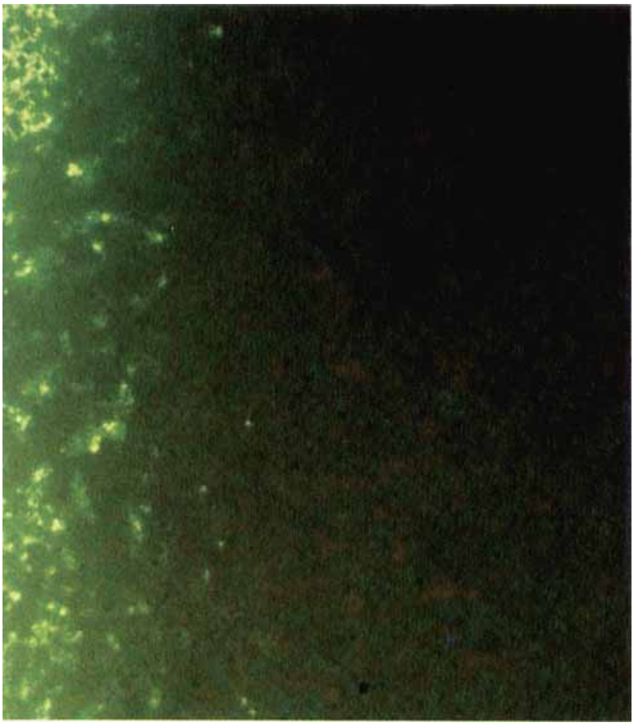


Figure 3. Annealed BPI texture of the 60 per cent chiral base, 40 per cent PG296 mixture at 113·3°C.

to field-induced cholesteric transitions. Then, following the analysis of Jakeman and Raynes [10], we should expect the rise and decay times of all the transitions to be of the form

$$\tau_{\text{on}} = \frac{\eta}{\varepsilon_0 \Delta\varepsilon E^2 - kq^2}, \tag{1}$$

$$\tau_{\text{off}} = \frac{\eta}{kq^2}, \tag{2}$$

where η is the twist viscosity γ_1, k is the twist elastic constant k_{22}, $\Delta\varepsilon$ is the dielectric anisotropy $(=\varepsilon_\parallel - \varepsilon_\perp)$ and q is the wave vector $(=\pi/\text{pitch})$. It is more difficult to justify the use of analogies to determine the form of the equation describing the threshold field for the blue-phase transitions, since the only transitions which are obviously equivalent in both the cholesteric and blue phases are Ch → N and BP → N. In this case the threshold field E_c is given by [11, 12]

$$E_c^2 = \frac{\pi^2}{p^2}\frac{k}{\varepsilon_0 \Delta\varepsilon}, \tag{3}$$

where p is the pitch of the cholesteric phase. Other threshold fields in the cholesteric phase differ by constants related to the elastic constants [13]. Using these equations, we may analyse the data obtained for both the BPIII → BPII and BPIII → N phase transitions to determine whether or not they may be considered as purely field-driven.

From equations (2) and (3), it can be shown that

$$\tau_{\text{off}} = \frac{\eta}{E_c^2 \varepsilon_0 \Delta\varepsilon}. \tag{4}$$

Rearranging equation (1), we have

$$\tau_{\text{on}} = \frac{E_c^2 \tau_{\text{off}}}{E^2 - E_c^2} = \frac{V_c^2 \tau_{\text{off}}}{V^2 - V_c^2}. \tag{5}$$

