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Supercritical Conversion of the Third Blue Phase to the Isotropic Phase in a Highly Chiral Liquid Crystal

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The results of two independent experiments in the vicinity of the "transition" from the third blue phase (BP_{III}) to isotropic phase (*I*) are reported for a highly chiral liquid crystal. Heat capacity measurements using a high-resolution calorimeter and dynamic light-scattering measurements using circularly polarized light have been performed. The data show a continuous evolution of BP_{III} into *I* with no critical fluctuations. This is strong evidence that the BP_{III}-*I* transition in this compound is supercritical, indicating that the BP_{III} and *I* phases possess the same macroscopic symmetry.

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The effect of chirality on liquid crystal phases and their transitions has been a subject of intense interest and surprising results. New liquid crystal phases that possess a regular array of "defects" become stable if the chirality is high. These include the blue phases between the chiral nematic (*N*^{*}) and isotropic (*I*) phases; two of the blue phases have cubic lattices of defects and one blue phase has a seemingly amorphous array of defects [1]. These defects are lines between double-twist cylinders where the orientational order goes to zero and the direction of preferred orientation is undefined. Other examples are the twist-grain-boundary phases in chiral systems with smectic phases [2]. The defects in these phases are grain boundaries between smectic blocks. The amorphous blue phase (BP_{III}), which exists at temperatures just below the isotropic phase in highly chiral liquid crystals, is not well understood. Suggestions have been made that it is a "melted" version of the cubic blue phases [3], or that it is a phase possessing random double-twist cylinders [4], icosahedral or quasicrystalline order [5], or bond orientational order [6].

The effect that chirality has on liquid crystal phase transitions is more subtle. While fluctuations play an important role in the weakly discontinuous transition from a nonchiral nematic liquid crystal to the isotropic liquid phase, chirality introduces modes that fluctuate more strongly [7]. There is considerable evidence that chirality tends to drive the system toward a continuous transition [8–11], but there is only a small amount of indirect evidence that the BP_{III}-*I* transition actually is continuous in any liquid crystal system [11–13.]

To be more specific, Voets and Van Dael have shown through adiabatic scanning calorimetry experiments that the BP_{III}-*I* transition in *S*-(+)-4-(2-methylbutyl)phenyl-4-decyloxybenzoate (CE6) is discontinuous with a latent heat that decreases from 1627 mJ/g in the racemic mixture (an *N*^{*}-*I* transition) to 785 mJ/g in the chiral enantiomer [10]. An even smaller BP_{III}-*I* latent heat

(but still a discontinuous transition) was observed in the pure chiral material *S*-(+)-4-(2-methylbutyl)phenyl-4-hexyloxybenzoate (CE4), where the latent heat decreased from 957 mJ/g in the racemic mixture (an *N*^{*}-*I* transition) to 147 mJ/g in the chiral enantiomer [13]. Becker and Collings confirmed these CE4 measurements optically by showing that the discontinuity in the intensity of static light scattering decreased with increasing chiral fraction but was still discontinuous for the pure chiral isomer [11]. A similar static light scattering experiment on the more chiral compound *S,S*-(+)-4''-(methylbutylphenyl)-4'-(methylbutyl)-4-biphenylcarboxylate (*S,S*-MBBPC [14]) showed no discontinuity at all [11].

In this Letter we report the results of two different types of experiments performed in the vicinity of the BP_{III}-*I* transition in *S,S*-MBBPC: (1) heat capacity measurements using a new high-resolution calorimeter, and (2) improved static and new dynamic light-scattering measurements. The heat capacity and the light-scattering data evolve continuously in the BP_{III}-*I* region for this compound with no evidence for critical fluctuations. As discussed below, our results indicate a supercritical BP_{III}-*I* evolution in *S,S*-MBBPC, i.e., a continuous but nonsingular variation in properties analogous to what occurs in a simple fluid at pressures above the liquid-gas critical pressure. The implication of this is that the macroscopic symmetry of the BP_{III} and isotropic phases is the same.

The calorimeter is capable of measuring the heat capacity C_p using an ac technique with excellent signal-to-noise ratio and very high resolution. In addition, a new nonadiabatic scanning technique can be used to measure C_p in the absence of two-phase coexistence and also quantitative latent heats at first-order transitions [15]. The investigated temperature range (388–393 K) includes the chiral nematic to first blue phase (BP_I) transition, the BP_I to BP_{III} transition, as well as the supercritical evolution from BP_{III} to the isotropic phase, as shown in Fig. 1.

