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Nearly-second-order nematic-isotropic phase transition in a cyclic thermotropic liquid crystal

Jian-Feng Li

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079

Virgil Percec

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Charles Rosenblatt*

Department of Physics and Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7079

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Kerr measurements are reported for a cyclic trimeric liquid crystal above the uniaxial nematic-isotropic phase transition temperature T_{NI} . The inverse of the order-parameter susceptibility is found to be linear in temperature, such that the quantity $T_{NI} - T^*$ is less than 200 mK, where T^* is the supercooling limit of the isotropic phase. Well below T_{NI} we observe textures consistent with a biaxial nematic phase.

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The nematic-isotropic ($N-I$) phase transition can exhibit an isolated critical point on a temperature- Γ phase diagram, where Γ corresponds to an experimentally adjustable parameter such as concentration or molecular architecture. This so-called Landau point separates a high-temperature isotropic phase from three nematic phases, viz., two uniaxial nematic phases segregated by a biaxial nematic phase [1–4]. Although extensive work on the nematic-nematic phase transitions in lyotropic systems has been reported [5–7], only recently was the Landau point actually observed. Using a ternary surfactant-cosurfactant-water system, Melnik, Photinos, and Saupé used magnetically induced birefringence to observe a diverging susceptibility above the $N-I$ transition temperature T_{NI} [8]. In this, as in other micellar systems, the shape of the micelle is dependent on the concentration; in consequence, one can achieve a biaxial micelle architec-

ture and/or a distribution of micelle shapes, which makes possible the existence of biaxial phases and a Landau point. To date, however, this scenario has not been achieved with single-component thermotropic liquid crystals. Although the thermotropic $N-I$ transition is often considered as “weakly” first order because of its relatively small latent heat, the discontinuity of the order parameter $S [\equiv \langle P_2(\cos\theta) \rangle]$ is actually quite large, typically 0.3–0.4. Additionally, the quantity $\delta T = T_{NI} - T^*$, where T^* is the supercooling limit of the isotropic phase,

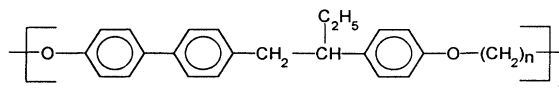


FIG. 1. The monomer that constitutes TPB-(c)9(3). ($X=3$; $n=9$.)

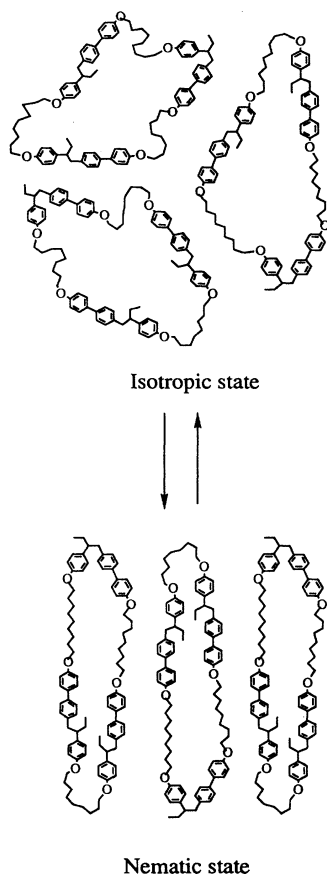


FIG. 2. Schematic representation of the probable isotropic and nematic phases.

is typically 1–2 K [9].

Very recently a new class of cyclic thermotropic liquid crystals has been synthesized, which promises a medley of intriguing new phenomena [10–12]. Typically composed of several monomers arranged in a closed loop, these molecules are inherently highly biaxial, and might be expected to exhibit bulk biaxial nematic phases, and perhaps even a continuous transition at a Landau point. In this light we have begun to investigate members of this class of molecules near the N - I phase transition. In this paper we report on Kerr measurements in the isotropic phase, in order to determine the susceptibility as a function of temperature for a member of this class. Additionally, we are able to extract the relaxation time τ near T_{NI} for long-wavelength order parameter fluctuations. We find that the susceptibility exhibits mean-field-like behavior near the N - I transition, but more importantly, that δT is less than 200 mK, a figure far smaller than observed in any other thermotropic liquid crystal extant.