It can easily be shown from equation (5) that the rise time τ_{on} is greater than the decay time τ_{off} in the voltage regime $V_c \leqslant V \leqslant \sqrt{2}\, V_c$. For the BPIII → BPII transition we have $V_c = 25\,\text{V}$, $\tau_{\text{on}} = 40\,\text{ms}$, $\tau_{\text{off}} = 5\,\text{ms}$ for $V = 30\,\text{V}_{\text{rms}}$. From this, we can see that $\tau_{\text{on}} \approx 8\tau_{\text{off}}$. However, from equation (5) the predicted value of the rise time would be $\tau_{\text{on}} = 2{\cdot}3\tau_{\text{off}}$ $(= 11{\cdot}5\,\text{ms})$. It can be seen that there is rather poor agreement between the observed and predicted rise times. We now consider the BPIII → N transition. In this case we have $V_c = 55\,\text{V}$, $\tau_{\text{on}} = 20\,\text{ms}$, $\tau_{\text{off}} = 800\,\mu\text{s}$ and $V = 70\,\text{V}_{\text{rms}}$. Thus we observe that $\tau_{\text{on}} = 25\tau_{\text{off}}$. However, the analysis implies that $\tau_{\text{on}} = 1{\cdot}6\tau_{\text{off}}$ $(= 1{\cdot}3\,\text{ms})$. Again the agreement between the observed and calculated values of τ_{on} is extremely poor, and we can conclude that the transitions observed cannot be simply field-driven.

As an alternative explanation we suggest that for (*b*) and (*d*) the influence of the field is to induce long-range order in the liquid-crystal structure where it did not previously exist. Therefore the growing of BPII in BPIII on application of a field may be interpreted as a seeding and propagation of structure, analogous to that observed in the relaxation of the homeotropic texture to BPII, reported previously [8]. Similarly, the formation of long-range nematic order from BPIII would take longer than in the case of BPI or BPII, which themselves have long-range order. In both cases relatively long response times would be expected. The relaxation response times are comparable to those measured for the field-induced phase transitions in the other blue phases. These observations lend further credence to the postulation that the structure of BPIII is locally similar to that of BPII, but lacks any long-range order [8, 14]. This second explanation also fits with the observation that the BPIII → BPII transition did not occur in a uniform manner across the electrode area, but rather took place as a nucleation and growth of BPII texture in the BPIII.

4. Electric-field effects in the polymer blue-phase mixture

As already noted, the polymer blue-phase mixture exhibited a blue-phase range of 4·6°C. However, sub-classification of the blue phases within this range proved difficult; it was only after several hours of annealing that the typical blue-phase textures were observed. The classification of the whole range as BPI was confirmed by (*a*) annealing studies and heating or cooling cycles, which revealed no further phase transitions optically, and (*b*) a contact-method determination of the phase diagram of the chiral base and PG296 mixtures, which showed that in this system both BPII and BPIII were unstable with increasing proportions ($\geqslant 10$ per cent) of PG296. It should be noted that the contact method was not accurate enough to determine the exact phase diagram of the system, but only indicated trends.

The appearance of the annealed blue phase texture at 113·3°C is shown in figure 3. On application of an electric field, all of the effects (i), (ii) and (iii) described above were observed. The occurrence of each of the effects with respect to applied r.m.s.

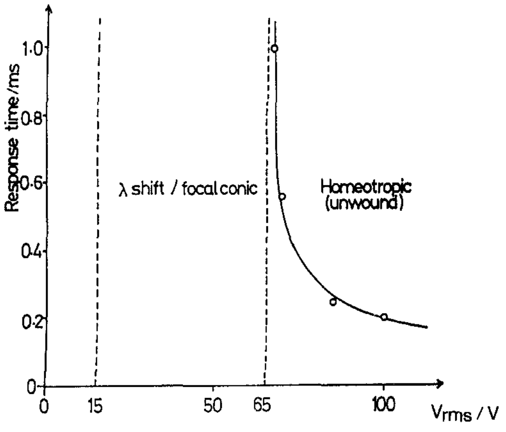


Figure 4. Voltage dependence and response times of the electro-optic effects in BPI of the 60 per cent chiral base, 40 per cent PG296 mixture. The frequency of the a.c. signal was 1 kHz.

