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Observation of an electric field-induced metastable blue phase in supercooled liquid crystalline systems

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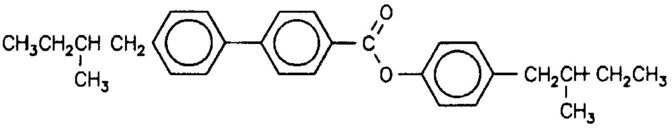
In this preliminary communication, the influence of an electric field on the metastable blue phase BPS is reported. Experiments involved both supercooling of the BP I at constant applied field and increasing the electric field strength applied to BPS at constant temperature, and resulted in the observation of a new field induced metastable phase BPES.

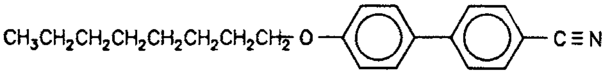
Among the three thermodynamically stable zero-field blue phases (BP), the low temperature one (BP I) can be supercooled with respect to the cholesteric phase to a large extent [1–3]. Recently, we have shown that a new metastable blue phase BPS transforms reversibly from the supercooled BP I [4, 5]. The BPS is thermodynamically stable with respect to the BP I, but metastable with respect to the cholesteric phase. The BPS only exists in liquid crystalline systems with a smectic A phase and if the temperature range of the cholesteric phase is small. We could demonstrate that smectic fluctuations are responsible for the occurrence of the BPS [5]. In this preliminary communication we report the influence of an electric field on the supercooled BPS.

Additionally to the conditions which have to be fulfilled for the existence of a BPS (high chirality, short cholesteric temperature range, smectic A phase), the liquid crystalline system must exhibit a sufficiently high dielectric anisotropy in order to obtain a strong coupling to the electric field. We found that a mixture of 35·4 wt% of the chiral compound CE 2 and 64·6 wt% of the smectic compound M 24 was a suitable mixed system for our experiments. The compounds were a gift of Merck Ltd, UK with the following formulae:

4-(2-Methylbutylphenyl) 4′-(2-methylbutyl)biphenyl-4-carboxylate, CE2 [BDH]



4-Cyano-4′-*n*-octyloxybiphenyl, M24 [BDH]



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The mixture mentioned above exhibits the following phase sequence (temperature in °C):

S_A 93·00 S_A/chol 95·30 chol 96·95 BP I 97·45 I.

The BPs were characterized by their Bragg reflections of visible light which have been measured by means of transmission and reflection spectroscopy in a microscope-spectrometer (Leitz Ortholux Pol II BK microscope combined with a computer controlled Jarrel Ash monochromator). The temperature was controlled with a modified Mettler F 5/52 hot stage. The ITO coated cells (E.H.C.) of 30 μm sample thickness were supplied with an AC electric field of frequency 1 kHz [6].

To study the influence of electric fields on the supercooled BPS, two kinds of measurements have been carried out:

(i) Supercooling the BP I at constant applied electric field strength (E).
(ii) Increasing the electric field strength applied to the BPS at constant temperature (T).

In both cases the dependence of the BP lattice constants has been observed by measuring the Bragg reflection wavelength (λ_B).

Figure 1 shows the temperature dependence of the selective reflection bands at four different applied electric field strengths. In order to be able to compare the results for different field strengths, it is necessary to keep an equal cooling rate; this was 0·01°C min^{-1}. The Bragg wavelength of the (110)-peak in the region of the stable BP I (96·95°C–97·45°C) shows only a small shift for weak electric fields. Therefore only one curve is representative in this temperature interval. A saturation effect of the temperature dependence of λ_B is observed in the metastable region of the BP I [5]. At $T \approx 95·8$°C at zero field, a jump in the Bragg wavelength was observed, indicating a

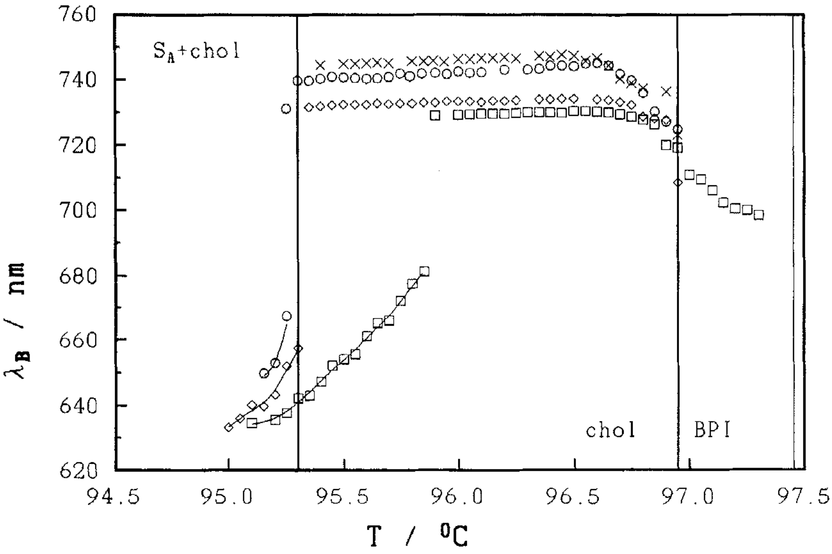

Figure 1. Temperature dependence of the Bragg reflection wavelength in the various blue phases formed by 35·4 wt% CE 2 in M 24 for various applied electric field strengths. Cooling rate: 0·01°C min^{-1}. □, $E = 0$ V μm^{-1}; ◇, $E = 1·0$ V μm^{-1}; ○, $E = 1·4$ V μm^{-1}; ×, $E = 2·0$ V μm^{-1}.

