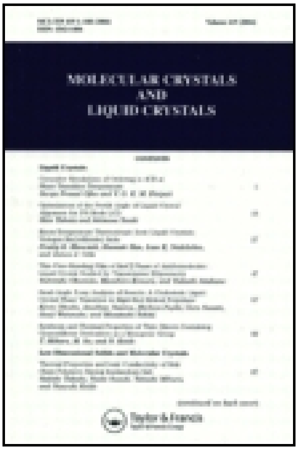

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A Complete Phase Diagram for the Blue Phases in CB15-E9 Mixtures

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A Complete Phase Diagram for the Blue Phases in CB15-E9 Mixtures

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We used polarized light microscopy and optical activity measurements in order to determine the BPIII-Isotropic critical point in CB15-E9 mixtures. The complete phase diagram is compared with that of mixtures of S,S-4"(methylbutyl)phenyl-4'-(methylbutyl)biphenylcarboxylate (CE2) and its racemate in which the BPIII-isotropic critical point was first observed. The effect of electric fields on the critical point was also investigated.

Keywords: blue phase; critical point; phase diagram; electric-field effects

INTRODUCTION

Short-pitched chiral nematics may form up to three blue phases[1-2], two cubic (BPI and BPII) and one amorphous (BPIII). BPI and BPII are unique examples of regular three-dimensional lattices composed of disclination lines. In BPI and BPII the disclination lines form body-centred and simple cubic lattices respectively. BPII and BPI have similar optical properties. These include optical activity, non-birefringence, selective reflection of circularly polarized light and Bragg peaks in the visible region. BPIII differs from BPI and BPII in that it does not show Bragg peaks. Keyes[3] was the first to point out that the BPIII and isotropic phases may be analogous to the liquid and gas phases and as such, there could be a continuous path around the BPIII-isotropic critical point terminating a line of coexistence.

This critical point has been observed recently in a mixture of CE2 (mole fraction ~0.45) and its racemate[4]. The CE2/CE2R phase diagram[5] is consistent with theoretical[6] predictions. The essential features of these phase diagrams include a critical chirality for the existence of a blue phase, the relative instability of BPII with respect to the other two phases with increasing chirality and the existence of the isotropic-BPIII critical point.

We could not study the effects of electric fields on this critical point unless a new system which exhibits such a critical point was established as CE2R is no longer commercially available. Since a 60% CB15- 40%E9 mixture[7] forms three blue phases and pure CB15 forms only BPI[8,9], one can deduce, assuming a universal phase diagram, that a critical point exists in these mixtures at a CB15 concentration intermediate between 60-100%. Previous data on these mixtures have been limited to pure CB15 and mixtures in the range 40-60% of CB15[10-12].

THEORY

The orientational order in BPI and BPII has been described in terms of a spatially averaged nematic alignment tensor $\langle \mathbf{Q(r)} \rangle$. However, this order parameter is zero in both BPIII and the isotropic phases and cannot be used to describe the isotropic-BPIII transition. The phenomenological theory of Stark and Lubensky[6] introduced a new scalar order parameter which is not zero in both these phases: $\langle \psi(\mathrm{r}) \rangle = \langle (\nabla \times \mathbf{Q(r)}) \cdot \mathbf{Q(r)} \rangle$

The free energy density can be expressed as:

$$f = \tfrac{1}{2} a_0 r \langle \phi \rangle^2 + \tfrac{1}{4} u_0 \langle \phi \rangle^4 - h \langle \phi \rangle \qquad (1)$$

where the theoretical temperature and its conjugate field are r and h respectively; $\langle \phi \rangle$ is the difference between $\langle \psi \rangle$ and its value at the critical point, $\langle \psi \rangle_c$; a_0 and u_0 are constants. The parameters r and h go linearly to zero as the critical point is reached. The measurable quantities, temperature T and the chiral fraction X are assumed to be linearly related to r and h:

$$r = a_1\,\Delta T + b_1\,\Delta X$$
$$h = a_2\,\Delta T + b_2\,\Delta X \qquad (2)$$

where $\Delta T = T - T_C$ and $\Delta X = X - X_C$ (the subscripts refer to the quantities at the critical point). The equilibrium value of the order parameter can be determined by the minimization of the free energy density with respect to the order parameter. The resulting cubic equation can be solved for $\langle\phi\rangle$ at various values of ΔX and ΔT. Curves of $\langle\phi(-\Delta T)\rangle$ vs. T look qualitatively like measured optical activity curves. By suitably choosing a_1, b_1, a_2 and b_2 (in terms of u_0 and u_0/a_0) one can produce curves which closely resemble optical activity measurements near the critical point.

