

Apparent tricritical behavior at a nearly second-order nematic-isotropic phase transition of a cyclic liquid crystalline trimer

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The cyclic liquid crystalline trimer TPB-(c)9(3) was investigated by optical retardation and Fréedericksz techniques within a few tens of millikelvins of the superheating limit of the nearly second-order nematic-isotropic phase transition. Both the optical retardation and the Fréedericksz bend threshold voltage are in good agreement with tricritical behavior for the transition.

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The nature of the nematic-isotropic (NI) liquid crystal phase transition has long been an enigma. Earlier, Poggi *et al.* measured a value for the order parameter exponent $\beta = \frac{1}{2}$ [1], consistent with the mean-field value, although Keyes showed that one can fit the data quite well with a tricritical exponent $\beta = \frac{1}{4}$ [2]. Other workers who have examined this problem have tended to find a tricritical-like exponent β [3,4], with additional support for tricritical behavior coming from measurements of the heat capacity exponent α [5]. Recently, Mukherjee reexamined this issue theoretically in the context of a Landau model, and showed that values for $T_{NI} - T^*$, where T_{NI} is the NI phase transition temperature and T^* is the supercooling limit of the isotropic phase, which are observed for low molecular weight liquid crystals tend to be more consistent with tricritical behavior [6] as compared to the mean-field behavior. The preponderance of evidence clearly seems to favor tricritical-like behavior, whereby the quartic term in a Landau free energy expansion,

$$F = \frac{1}{2} a_o (T - T^*) \text{Tr} \mathbf{Q}^2 - \frac{1}{3} B \text{Tr} \mathbf{Q}^3 + \frac{1}{4} C (\text{Tr} \mathbf{Q}^2)^2 + \frac{1}{5} D (\text{Tr} \mathbf{Q}^2)(\text{Tr} \mathbf{Q}^3) + \frac{1}{6} E (\text{Tr} \mathbf{Q}^2)^3 + E' (\text{Tr} \mathbf{Q}^3)^2, \quad (1)$$

in the tensor order parameter \mathbf{Q} is small relative to the sixth-order term(s). However, analyses have always been plagued by the non-negligible magnitude of $T_{NI} - T^*$, which usually is ~ 1.5 K [7], i.e., the difficulty in closely accessing the region near T^* can lead to ambiguous interpretation of experimental results.

About ten years ago, Li *et al.* reported a nearly second-order NI transition for a cyclic thermotropic liquid crystal [8], where the quantity $T_{NI} - T^* < 200$ mK. This was the first and, to our knowledge, only report of such a small value of $T_{NI} - T^*$ for a thermotropic liquid crystal. It turns out that the nematic-isotropic transition becomes second order when both the coefficient B vanishes and $T = T^*$. This is the so-called Landau point [9,10] that separates the isotropic phase from two uniaxial nematic phases, and possibly a biaxial phase as well [11–13], depending upon the relative values of

the coefficients E' and C . Based on the small value of $T_{NI} - T^*$ (and thus the possibility of a nearby Landau point), and owing to the highly biaxial shape of the cyclic trimer molecule TPB-(c)9(3) (Fig. 1), the intriguing prospect arose that the bulk nematic phase of this material may exhibit biaxial character. Subsequently, Li *et al.* examined the behavior of TPB-(c)9(3) deep inside the nematic phase, finding behavior suggestive of a transition from a uniaxial to biaxial nematic ≈ 25 K below T_{NI} [14]. Although a biaxial phase has been observed in a lyotropic liquid crystal [15], and there are numerous reports of thermotropic biaxial phases [16–21], nuclear magnetic resonance (NMR) measurements on several of the thermotropic materials have shown that many of these nematics are, in fact, uniaxial [22]. Because the tiny extant quantity of the difficult-to-synthesize liquid crystal TPB-(c)9(3) has not been deuterated (and contains no other spin one nuclei), no such NMR measurements have been performed on TPB-(c)9(3). Nevertheless, the small value of $T_{NI} - T^*$ indicates that the coefficient B is small and that the first-order character of the uniaxial nematic-isotropic transition is considerably weaker than for most other low molecular weight thermotropic materials. Thus, TBP-(c)9(3) may serve as an ideal candidate for critical behavior investigations.