We studied the cyclic trimer TPB-(c)9(3), which is composed of the monomer shown in Fig. 1, with $n=9$ and $X=3$; in Fig. 2 we show schematic representations of the isotropic and nematic phases. Details of the synthesis are described elsewhere [13,14]. T_{NI} was found to be about 90°C, and the nematic-glass transition temperature approximately 36°C. Before proceeding, we examined a cell filled with TPB-(c)9(3) by optical microscopy. The

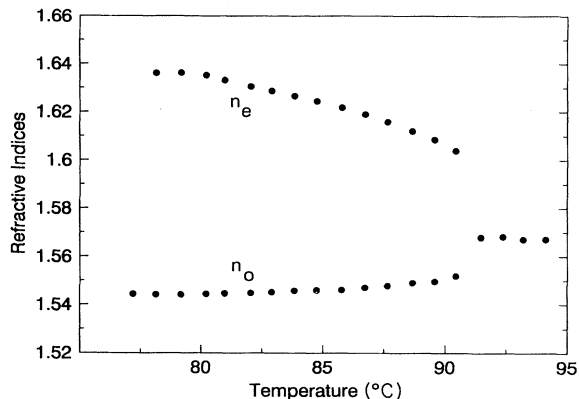


FIG. 3. Refractive indices vs temperature at wavelength $\lambda=6328$ Å. Note that the temperature scale is shifted slightly from Figs. 3 and 4 because of the use of different thermistors.

cell was treated for homeotropic alignment using the surfactant hexadecyl trimethylammonium bromide, and a good monodomain was observed in the nematic phase. On cooling to approximately 58°C we observed the onset of very-long-wavelength (on the order of hundreds of μm) Schlieren textures. Further cooling resulted in an increased contrast. Compression and dilation of the cell induced a rearrangement of the pattern, although we were unable to induce textures, such as focal conics, which are characteristic of a smectic- C phase. The observed texture is consistent with a low-temperature biaxial nematic phase [15,16]. Further evidence of a biaxial phase can be gleaned from the small value of δT (see below). This is consistent with a nearby Landau point, which in turn exhibits the phase sequence on cooling (isotropic \rightarrow uniaxial nematic \rightarrow biaxial nematic). Using an Abbe refractometer, we then measured the refractive indices in the uniaxial nematic phase much closer to T_{NI} ; these results are shown in Fig. 3. Since $n_e > n_o$ it is highly unlikely that the molecules form a discotic uniaxial phase. Instead, we conclude that the ring structure is elongated, especially in the nematic phase. These anisometric rings in turn form a uniaxial nematic phase, with the long axes of the rings parallel to the nematic director (see Fig. 2).

We now turn to the orientational susceptibility measurements. The phenomenological Landau free energy for uniaxial order is given by

$$F = \frac{1}{2}a(T - T^*)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 - \frac{1}{2}\Delta\chi E^2 S, \quad (1)$$

where $\Delta\chi$ is the volumetric susceptibility anisotropy and E is the applied electric field. Note that a necessary condition for a Landau point is that the coefficient b vanish. For small induced order we find that

$$S = \Delta\chi E^2 / 2a(T - T^*), \quad (2)$$

and thus the dc ($\omega=0$) order parameter susceptibility $dS/dE^2|_{dc} = \Delta\chi / 2a(T - T^*)$. The dynamical equation for S is $\eta(dS/dt) = -(dF/dS)$, when η is a kinetic coefficient. From Eq. (1) we obtain

$$\eta \frac{dS}{dt} + a(T - T^*)S = \frac{1}{2}\Delta\chi E^2. \quad (3)$$

Assuming $E = E_0 \cos \omega t$, we expect a dc order parameter S_{dc} given by one-half the value in Eq. (2), plus a component of S at frequency 2ω given by

$$S_{2\omega} = \frac{\Delta \chi E_0^2}{4a(T - T^*)[1 + 4\omega^2 \tau^2]} (\cos 2\omega t + 2\omega \tau \sin 2\omega t). \quad (4)$$

$S_{2\omega}$ has in-phase and quadrature components, such that the relaxation time τ is given from Eqs. (3) and (4) by

$$\tau = \frac{\eta}{a(T - T^*)} = \frac{S_{2\omega}^{\text{quad}}}{2\omega S_{2\omega}^{\text{in-phase}}}. \quad (5)$$