EXPERIMENT

Polarized light miscroscopy was used to detect transitions which occurred above room temperature, namely, those in mixtures whose CB15 weight concentrations were ≤ 50%. A Melcor annular thermoelectric cooler inserted between the sample and the hot stage (Instec) provided sufficient cooling in order to study mixtures in the range 60-70% of CB15. The above transition temperatures are accurate to at least ± 0.005 K.

Optical activity measurements were used to study transitions for those mixtures with CB15 concentrations > 70% and these samples were cooled with liquid nitrogen. We used a phase modulation technique (described elsewhere[8]) in order to measure the optical activity to ± 0.05°. The samples were attached to large metal towers which were cooled with liquid nitrogen vapour. The portions of the metal towers in contact with the surroundings were insulated with fibre glass (2″ thick). We found that we could control temperatures to ± 0.05 K by using an Instec MK1 temperature controller which controlled the output of two small heaters that were attached to the metal plates. The sample was sandwiched between untreated but thoroughly cleaned glass slides which were separated by strips of aluminum. These served as both spacers and electrodes. Readings were taken only after temperatures remained constant for at least five minutes.

RESULTS AND DISCUSSION

The CB15-E9 phase diagram shown in figure 1 possesses a BPIII-isotropic liquid critical point at a 75% weight concentration of CB15. The transition temperatures were taken when a given blue phase first appeared. In the 50% and 60% CB15 mixtures, areas identified as blue phases include two phase isotropic-blue phase regions as well. Thus, these blue phase temperature intervals appear unusually broadened. However, pure blue phases existed for only a fraction of the observed temperature intervals. For the 50% mixture, pure BPII existed over a temperature interval of ~ 0.35 K; while the pure BPIII range in the 60% mixture was ~ 0.20 K. This resulted in the unusual shape for the BPII domain accounts for any apparent difference between this phase diagram and that of the CE2/CE2R system. It is unclear at present why two phase regions were not observed in the 55% CB15 mixture and if supercooling was completely eliminated. CE2 and CE2R are chemically similar differing only in their optical activities and that phase diagram is more likely to correspond to the theoretical phase diagram.

The samples which were viewed with the polarizing microscope appeared to be completely miscible in the isotropic phase but especially in the 50-50 mixture, the isotropic and blue phase coexisted over several tenths of a degree. Two phase regions are typical of discontinuous transition and this coexistence progressively decreased with increasing CB15 concentration.

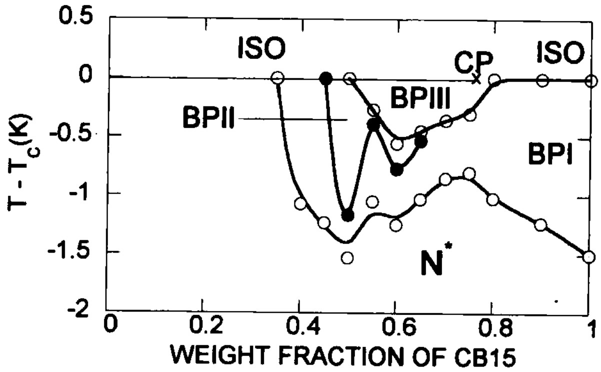

FIGURE 1, The complete phase diagram for CB15-E9 mixtures. The wavelength of the light used in the optical activity experiment is 633 nm.

Nevertheless, the location of the critical point in a new system was achieved and it was thus possible to study, on a preliminary basis, the effect of applied electric fields.

The optical activity data for a 75% CB 15 mixture is shown in figure 2. A discontinuous change is observed at the BPIII-BPI transition and there are no obvious signs of pretransitional effects. This behaviour is similar to that seen in the CE2/CE2R system[4,5]. We could not follow the fitting procedure given in reference 5 owing to the large number of fitting parameters (8) and the limited number of data points. The data of reference 5 contained 50 data points within a fraction of a degree.