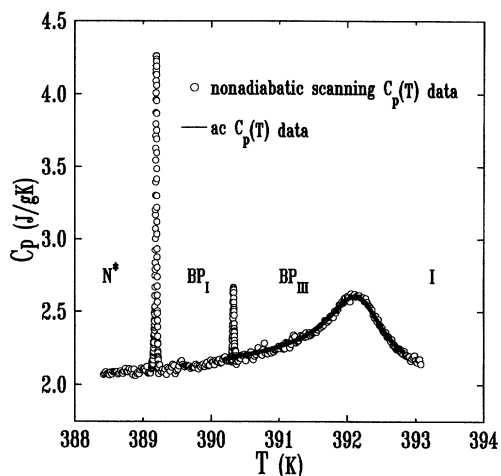


FIG. 1. The specific heat-capacity variation in the N^* - BP_I - BP_{III} - I transition region for S,S-MBBPC. The heat peaks for the scanning data at the N^* - BP_I and BP_I - BP_{III} transitions are artificial $C_p(\text{eff})$ values due to two phase coexistence and latent heat effects. Note the absence of latent heat peak at the BP_{III} - I transition. The heating rate for the nonadiabatic scanning run (open circles) was 4 K/h, while the heating or cooling rates for the ac calorimetry run at $\omega_0 = 0.196 \text{ s}^{-1}$ (solid line) were 50 mK/h.

Data from an ac calorimetry run and a nonadiabatic scanning run are both given in this figure.

The heat capacity data obtained in the ac calorimetry run show very little scatter, and the 450 data points are represented by a smooth curve $C_p(T)$. It must be stressed that the ac calorimetry technique does not measure enthalpy and cannot provide a quantitative measure of latent heats. However, characteristic changes in the phase shift ϕ between the input ac power $P_0 \exp[i\omega t]$ and the observed oscillatory sample temperature $T_{ac} \exp[i(\omega t + \phi - \pi/2)]$ do provide qualitative indications of two-phase coexistence at discontinuous transitions [15,16]. In the present study, an ac phase shift anomaly was seen at the BP_I - BP_{III} transition but was not present in the temperature range 391–393 K (note that no ac C_p data were taken below 390.2 K).

The nonadiabatic scanning technique measures an effective heat capacity C_p defined by

$$C_p = \frac{dH/dt}{dT/dt} = \frac{P - (T - T_b)/R}{dT/dt}, \quad (1)$$

where P is the dc power input, T is the time-dependent temperature of the sample, T_b is the time-independent temperature of the heat bath, and R is the thermal resistance between the sample and bath. Thus $(T - T_b)/R$ represents the rate of heat leak between sample and bath. For a one-phase system, this method yields the true C_p value. However, if two coexisting phases are interconverting at a first-order transition, Eq. (1) yields an apparent value $C_p(\text{eff})$ reflecting latent heat effects. The

latent heat L is then given by

$$L = \int_{T_1}^{T_2} [C_p(\text{eff}) - C_p(\text{coex})] dT, \quad (2)$$

where $C_p(\text{coex})$ is the heat capacity that a two-phase coexisting mixture would have in the absence of phase conversion. Thus $C_p(\text{coex})$ accounts for the heat effects associated with raising the temperature of a two-phase mixture over the narrow coexistence range from T_1 to T_2 and is well represented by the ac $C_p(T)$ data. Note that the coexistence range $T_2 - T_1$ is only 88 mK for N^* - BP_I and 40 mK for BP_I - BP_{III} . The nonadiabatic scanning technique is completely analogous to the well-established adiabatic scanning method [17] and is closely related to the relaxation method described in Ref. [16].

Figure 1 clearly shows the excess $C_p(\text{eff})$ peaks at 389.20 ± 0.05 and 390.34 ± 0.02 K which are associated with latent heat effects at the N^* - BP_I and BP_I - BP_{III} transitions. No such latent heat peak is observed at the BP_{III} - I transition (C_p maximum at 392.12 ± 0.08 K). The latent heats were determined to be 56.4 and 11.3 mJ/g for the N^* - BP_I and BP_I - BP_{III} transitions, respectively, which agree well with values reported for other chiral liquid crystals. The N^* - BP_I latent heat is 34 mJ/g for cholesteryl nonanoate (CN) [18] and 87 mJ/g for CE6 [10]. The sum of the latent heats for the BP_I - BP_{II} and BP_{II} - BP_{III} transitions is 14.6 mJ/g for CN [18] and 71 mJ/g for CE6 [10]. The essential new feature for S,S-MBBPC is the absence of any indication of a BP_{III} - I latent heat. This is in contrast to the reported BP_{III} - I latent heat values in less chiral materials: 323 ± 50 mJ/g for CN [18], 785 mJ/g for CE6 [10], and 147 mJ/g for CE4 [13]. The value for CE4 is the smallest BP_{III} - I latent heat ever reported.