voltage at a frequency of 1 kHz is shown in figure 4. Although the shift in the wavelength of the Bragg-reflected light and the field-induced transition to a cholesteric phase were clearly visible by eye, neither has been timed so far, since the uneven optical texture made accurate measurement difficult. However, it was possible to record the electro-optic response times of the transition from BPI to the homeotropic texture, and these are shown with respect to applied voltage in figure 4. The data in this figure show that (i) there is a dependence of τ_{on} on applied voltage and (ii) that the measured response times are still extremely fast (<1 ms). The observation of the voltage dependence contrasts with measurements on equivalent field-induced phase transitions in low-molar-mass materials [8]. The voltage variation is significant close to the threshold for the BPI-to-homeotropic transition (about 65–70 V), but there is little variation of τ_{on} above 70 V_{rms}, where it remains about 200 μs. The graph in figure 5 shows the relationship log τ versus log $(V^2 - V_c^2)$ with $V_c = 66$ V. It can be seen from the figure that the data fit the dependence

$$\tau = \frac{A}{(V^2 - V_c^2)^{0\cdot425}}$$

rather well. This is unexpected; the response time in a field-driven transition normally varies simply as $(V^2 - V_c^2)^{-1}$. Further measurements are currently being undertaken to determine this relationship more accurately.

The measurement of response times for the polymer/monomer system in this high-voltage regime, which were only a factor of two to three greater than those of the low-molar-mass materials measured previously, was very surprising. Certainly the bulk viscosity of the polymer mixture was much greater than the low-molar-mass mixtures; comparison with other data for PG296 in nematic hosts [9, 15] indicates that for a 40 per cent mixture the twist viscosity should be increased by a factor of approximately 75. From both equations (4) and (5) it can be seen that the effect of such a high viscosity could be counteracted by large changes in either E_c or the dielectric anisotropy or both. However, the literature [9] has shown that for a low-molar-mass liquid crystal doped with approximately 40 per cent by weight of PG296, $\Delta\varepsilon$ and the splay, twist and bend elastic constants are reduced by a factor of

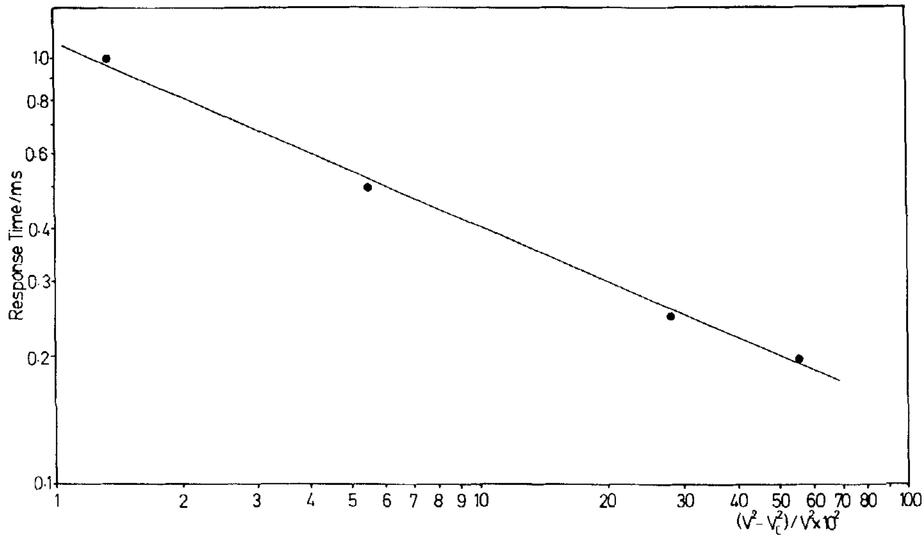


Figure 5. Logarithm of the response time of the BPI → N phase transition plotted against logarithm of $V^2 - V_c^2$, $V_c = 66\,\mathrm{V}$. The gradient is $-0{\cdot}425$.

approximately 0·6. If we assume that this will also be true in BPI of these systems then the data can be analysed as follows.