Given this serendipitous happenstance of a nearly second-order thermotropic NI phase transition, and having recently come across the only known cache (< 1 mg) of TPB-(c)9(3), we have examined this liquid crystal as a function of temperature in the nematic phase in order to better understand the nature of the phase transition. Our earlier Kerr measurements in the isotropic phase yielded a susceptibility exponent $\gamma = 1$, which is consistent with both tricritical and classical mean-field behavior [8]. A measurement of the order parameter exponent β , however, would be able to distinguish between the two behaviors. Thus, both optical phase retardation measurements and Fréedericksz transition measurements

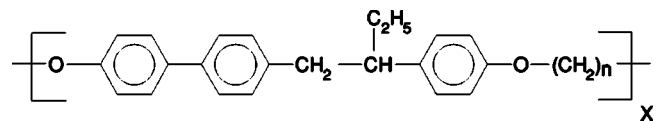


FIG. 1. The monomer that constitutes TPB-(c)9(3). ($X = 3$, $n = 9$.)

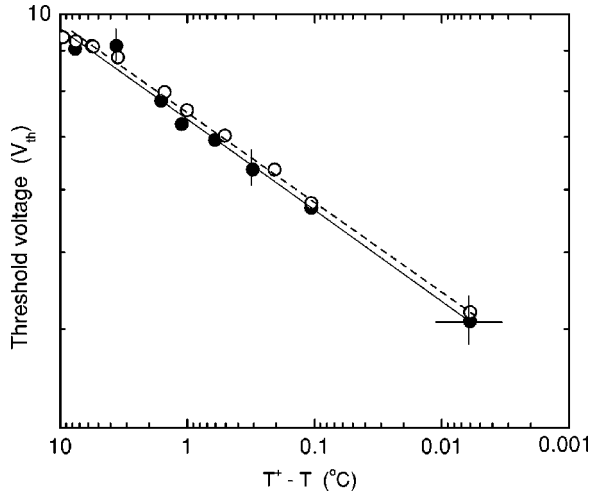


FIG. 2. Fréedericksz threshold voltage V_{th} vs $T^+ - T$ for two sets of data. The solid line corresponds to an algebraic fit for the solid circles using all nine points; the dashed line corresponds to the open circles.

were performed. Our central result is that the order parameter exponent β is consistent with, but perhaps slightly smaller than, the value $\frac{1}{4}$ associated with the tricritical behavior.

Details of the synthesis of the cyclic trimer TPB-(c)9(3), which is composed of the monomer shown in Fig. 1 with $n = 9$ and $X = 3$, are described elsewhere [23,24]. T_{NI} was found to be about 84°C for this batch, and the glass transition temperature $\approx 36^\circ\text{C}$.

For the Fréedericksz measurements, two glass slides coated with semitransparent indium tin oxide (ITO) first were spin coated with the polyimide SE1211 (Nissan Chemicals Ltd.) and baked at 180°C for 1 h to ensure homeotropic alignment. The slides were then placed together, separated by a pair of Mylar spacers of approximate thickness $t = 2\ \mu\text{m}$, and cemented. Two electrodes were attached to the two ITO surfaces so that electric field could be applied across the cell. The cell was then placed in a temperature-controlled oven and filled with the material TPB-(c)9(3) in its isotropic phase and cooled slowly to the nematic phase. Good homeotropic alignment was obtained. A beam from a 5-mW He-Ne laser focused to a diameter of $60\ \mu\text{m}$ passed consecutively through a light chopper, a polarizer, the cell, an analyzer, and into a detector. The polarizer and analyzer were oriented at 45° with respect to the vertical. The detector signal was fed into a lock-in amplifier, which was referenced to the chopper frequency of 783 Hz. For a given temperature in the nematic phase, the amplitude of the 1-KHz ac voltage was ramped from 0 to 15 V at a rate of $3.33 \times 10^{-4}\ \text{V s}^{-1}$ —this was sufficiently slow to avoid hysteresis on ramping up and down—and the detector intensity was computer recorded. The Fréedericksz threshold voltage was obtained from the curve of intensity vs V . Several sets of measurements were made from 75°C up to within about 10 mK of T_{NI} ; two sets of data are shown in Fig. 2 as a function of $T^+ - T$, where T^+ is the calculated superheating limit of the nematic phase (see below).