Static and dynamic light-scattering measurements were performed on S,S-MBBPC using 488 nm light and a 90° scattering angle for an 8 K interval that included the BP_I , BP_{III} , and I phases. Two polarization arrangements were used: (1) right circular polarized (RCP) incident light and right circular polarized detected light, and (2) left circular polarized (LCP) incident light and left circular polarized detected light. The first polarization arrangement is sensitive to the most strongly fluctuating mode (a chiral mode) in S,S-MBBPC, and the second arrangement is sensitive to the most weakly fluctuating mode (a chiral mode) in S,S-MBBPC [7]. In each case, a nonchiral fluctuating mode contributes to the detected light at the 2% level and another chiral fluctuating mode contributes at less than the 0.1% level. In this temperature region, S,S-MBBPC has some of the shortest relaxation times measured in liquid crystals. In order to measure these submicrosecond times, a cross-correlation technique employing a beam splitter and two photomultiplier tubes (PMTs) was used to eliminate the effects of afterpulsing in the PMTs. The correlator was a Malvern 7032ES set to a 50 ns sample time. Exponential fits to the correlation

function allowed the relaxation times to be measured with an uncertainty of between 10 and 30 ns.

The thermistor used for temperature control in these light-scattering experiments was not individually calibrated. Instead, parameters supplied by the manufacturer were used. This is probably the reason why all the transition temperatures measured via light scattering are 2 K lower than those measured in the heat-capacity experiments. The widths of the BP_I and BP_{III} phases measured with the uncalibrated thermistor (1.0 and 1.5 K, respectively) correspond nicely to those measured previously in optical activity experiments (1.1 and 1.6 K, respectively) [12] and to those measured in the heat-capacity measurements reported here (1.14 and 1.78 K, respectively).

The intensity of the scattered light I_s as a function of temperature for both polarization arrangements is shown in Fig. 2. Because of a combination of stray light reaching the detector and impurity scattering from the sample, there is a background intensity of about 20 000 counts/s. When this background intensity is subtracted from I_s , the inverse intensity in the isotropic phase is linear, which is the mean-field result and has been verified previously [9]. A discontinuity in the scattering for both chiral modes is apparent at the BP_I-BP_{III} phase transition at 388.2 ± 0.1 K, but only a change in temperature dependence is observed at the BP_{III}-*I* transition around 389.7 ± 0.2 K. The N^* -BP_I transition is easily measured (387.2 ± 0.1 K), since the 1 cm thick sample is opaque in the N^* phase. The lack of a discontinuity in the BP_{III}-*I* transition in the high-quality data of Fig. 2 confirms previous optical results on this compound [11,12]. In fact,

the temperature over which the data changes from mean-field behavior to a more or less linear dependence is about 0.5 K, which is roughly the width of the heat-capacity peak in Fig. 1. Similar measurements on CE6 reveal a clear discontinuity at the BP_{III}-*I* transition, with mean-field behavior followed right up to the discontinuity [19].

The relaxation time of the fluctuations for both chiral modes is displayed in Fig. 3. Again, a discontinuity is evident at the BP_I-BP_{III} transition but not at the BP_{III}-*I* transition. Graphing the inverse of the relaxation time vs temperature for the data in the isotropic phase yields a linear relationship as expected from mean-field theory. However, the divergent behavior in the isotropic phase shown in Figs. 2 and 3 is no stronger than is seen in similar experiments on CE6 [19], indicating that the fluctuations in the neighborhood of the BP_{III}-*I* transition are not critical. This also suggests the evolution of one phase to another typical of a supercritical region.

