Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Porsch, F. and Stegemeyer, H.(1987) 'Electric Field Induced Phase Transitions in Liquid-Crystalline Blue Phases', Liquid Crystals, 2: 3, 395 — 399
To link to this Article: DOI: 10.1080/02678298708086684
URL: http://dx.doi.org/10.1080/02678298708086684

LIQUID CRYSTALS, 1987, VOL. 2, NO. 3, 395–399

PRELIMINARY COMMUNICATIONS

Electric field induced phase transitions in liquid-crystalline blue phases

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(*Received 6 June 1986; accepted 31 December 1986*)

Voltage/temperature phase diagrams of liquid-crystalline blue phase (BP) systems CB 15/M 18 and CB 15/E 9 have been determined by means of polarizing microscopy. Above a certain threshold voltage a field-induced BP occurs which is stable in a region of the U/T diagram between the BP I and BP II.

In cholesterics of sufficiently small pitches up to three blue phases occur two of which show a cubic structure (BP I and II). The BP properties have been reviewed in this Journal [1]. Electric field effects on BPs were studied by several groups [2–9]. Recently, Pieranski *et al.* [4] observed electric field induced BP single crystals of hexagonal habit (BP H) which are comparable with hexagonal weak field BP predicted theoretically by Hornreich *et al.* [8] and another field induced phase which they named BP X although they could not exclude that it is identical with the BP I [4]. Both field induced BPs have been observed in the two-phase region BP II/isotropic. In this communication we report voltage/temperature phase diagrams of BP systems with an electric field induced blue phase occurring between the BP I and BP II above a definite field strength.

To obtain a large dielectric anisotropy we used mixtures of the chiral 4-cyano-4′-(2-methylbutyl)-biphenyl (CB 15; designation of BDH Chemicals) with the nematogenic 4-cyano-4′-hexoxy-biphenyl (M 18) and the nematogenic cyano-biphenyl mixture E 9. Tin dioxide coated glass cells with 12 μm spacers were driven by a square-wave a.c. voltage source (200 Hz) and thermostated in a modified Mettler heating stage FP 52/5 which allows reproducible temperature changes of 10 mK.

The voltage/temperature (U/T) phase diagrams were obtained by means of microscopic texture observations parallel to the field direction (polarizing microscope Leitz SM-Lux Pol). A small temperature gradient was generated across the observed sample area. Thus, the phase boundary between BP I and II was observed by the different colours of the two phases in transmitted light as well as by the typical striations of the BP I grown from the BP II. In an applied electric field the colour of both BP I and II is red-shifted on increasing field strength at constant temperature. Simultaneously the birefringence of the BP I striations increases but the phase boundary BP I/BP II remains fixed indicating that the temperature for this phase transition is field independent. However, above a certain threshold voltage a different texture develops between the BP I and BP II (cf. figure 1). This texture exhibits neither striations nor birefringence but shows the same colour in reflection as the BP I. The photograph of figure 1 is