transformation of the BP I into the BPS. The time for complete relaxation of the BPS into the cholesteric phase in the zero-field experiment was several days at $T \approx 95{\cdot}7°C$. The Bragg wavelength maximum reached in the supercooled BP I increases with increasing field strength. Also the temperature of the phase transition into the BPS strongly depends on the field strength. For higher field strengths, the transition is shifted to lower temperatures and the temperature interval of BPS becomes smaller. Finally, the BPS does not occur at electric field strengths higher than $E \geqslant 2\,\mathrm{V\,\mu m^{-1}}$.

Figure 2 shows the electric field dependence of the lattice constant of the BPS for five different temperatures. As was shown in [4], after the phase transition BP I–BPS, we can heat the BPS into the interval of the supercooled BP I to the temperature of the phase transition cholesteric–BP I without any structure relaxation to the BP I. We have now heated the BPS inside the temperature interval of supercooled BP I but far away from the two phase region cholesteric–smectic A, and measured the field dependence of the selective reflection. For weak field strengths, a red shift of the selective reflection is observed and the Bragg wavelength is proportional to E^2 (positive electrostriction). Further, for larger field strengths, a discontinuity of the function $\lambda_B(E)$ occurs, combined with a sign reversal of the slope (negative electrostriction). These observations indicate a field-induced phase transition, as has been observed in other BP systems [7]. For a review of electric field effects on BPs cf. [8]. We call this new field induced blue phase, arising from the BPS in the supercooled region, BPES. The field-induced transition to the BPES has also been observed using the polarizing microscope and is demonstrated in the photomicrographs of figure 3. The Bragg wavelength of the BPES is also proportional to E^2. At higher temperatures (96·3°C), the BPS coexists with the BPES over an extensive interval (3·5–6·3 $\mathrm{V^2\,\mu m^{-2}}$). At the lowest investigated temperature (95·5°C), the BPES does not occur. The ends of the curves are in accordance with the transition to the cholesteric phase with the focal-conic texture.

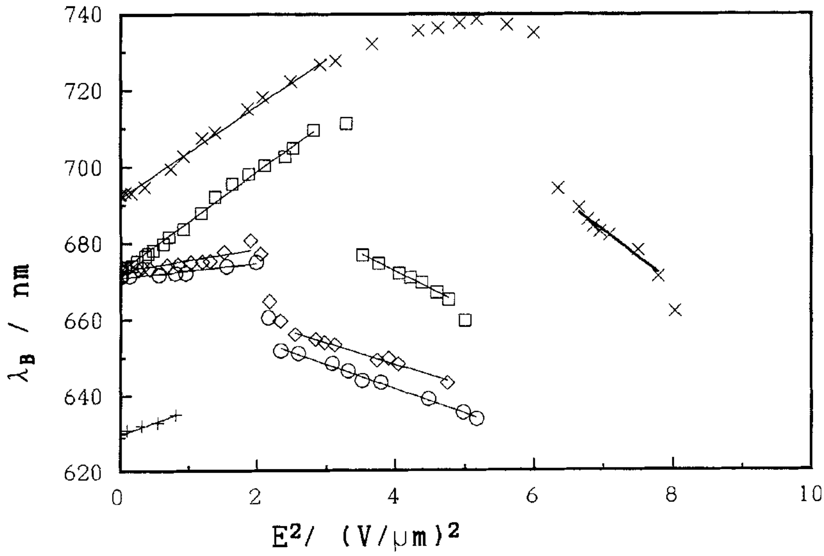

Figure 2. Bragg wavelength versus square of applied field strength for the BPS formed by 35·4 wt% CE 2 in M 24 at various temperatures. The lines are guides for the eye where λ_B is proportional to E^2. +, $T=95{\cdot}5°C$; ○, $T=95{\cdot}7°C$; ◇, $T=95{\cdot}9°C$; □, $T=96{\cdot}0°C$; ×, $T=96{\cdot}3°C$.