We applied electric fields large enough to produce a measurable effect but not large enough to induce new phases[10,11,13-15] (figure 3). The isotropic-BPIII transition is now characterized by a small but finite discontinuity which was not detected at the smaller fields. The optical activity in the blue phases appear to be enhanced by the applied field and BPIII is thermodynamically stable over a range of ~ 0.7 K as compared with ~ 0.3 K at zero fields; while

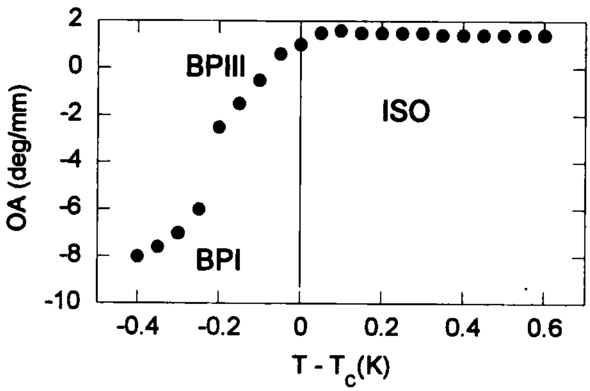

FIGURE 2, The optical activity of a 75% CB15-25% E9 mixture. The BPIII-BPI transition is discontinuous and the BPI-N*transition is not shown.

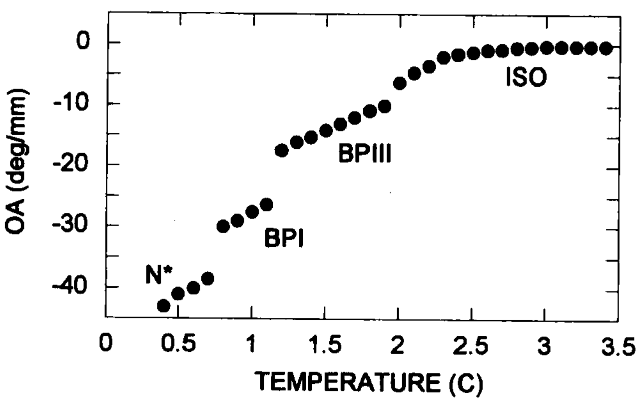

FIGURE 3, The optical activity when a d.c. field of 8 kV/cm is applied normal to the direction of the laser. The sample is 1.07 ± 0.01 mm thick and has a gap between the electrodes of 2.45 ± 0.01 mm.

at the same time there is a decrease in the stability of BPI. This stabilizing of BPIII by small electric fields has been recorded in MBMBAC[16]. Both MBMBAC and CB15 possess large and positive dielectric anisotropies[16] and they couple strongly with the electric fields.

The transition temperatures shifted to lower temperatures as the field was increased. This shift is proportional to V^2 as evident in figure 4. Both the isotropic and BPIII phase are characterized by short-range order (though of different types) which are not expected to be preserved in the presence of electric fields. Molecules characterized by positive anisotropies tend to align parallel or near parallel to applied fields and this reduces the energy of the system. However, our data is consistent with the preservation of this short range order in the presence of weak electric fields (the isotropic phase is stable at a lower temperature and BPIII has an extended temperature range). We know of no explanation as to why both phases are stabilized by electric fields. The effect of much larger fields ~ 30-40 kV/cm (which are known to break the symmetry in BPII and BPI) still need to be investigated.

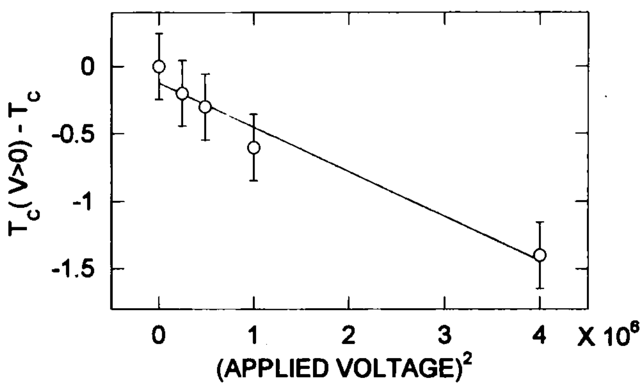

FIGURE 4, The shift in transition temperatures versus the square of the applied voltage. The applied voltages were 500, 707, 1000 and 2000 V.

CONCLUSION

We have established that a BPIII-isotropic liquid critical point exists in a 75% CB15-25% E9 mixture and have studied for the first time, the effect of electric fields on this critical point. The fields appear to enhance the stability of BPIII and reduce that of BPI. Also, the isotropic-BPIII transition temperature shifts to lower temperatures with increasing fields.

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