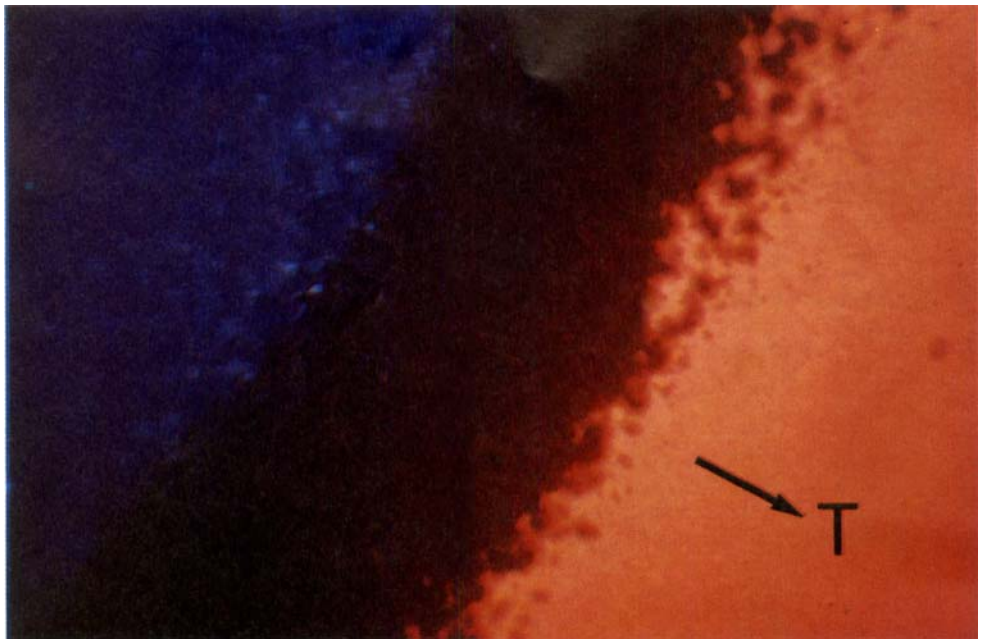

Figure 1. Microphotograph showing the phase sequence BP I/BP E/BP II (from the left to the right) in an electric field with a small temperature gradient from the left to the right. Magnification 250×. CB 15/E 9 mixture with 48·4 wt % CB 15; sample thickness 12 μm; voltage 23·8 V; temperature 33·56°C.

taken in transmitted light for which reason the BP I exhibits a slightly different colour as a result of its birefringence. On increasing field strength the new texture grows at the expense of the BP I and finally supersedes the BP I completely. The phase boundary between the BP II and the new texture, however, remains fixed. Best developed boundaries between the different textures were obtained by annealing the sample for several minutes. All transitions are reversible and reproducible with increasing and decreasing temperature. However, at high field strengths the BP II and the new texture appear dark and the transition is therefore rather difficult to detect. At slightly higher field strengths the new texture transforms into the cholesteric phase.

The voltage/temperature phase diagrams were obtained by measurements at constant temperature as well as at constant voltage. The temperature data of both these methods have been scaled with respect to the BP I/II transition as a suitable fixed point. The U/T diagram for two mixtures, CB 15 with M 18 and E 9 are given in figures 2 and 3, respectively.

The U/T area where the new texture occurs has been designated preliminarily as BP E indicating that it exists only in the presence of an electric field. The composition of the CB 15/E 9 mixture of figure 3 is nearly the same as that for which the field-induced BP H and BP X have been reported [4]. However, we neither found hexagonal platelets in the two-phase region nor observed a wave-length jump in the BP II on increasing voltage in our mixture even at higher a.c. frequencies (up to 10 kHz). In a CB 15/E 9 mixture of higher chirality (with 60·7 wt % CB 15) we did observe hexagonal platelets growing from the fog phase (BP III) but only at a.c. frequencies above 1 kHz.

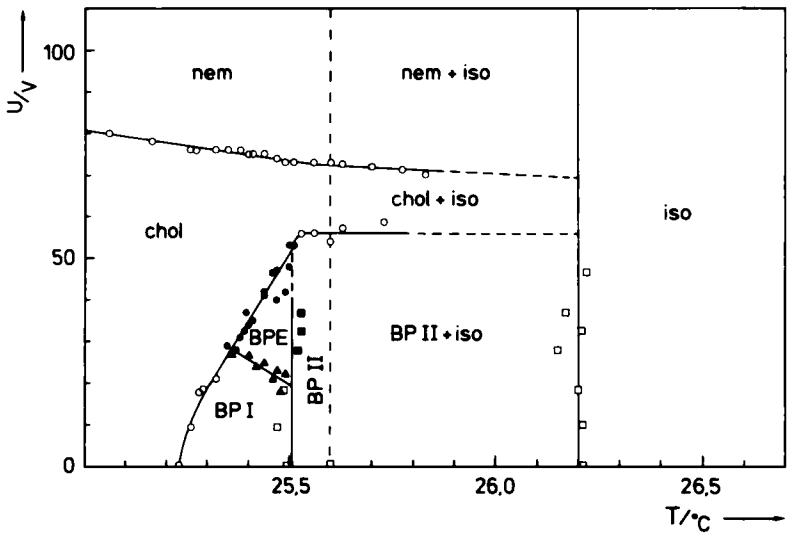

Figure 2. A phase diagram showing voltage against temperature for a CB 15/M 18 mixture 57·6 mol % CB 15; sample thickness 12 μm. (Different symbols of phase transition points represent data for the transitions between the different BPs concerned; full symbols: transitions of the BP E.)