For the optical retardation measurements, the cell was

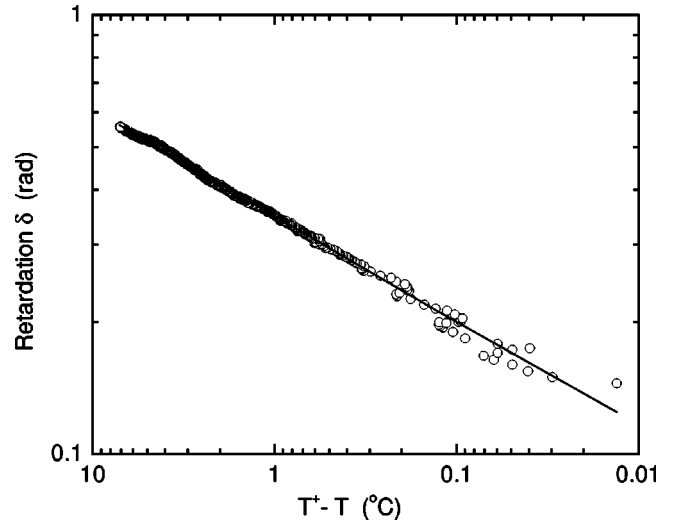


FIG. 3. Optical retardation δ vs $T^+ - T$. The solid line corresponds to an algebraic fit.

mounted such that its normal made an $\approx 45^\circ$ angle with the vertical. The temperature was then ramped downward from the isotropic into the nematic phase at a rate of $5.55 \times 10^{-4}\ \text{K s}^{-1}$ and the lock-in amplifier output, proportional to the intensity, was computer recorded. A Babinet-Soleil compensator was then inserted after the sample and the retardation difference $\Delta\delta$ between a temperature just inside the isotropic phase and temperature $T_{NI} - 7^\circ\text{C}$ was measured for calibration purposes. The intensity at the detector is given by $I = I_o - I_1 \cos \delta$, where δ is the temperature-dependent phase retardation and I_o and I_1 are constants. The two constants I_o and I_1 were obtained empirically from intensity measurements in the isotropic phase and at $T_{NI} - 7^\circ\text{C}$, along with a measurement of the retardation at $T_{NI} - 7^\circ\text{C}$. (The retardation $\delta = 0$ in the isotropic phase.) Thus, the intensity measurements could be converted to retardation values; data are shown in Fig. 3.

The Fréedericksz threshold voltage V_{th} for a cell is proportional to $\sqrt{K_{33}/\Delta\chi}$, where K_{33} is the bend elastic constant, $\Delta\chi$ is the dielectric anisotropy of the liquid crystal (which is negative for this material), and infinitely strong surface anchoring is assumed [7]. $\Delta\chi$ can be taken as proportional to $Q_{zz} - Q_{xx}$, i.e., proportional to the scalar order parameter S for a uniaxial nematic phase [7]. K_{33} is more complicated. For a simple model in which the free energy contains terms up to second order in \mathbf{Q} and for which there are two gradient terms with two coefficients, all three elastic constants are proportional to S^2 [25]. Deviations from this form, particularly for the bend elastic constant, are not uncommon [26], however. Given the insufficient quantity of liquid crystal to permit an independent measurement of $\Delta\chi$ (and thus S), we have chosen to examine V_{th} vs temperature and assume that $V_{th} \propto S^{1/2}$. Data for V_{th} in Fig. 2 were fitted to the three-parameter algebraic form $V_{th} = a(T^+ - T)^x$. In principle, there should also be a constant added to the algebraic part owing to the inherent first-order nature of the transition. However, using the technique of range shrinking, whereby the first Z points are fitted, then the first $Z + 1$