As TPB-(c)9(3) and related molecules are synthesized in only milligram quantities, we chose to perform an electric-field-induced birefringence measurement rather than one based on a magnetic field, which requires far more material. Two glass slides coated with indium tin oxide (ITO) were separated by Mylar spacers of nominal thickness $3 \mu\text{m}$ and adjusted for optimum parallelism under monochromatic light. Since the two regions of ITO had a well-defined overlap area $A = 0.20 \pm 0.01 \text{ cm}^2$, we found from a measurement of the cell capacitance that the cell thickness $d = (3.3 \pm 0.1) \times 10^{-4} \text{ cm}$. The cell was filled with TPB-(c)9(3) and placed in an oven that was temperature controlled to 10 mK. The beam from a 5-mW He-Ne laser was directed along the \hat{z} axis and passed consecutively through a polarizer oriented at 45° with respect to the \hat{x} axis, a Babinet-Soliel compensator, the sample, a crossed analyzer, and into a photodiode detector. In order to detect the electrically induced optical phase shift α through the cell, the cell was tilted by $\varphi_i = 45^\circ$ in the \hat{x} - \hat{z} plane, thereby making the \hat{x} axis the extraordinary optical axis.

Owing to the very small magnitude of the induced phase shifts ($\alpha < 10^{-4}$), a phase-sensitive detection scheme was used to measure the susceptibility. The detector intensity I is given by $I = I_0 \sin^2 \alpha$, where I_0 is the maximum intensity and $\alpha = \alpha_{\text{cell}} + \alpha_{\text{comp}}$. α_{comp} is the optical phase shift of the compensator. The phase shift associated with the cell is $\alpha_{\text{cell}} = k(n_e^{\text{eff}} d_e - n_o d_o)$, where k is the wave vector of light ($k = 9.93 \times 10^4 \text{ cm}^{-1}$), n_e^{eff} is the effective extraordinary refractive index, n_o is the ordinary refractive index, and d_e and d_o the optical path lengths through the cell for extraordinary and ordinary light, respectively. As usual,

$$n_e^{\text{eff}} = [(\cos^2 \varphi_e) / n_o^2 + \sin^2 \varphi_e / n_e^2]^{-1/2},$$

where φ_e , the extraordinary angle of refraction inside the tilted cell, is determined implicitly from Snell's law, viz., $\sin \varphi_i = n_e^{\text{eff}} \sin \varphi_e$. The ordinary refractive angle φ_o in the cell is likewise obtained from $\sin \varphi_i = n_o \sin \varphi_o$, and the path lengths are given by $d_o = d / \cos \varphi_o$ and $d_e = d / \cos \varphi_e$. Finally, we have the usual relationship that $\frac{1}{3} n_e^2 + \frac{2}{3} n_o^2 = n_{\text{iso}}^2$, where the isotropic refractive index n_{iso} can be obtained from Fig. 3. From this set of seven equations we uniquely obtain the birefringence $\Delta n = n_e - n_o$ from a measurement of α_{cell} , where $\Delta n \propto \alpha_{\text{cell}}$ for small phase shifts. (Indeed, we actually ob-

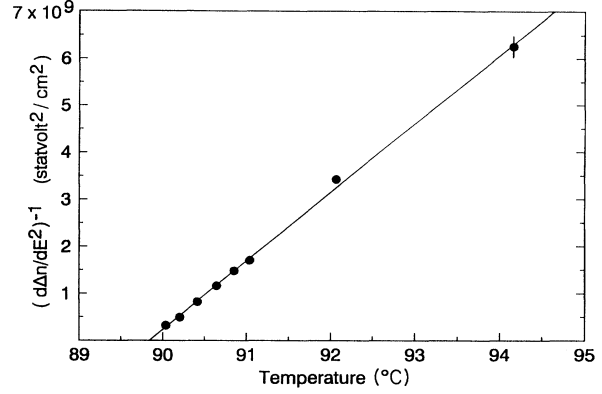


FIG. 4. Inverse susceptibility vs temperature. x -intercept of fit corresponds to $T^* = 89.84$, with $T_{NI} < 90.03$. Error bars are shown.

tain n_e and n_o separately.) We thereby can extract the quantity $d\Delta n/dE^2$, which is proportional to the order parameter susceptibility dS/dE^2 since $\Delta n \propto S$ for small S .