We feel that the evidence supporting a supercritical (continuous but nonsingular) evolution of BP_{III} to *I* in S,S-MBBPC is very strong. There is no indication of two-phase coexistence or latent heat in the thermal studies of the BP_{III}-*I* transition. There is the continuous evolution of both intensity and relaxation time in the optical studies. One possible concern is that our thermal results are artificial due to rate effects if the BP_{III}-*I* transition is kinetically very sluggish compared to the N^* -BP_I and BP_I-BP_{III} transitions. This possibility has been tested in three ways. First, as shown in Fig. 1, the nonadiabatic scanning results and ac calorimetry data are in excellent agreement, even though the scanning rates

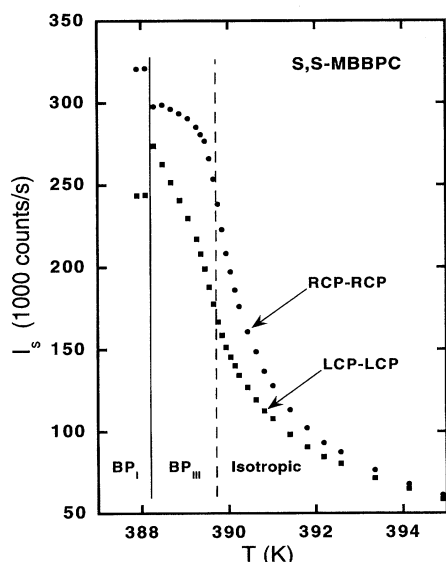


FIG. 2. Light-scattering intensity I_s for both polarizations in the BP_I-BP_{III}-*I* transition region for S,S-MBBPC. The wavelength was 488 nm and the scattering angle was 90°. Note the discontinuity in I_s at the first-order BP_I-BP_{III} transition and the continuous change in temperature dependence with no discontinuity at the BP_{III}-*I* transition.

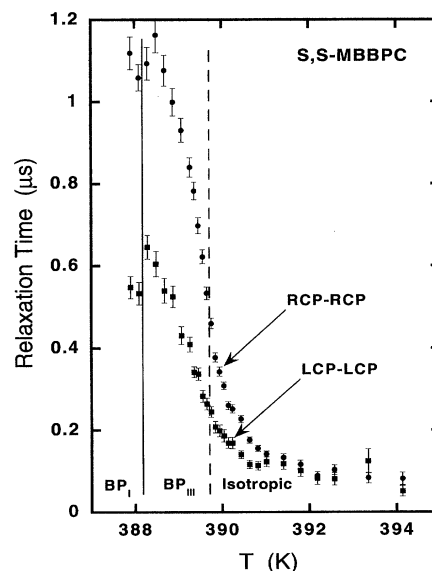


FIG. 3. Relaxation time τ of the scattered light for both polarizations in the BP_I-BP_{III}-*I* transition region for S,S-MBBPC. The wavelength was 488 nm and the scattering angle was 90°. Note the discontinuity in τ at the first-order BP_I-BP_{III} transition and the continuous change in temperature dependence with no discontinuity at the BP_{III}-*I* transition.

differ by a factor of 80. Second, the ac calorimetry experiment was repeated with an oscillation frequency 9 times smaller and a scanning rate half as large, yielding identical results. Third, there is no change in the ac heat capacity at the peak of the BP_{III}-*I* transition when the temperature is held constant for 2×10^5 s. Thus the idea of a discontinuous transition but very slow BP_{III}-*I* conversion is not consistent with our data.

The existence of a first-order BP_{III}-*I* coexistence line that terminates at an isolated critical point is confirmed by preliminary C_p measurements on mixtures of S,S-MBBPC and its racemate. Two-phase coexistence and a latent heat are observed at low concentrations of S,S-MBBPC, and both these features disappear for high concentrations of S,S-MBBPC. Further work to locate and characterize the critical mixture is in progress.

The existence of a critical point for the BP_{III}-*I* transition has extremely important implications for the structure of BP_{III}. Any structure proposed for BP_{III} must possess isotropic symmetry macroscopically, since only then could a critical point be present. Yet the existence of optical activity in both BP_{III} and *I* indicates that the symmetry of neither phase is completely isotropic [11,12]. Obviously, some order parameter is discontinuous at the BP_{III}-*I* transition in low chirality compounds but continuous in the more highly chiral S,S-MBBPC.

Lubensky and Stark have introduced a scalar order parameter $\langle \psi \rangle$ to describe both BP_{III} and *I*. This model, in which $\langle \psi \rangle = \langle (\nabla \times \vec{Q}) \cdot \vec{Q} \rangle$ with $\vec{Q}(\mathbf{r})$ being the alignment tensor, predicts that the BP_{III}-*I* transition is in the same Ising universality class as the liquid-gas transition [20].

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