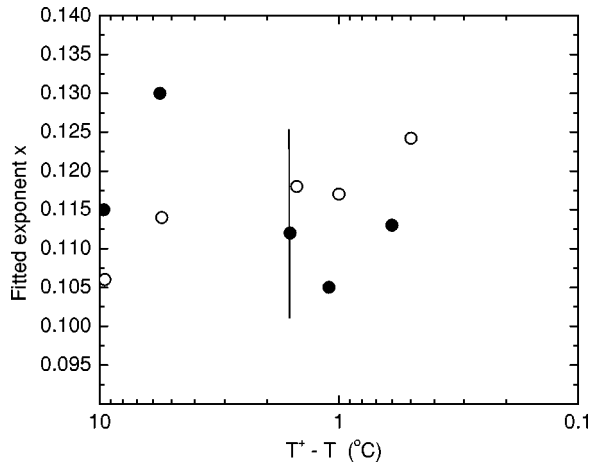


FIG. 4. Range shrinking fits for exponent x for the two sets of data shown in Fig. 2. The points correspond to a fit using all data between T^+ and $T^+ - T$.

points, and so on, we found that the exponent x tended to hover in the vicinity of $x = 0.115 \pm 0.01$. Figure 2 shows two sets of data where each of the two fits uses all data points for a given set, and Fig. 4 shows the exponents x obtained by the range shrinking technique. Note that the highest temperature data points ($T^+ - T < 10$ mK) in Fig. 2 are somewhat uncertain. First, temperature control is $\approx \pm 2$ mK. Second, there is likely to be a temperature differential across the beam spot of about the same magnitude. Finally, the position of T^+ was determined based upon the algebraic fit, which has an uncertainty of $\approx \pm 3$ mK. Although we have plotted these two data points and have included them in the fit, we are somewhat skeptical that one can approach the superheating limit so closely. Nevertheless, omission of these points does not affect the quantitative results in any significant way, nor does it affect our interpretation of the critical behavior. Turning now to Fig. 4, it is clear that even with data scatter caused by the difficulty in precisely locating V_{th} , there is no clear trend in x as additional points are used for the fit. This behavior would imply that omitting a constant offset in the fit is a reasonable approximation, that T^+ is nearly equal to T_{NI} , and thus the first-order nature of the transition is extremely weak. Based on the simple model for V_{th} , the critical exponent for the order parameter $\beta = 2x = 0.23 \pm 0.02$. This value is slightly smaller than, but consistent with, tricritical behavior, in which the quartic term in Eq. (1) is much smaller than the sixth-order term. Our results also exclude the mean-field value of $\beta = \frac{1}{2}$, and render the Ising value $\beta = 0.312$ highly unlikely.

Let us now turn to the retardation data. The phase retardation is given by $\delta = \int k(n_e^{eff} d\zeta_e - n_o d\zeta_o)$, where n_e^{eff} is the effective (angle-dependent) extraordinary refractive index, n_o is the ordinary refractive index, ζ_e and ζ_o are the paths in the sample taken by the two eigenmodes, and k is the wave vector of light in vacuum. An expansion of δ reveals that $\delta \propto S$ to lowest order in S ; thus, the data in Fig. 3 should scale as the scalar order parameter. The solid line in Fig. 3 is a fit to the form $\delta = a(T^+ - T)^y$, where again we have omitted a constant offset term. As was done for the Fréedericksz data,

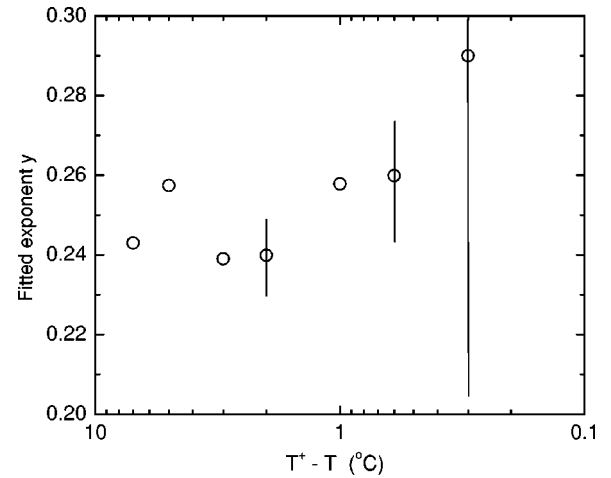


FIG. 5. Range shrinking fits for exponent y for the data shown in Fig. 3. The points correspond to a fit using all data between T^+ and $T^+ - T$.

we have performed fittings over the temperature ranges $T_{NI} - 0.3 \text{ K} < T < T_{NI}$, $T_{NI} - 0.6 \text{ K} < T < T_{NI}$, etc. The calculated exponents y are shown in Fig. 5. The exponent y closest to the transition is somewhat larger than the tricritical value 0.25, although the scatter in the data close to the transition gives rise to a large uncertainty (see Fig. 3). As we add more data points further from T_{NI} to the fit, we find that the exponent y settles down very quickly to a value $y = 0.25 \pm 0.01$; this corresponds to the order parameter exponent β , and is very close to the tricritical value.