The sample was driven with a low-frequency envelope at $f = 20.5 \text{ Hz}$ (corresponding to $\omega = 128.8 \text{ s}^{-1}$), which was modulated at 4 kHz. The high-frequency modulation ensured that charge conductivity would not be a problem, and the low-frequency envelope allowed us to study the dynamic behavior of the order parameter near the transition. For a fixed α_{comp} the intensity for the small α_{cell} is given by

$$I = I_0 \sin^2 \alpha_{\text{comp}} + I_o \alpha_{\text{cell}} \sin 2\alpha_{\text{comp}} + O(\alpha_{\text{cell}}^2), \quad (6)$$

where α_{comp} was chosen to be 0.6 and I_o was calibrated by measuring the change in detector output voltage for a given change in α_{comp} . A measurement of I thus yields α_{cell} , which in turn is proportional to Δn . The signal from the detector was input to a lock-in amplifier, which was referenced in the $2f$ mode by the low-frequency envelope [cf. Eq. (4)]. Both the in-phase ($I^{\text{in-phase}}$) and quadrature (I^{quad}) components of the signal were measured as functions of applied field E at eight discrete voltages up to 15 V (corresponding to $E = 150 \text{ statvolts/cm}$)

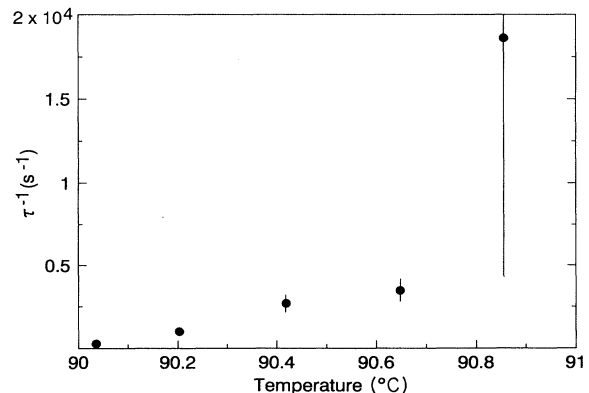


FIG. 5. Inverse relaxation time vs temperature for several points above T_{NI} . Error bars are shown.

at each temperature in the isotropic phase. As expected, $I^{\text{in-phase}}$ was found to be linear in E^2 , the quadrature component was generally much smaller and noisier, and therefore its linearity in E^2 could be verified only close to T_{NI} . The magnitude of the dc susceptibility is obtained from the slope of a linear least-squares fit of $\{(I^{\text{in-phase}})^2 + (I^{\text{quad}})^2\}^{1/2}$ vs E^2 [cf. Eq. (4)], where τ is obtained below. This quantity yields $d\Delta n/dE^2|_{\text{dc}}$, whose inverse is plotted against temperature in Fig. 4. Note that the $\omega\tau$ correction is generally of no consequence, except *very* close to T^* . Also, note that the small shift in temperature between Figs. 3 and 4 is due to the use of different equipment with different thermistors. From Fig. 4 we see that $[d\Delta n/dE^2|_{\text{dc}}]^{-1}$ is linear in temperature, which according to Eq. (2) indicates that mean field behavior is obtained. (Had critical behavior commensurate with an $N=5$, $d=3$ N -vector model been observed, we would have expected a susceptibility exponent $\gamma \approx 1.53$ [17].) In addition, we observe that δT is less than 200 mK, much smaller than found in traditional thermotropic liquid crystals. As pointed out above, this behavior is characteristic of a nearby biaxial phase, with the possibility of a nearby Landau point on the temperature- Γ phase diagram. It is entirely possible that even smaller values of δT might be achieved with other members of this class of molecules, most likely by varying the tail length n of the mesogen. Since we do not yet know the eccentricity of the ring, we do not know whether a longer or shorter tail is appropriate. Addition-

ally, we note that because of their extremely large error bars (of order 50%), we have not shown in Fig. 4 the data points for temperatures $T > 94^\circ\text{C}$. For these temperatures the data *suggest* some upward curvature in the inverse susceptibility, indicating the possibility of an anomalous falloff in the response to an applied field. If this is indeed the case, it may be due to conformational changes in the molecule at temperatures well above T_{NI} (see Fig. 2). Owing to the large uncertainty in the data, however, this speculation is neither warranted nor substantiated.

In light of Eq. (5) we can extract the relaxation time τ as a function of temperature. Unfortunately, owing to the small magnitude of I^{quad} , τ is completely unreliable in the region $T > T_{NI} + 1^\circ\text{C}$. Nevertheless, in Fig. 5 we show the inverse relaxation time vs temperature for the first few points in the isotropic phase. As expected, the response of the system appears to be slowing down, such that τ^{-1} appears to be vanishing as we approach T^* .

The results reported herein represent an exciting new class of material with many fascinating possibilities. In particular, we intend to study the N - I transition in other members of this class, as well as study the apparent uniaxial to biaxial phase transition.

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*Electronic mail: cxr@po.cwru.edu

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