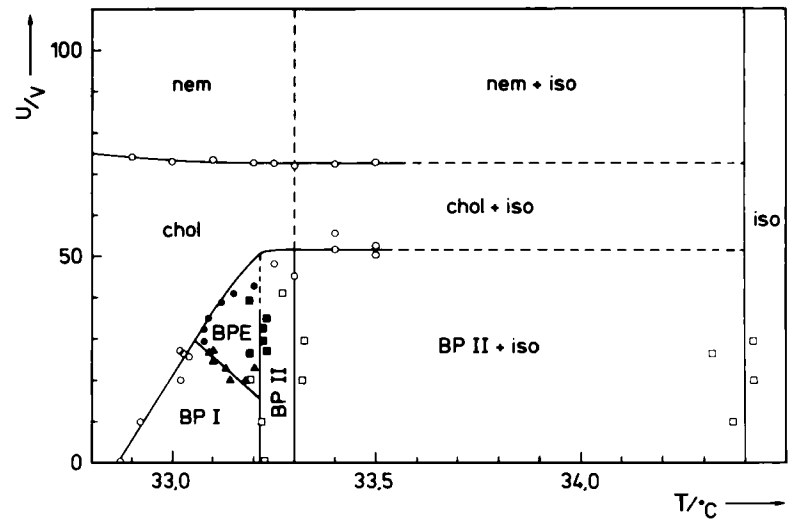

Figure 3. Voltage/temperature phase diagram of a CB 15/E9 mixture, 49·6 wt % CB 15, sample thickness 12 μm. (Different symbols of phase transition points represent data for the transitions between the different BPs concerned; full symbols: transitions of the BP E.)

The question arises if the observed E texture is only a special case of the BP I or BP II or a thermodynamically stable field induced BP. (i) The E texture and the BP II exhibit different selective reflection wavelengths (cf. figure 1). According to the Bragg equation this could indicate different orientations of the BP II lattice. But a lattice reorientation is not expected to respond reversibly to temperature changes and to be

independent of the field strength as we have found for this transition (cf. figures 2 and 3). Thus, the E texture is not identical with the BP II. (ii) May the E texture be a special case of the BP I? The same selective reflection colour mentioned previously could indicate this. But the birefringence as well as the striations of the BP I vanish on increasing voltage at a threshold field strength E_0 and do not reappear at higher fields. On decreasing field strength, however, they reappear sharply just at E_0. This indicates a change of the symmetry which is clearly due to a phase transition. Consequently, we come to the conclusion that the BP E is not identical with the known zero-field BPs but must be a thermodynamically stable field induced blue phase.

Because of the lack of birefringence the observed field induced BP seems to be a uniaxial phase belonging, for example, to the tetragonal or hexagonal crystal system. Therefore, it may be related to the BP H or BP X despite the fact that these phases have been found in quite different regions of the U/T diagram, namely at the BP II/isotropic transition [4]. The present state of our equipment does not allow us to determine the crystal system of the observed BP E by conoscopy; we shall report this problem in a forthcoming paper. However, it should be emphasized that the knowledge of the crystal system is not sufficient to specify a phase. This question can be answered by means of a precise U/T phase diagram containing the BP E as well as the BP H and BP X [4] which should be worked out.

The U/T diagrams (cf. figures 2 and 3) show a quite different field dependence for the three BP E phase transitions: The BP E → BP II transition is field independent, the BP E → Ch transition exhibits the same dependence as the BP I → Ch transition while the BP I → BP E transition temperature *decreases* with increasing field strength. As the enthalpy changes of all BP transitions are extremely small their transition temperatures are very sensitive to small changes of the dielectric permittivity during a phase transition. This has been discussed for BP systems [1, 7] in terms of a relation given by Kirkwood [10]. The field independence of the BP I/BP II as well as the BP E/BP II transition indicates no permittivity difference between these phases. But above the BP E threshold voltage the BP I and BP II do have different permittivities because the transition BP I/BP E is field dependent while BP E/BP II is not. Hence, BP E and BP II must have the same permittivity. The permittivity of the BP I, however, now assumes a smaller value than that of the BP II and BP E which could be accounted for by non-linear dielectric behaviour which has been detected by means of a field induced optical biaxiality [1, 6].

The variety of zero-field and field induced BPs is not surprising because all these blue phases are separated by very small transition enthalpies. Thus, external fields may easily change the stability of one molecular arrangement with respect to another.

This work has been supported by the Deutsche Forschungsgemeinschaft, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie.

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