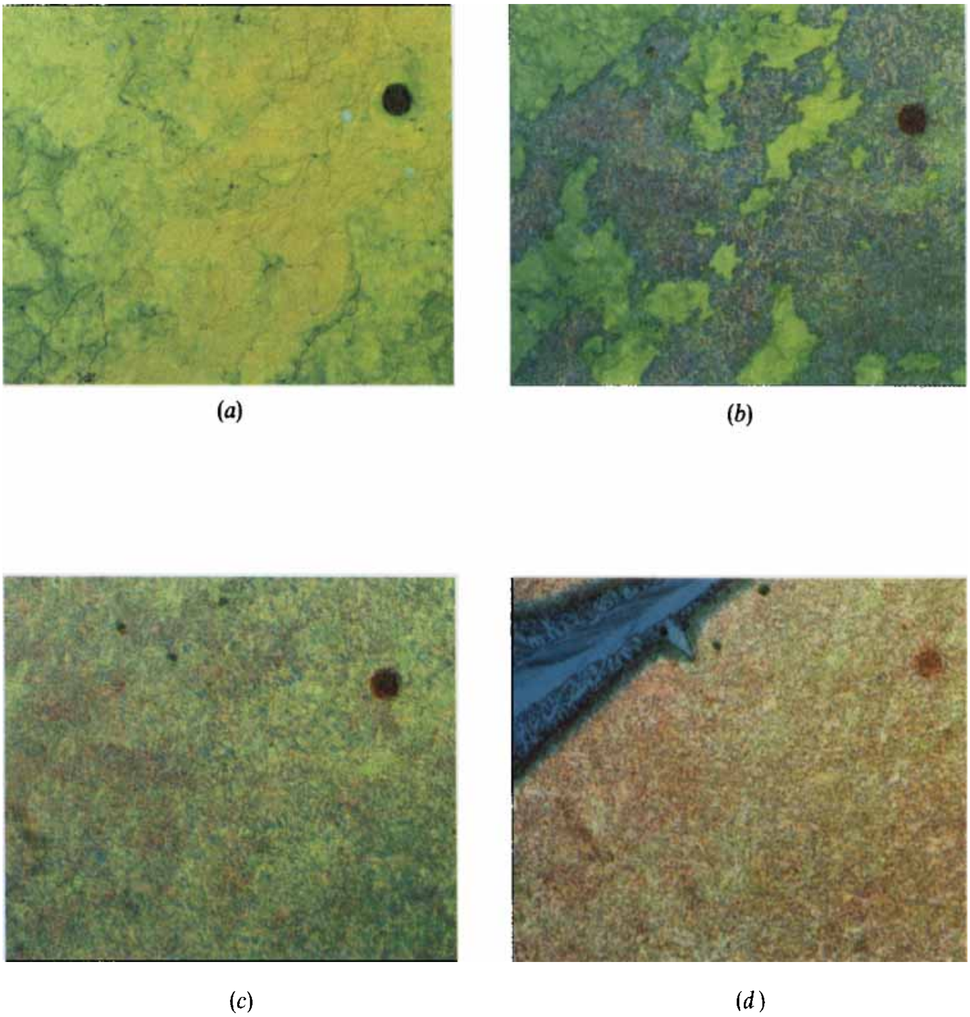

Figure 3. Electric field induced phase transitions at $T = 95{\cdot}7$°C: (*a*) $0\,\mathrm{V\,\mu m^{-1}}$, BPS + cholesteric; (*b*) $1{\cdot}46\,\mathrm{V\,\mu m^{-1}}$, transition BPS to BPES; (*c*) $1{\cdot}82\,\mathrm{V\,\mu m^{-1}}$, BPES + cholesteric; (*d*) $2{\cdot}27\,\mathrm{V\,\mu m^{-1}}$, transition to the focal-conic texture of the cholesteric phase.

Further observations characterize the BPES; heating of the BPES at constant applied electric field strength leads to a red-shift of the Bragg reflection wavelength, until finally the transition to BP I occurs. As for the BPS, we can also observe an anomalous temperature dependence of the Bragg wavelength in the BPES.

We can now generalize the statements given in [4, 5]. Two features of the metastable blue phases have to be underlined which are anomalous with respect to the behaviour of the other stable blue phases [6–8]: (i) the decrease in the lattice constant with decreasing temperature in the BPS and BPES and (ii) the sign reversal of the electrostriction during the transition BPS–BPES. The main results of [4, 5] and of this paper relate to the evidence for the fact that the free energy of our system (blue phases in the vicinity of a smectic A phase) exhibits new local minima in the T, E and q coordinate space (q is the structural wavevector). We can reach these states during the process of structure relaxation in the supercooled region of the BP I or by applying an electric field in the supercooled region.

An important feature of the new blue phases is that these metastable states are observed in the vicinity of the smectic A phase. The effects of smectic fluctuations on the cholesteric phase could be described by taking account of a conical structural mode [9]. But in the conventional Landau theory of blue phases [9], the effect of the conical mode results in a weak increase in the BP lattice constant with decreasing temperature. This means, that an explanation of the properties of metastable blue phases requires the application of qualitatively new ideas. Experimental development of this work should be a detailed investigation of the phase ordering process in chiral liquid crystals and this is now in progress.

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