We may consider the way in which the polymer influences the relevant constants in the blue-phase mixture by comparing threshold voltages for the BPI → N phase transition in this material (66 V) with analogous purely low-molar-mass systems (45 V) [8]. For this comparison we use equation (3). Assuming that the pitch of both systems is constant (since equivalent proportions of the chiral base mixture were present in each case), it can be seen that the ratio $k_{22}/\Delta\varepsilon$ in the polymer mixture is a factor of two greater than $k_{22}/\Delta\varepsilon$ in the low-molar-mass mixture. Since both the twist elastic constant and the dielectric anisotropy are likely to be decreased in the polymer mixture [9], we can determine the extent to which the 75-fold increase in viscosity can be counteracted by increases in E_c^2 and $\Delta\varepsilon$ by using equations (4) and (5). If all of the change in the ratio $k_{22}/\Delta\varepsilon$ was attributable to $\Delta\varepsilon$ then we have, for the same distance in applied field above threshold,

$$(\tau_{\mathrm{on}})_{\mathrm{lmm}} = \frac{\eta}{\Delta\varepsilon\varepsilon_0(E^2 - E_c^2)} \tag{4}$$

$$\Rightarrow (\tau_{\mathrm{on}})_{\mathrm{polymer}} \approx \frac{75\eta}{\frac{1}{2}\Delta\varepsilon\varepsilon_0(E^2 - E_c^2)} = 150(\tau_{\mathrm{on}})_{\mathrm{lmm}}. \tag{5}$$

Alternatively, if all of the change in $k_{22}/\Delta\varepsilon$ is attributed to k_{22} then we have

$$(\tau_{\mathrm{on}})_{\mathrm{polymer}} \approx \frac{75\eta}{\Delta\varepsilon\varepsilon_0(E^2 - E_c^2)} = 75(\tau_{\mathrm{on}})_{\mathrm{lmm}}.$$

In either case it can be seen that the polymer solution would be expected to have response times approximately two orders of magnitude greater than the low-molar-mass mixture. We may conclude that the analysis of the measured response times in this way does not explain the much smaller relative increase measured for the polymer-mixture response time ($(\tau_{\mathrm{on}})_{\mathrm{polymer}} \approx 3(\tau_{\mathrm{on}})_{\mathrm{lmm}}$).

It is possible that there is little increase in the measured reponse time in the polymer system either because the polymer side groups are not reoriented on application of the electric field or because the electro-optic response measured (i.e. the time taken for a 10–90 per cent change in light level) does not detect this reorientation. It is the latter explanation that is more probable; evidence indicates that the side groups of this particular polymer are easily oriented in high electric fields [9], and the red appearance of BPI confirms that the polymer is fully incorporated in the blue-phase structure since it has increased the pitch of the purely chiral component of the mixture. It is therefore unlikely that the low-molar-mass molecules are reorientated in preference to the polymer side groups where both are fully incorporated in the blue-phase structure. It is clearly necessary to examine the electro-optic properties of other polymer blue-phase mixtures, both with varying polymer concentrations and containing different polymer molecules, in order to fully understand these effects.

5. Conclusions

In this paper we have described the dynamic properties of electric-field effects in all of BPI, BPII and BPIII for low-molar-mass mixtures and in BPI of a 40 per cent polymer mixture. In both cases the response-time data were analysed analogously to the well-known Ch → N transition. We have shown that this analysis is not applicable to the blue-phase systems. Alternative interpretations of our observations of anomalous response times in BPII have indicated that its structure does indeed lack long-range order, but may be locally similar to the simple cubic structure of BPII, confirming previous suggestions [8, 14]. The electro-optic response times measured in the polymer blue-phase mixture revealed that the increased viscosity of the system had little influence on the values of τ_{on}, which were typically about 200 μs. Studies of the dynamics of the electric-field effects in blue phases are clearly providing significant additional information concerning these phenomena.

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