Simple theories based on molecular shape and computer simulations of simple shapes suggest that the transition for ordinary mesogens is mean-field-like with a large value of C [27] in the free energy [Eq. (1)]. However, we need to remember that TBP-(c)9(3) is a mixture of many isomers: TBP-(c)9(3) is a cyclic trimer and each monomer is chiral and has a direction. Because these are not controlled in the synthesis, TBP-(c)9(3) is a mixture of 16 isomers, each of which is likely to have several different common conformers with significantly different shapes. Consider now the C and E' terms in the free energy, which are written as the square of other scalars, viz., the a_o and B terms, respectively. [We note that the fifth-order term in Eq. (1) usually is neglected [6,9]. Provided the quartic coefficient C is small, both B and D must be small in order for the transition to be nearly second order. As we observe that the transition is nearly second order, we will neglect the fifth-order term in our analysis below.] If we consider a free energy that includes fluctuations in scalar quantities ρ (such as the concentration of chemical or conformational isomers), the resultant contribution to the free energy is $\frac{1}{2}a\rho^2 + \rho(\alpha[\text{Tr}(\mathbf{Q}^2)] + \kappa[\text{Tr}(\mathbf{Q}^3)])$. If we then eliminate these fluctuations, we find that this results in only negative contributions to the C and E' terms; this is not unlike the effect of density variations on a single-component monomeric liquid crystal [6,28]. (In fact, the coupling between density and \mathbf{Q} has been cited as a reason for the relatively small values of $T_{NI} - T^*$, even for ordinary monomers [6].) Therefore, it would be expected that this mixture, and even mixtures that contain fewer chemical

isomers [29], would tend to have smaller positive (or perhaps even negative) values of C and E' than would single component samples. The fact that C is likely to be especially small is consistent with the very weak first-order character of this material. Moreover, the fact that E' also is less positive may imply that the system is less likely to have a biaxial phase, consistent with the observation that the biaxial phase, if it exists, occurs some 25 K below T_{NI} [14]. This may help to explain why the search for biaxial nematics has been so difficult. If it tends to be the case that the C and the E' terms are small or negative, it would be quite difficult to observe biaxial phases, even if B could be adjusted to be small. The chemical structures that have been hypothesized to be biaxial nematics are routinely very complex structures that have many conformers that plausibly result in small or negative C and E' terms. If this hypothesis were correct, it would suggest that only materials in which most of the conformers have a similar tendency to align, i.e., similar values of the $\text{Tr } \mathbf{Q}^2$ term and similar and small values of the $\text{Tr } \mathbf{Q}^3$ (B) term (which is more difficult to describe “intuitively” in terms of molecular structure) would have nearly second-order transitions and biaxial nematic phases. Finally, we remark that if the α coupling term between ρ and \mathbf{Q} were sufficiently strong we would expect a two-phase region,

which indeed occurs. However, we believe that this is due to a small concentration of nonmesogenic impurities that cause phase separation, but do not significantly alter the magnitude of the order parameter in the ordered phase. If the κ term were sufficiently large, we would expect phase separation into two coexisting uniaxial phases. However, at low enough temperatures we observe a biaxial phase, rather than two uniaxial phases.

To summarize, our two measurements are a clear indication that for this material the transition exhibits a tricritical character. As with many other thermotropics, the quartic term is small compared to the sixth-order term E in Eq. (1). But, because the cubic term is also small, we are able to very closely approach the superheating limit of the nematic phase, facilitating an unambiguous algebraic fit of the data. Thus, as have many other workers, but now with the distinct advantage of having a nearly second-order phase transition because of the apparent biaxial shape of the mesogen, we conclude that the underlying character of the weakly first-order NI transition is tricritical in nature.

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