# Continuous Nematic-Isotropic Transition in Submicron-Size Liquid-Crystal Droplets

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Deuterium NMR of nematic droplets in a polymer matrix reveals the effect of confinement on molecular orientational ordering near the nematic-isotropic (N-I) phase transition. For large droplets of 0.35 $\mu$m in diameter, the N-I transition is first order. For droplets of less than 0.035 $\mu$m in diameter, the isotropic phase shows a paranematic order and the N-I transition is replaced by a continual evolvement from paranematic to nematic order. This result provides the first demonstration of Sheng's prediction that the N-I coexistence curve terminates at a critical enclosure size.

The effects of surface confinement on molecular ordering pose problems of both fundamental[1] and applied[2] interest. We report here the first nuclear-magnetic-resonance study of molecular order in a nematic liquid crystal confined to submicron-size spherical cavities in a rigid polymer where the surface at the cavity wall has a profound effect on ordering near the isotropic-nematic phase transition. Composites of polymers and droplets of low molecular weight liquid crystals of uniform size ranging from 2.0 to 0.02 $\mu$m in diameter were made with polymerization induced phase separation.[3,4] The high density of droplets allows for a sufficient signal-to-noise ratio for deuterium NMR measurements of the molecular orientational order parameter.[5] The results show that for sufficiently small droplets the isotropic phase is replaced by a paranematic phase where a small but finite order exists and that the isotropic-nematic transition is replaced by the continuous evolvement of order similar to that predicted by Sheng[6] in his theoretical work on nematics confined between two parallel ordering walls.

The pioneering work of Sheng[6,7] further predicted a first-order surface transition in the boundary layer (prewetting transition) at the walls at a temperature above but near the bulk isotropic-nematic transition. As the thickness of the film decreased, the boundary layer transition was predicted to first merge into the isotropic-nematic coexistence curve at intermediate thicknesses, and the coexistence curve then to terminate at a critical point at a smaller critical separation thickness. This theoretical work has since been extended by others.[8-10] Yokoyama[11] has reported birefringence measurements on planar films of varying thickness and demonstrated a predicted shift in the transition temperature but could not be conclusive that the nematic-isotropic (N-I) transition becomes continuous below a critical thickness because of the nonuniform configuration of the sample films.

Allender and Žumer,[12] and more recently Žumer, Vilfan, and Vilfan[13] applied the theory to spherical droplets which introduce elastic terms in the Landau-de Gennes approach. Assuming strong anchoring at the surface (i.e., a temperature-independent surface free energy) the expansion of the free energy density is expressed as

$$f = f_0 + \tfrac{1}{4} a(T - T^*)S^2 + \tfrac{1}{4} BS^3 + \tfrac{9}{16} CS^4 + \tfrac{3}{4} D_1(\nabla S)^2 + \tfrac{9}{4} S^2[D_2(\nabla \cdot \mathbf{n})^2 + D_2(\mathbf{n} \times \nabla \times \mathbf{n})^2 + L_1(\mathbf{n} \cdot \nabla \times \mathbf{n})^2]$$

$$+ \tfrac{3}{8} L_2[(\mathbf{n} \cdot \nabla S)^2 + 4S(\mathbf{n} \cdot \nabla S)(\nabla \cdot \mathbf{n}) + 2S(\nabla \mathbf{n}) \cdot (\mathbf{n} \times \nabla \times \mathbf{n})], \quad (1)$$

where $S$ is the orientational order parameter, $\mathbf{n}$ is the local nematic director, $D_1 = L_1 + L_2/6$, $D_2 = L_1 + L_2/2$, and $L_1$ and $L_2$ are related to the Frank elastic constants. The coefficients $f_0$, $a$, $B$, and $C$ in the expansion are temperature independent and $T^*$ is the temperature limit for supercooling.

The minimization of Eq. (1) was performed by Allender and Žumer for a droplet with a radial director configuration where the molecules at the droplet wall are anchored normal to the surface. For nominal values of material constants (typical of the compound 4'-pentyl-4-cyanobiphenyl, 5CB) it was found that there was a critical droplet radius, $R_c \approx 0.16$ $\mu$m, where the N-I transition became second order. Below this radius the transition completely vanished. Omission of the condition of very strong anchoring, the prewetting surface layer tran-

sition may occur, as well as a possible change of director configuration.[14]

Deuterium nuclear magnetic resonance is one of the most direct methods of measuring orientational order.[5] In a local region of a nematic droplet indicated by the position vector, $\mathbf{r}$, a compound deuterated at a specific site will yield a spectrum of two lines at the angular frequencies, $\omega_q$, given by the expression

$$\omega_q(\mathbf{r}) = \pm \pi \delta \nu \tfrac{1}{2} [3\cos^2\theta(\mathbf{r}) - 1], \quad (2)$$

where $\theta(\mathbf{r})$ gives the orientation of the local nematic director relative to the direction of the magnetic field. $\delta \nu$ is the quadrupole splitting in the bulk nematic given by $3e^2qQS/2h$, where $q$ is the electric field gradient created by the carbon-deuterium bond, $Q$ is the quadru-

pole moment of nuclear spin, and $S = \langle \frac{3}{2} \cos^2\beta - \frac{1}{2} \rangle$ is the degree of orientational order of the deuterium bond direction relative to the direction of the magnetic field. We are working with droplets of radius $R$, substantially less than the magnetic coherence length $\xi = (\mu_0 K / \Delta\chi)^{1/2}/B \sim 1.0$ $\mu$m, where $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility, and $B$ is the field of the NMR magnet (4.7 T). Therefore, our magnetic field has a negligible effect on nematic droplet structures.

In the case of strong parallel anchoring, droplets with bipolar structure are formed[15] (see inset of Fig. 1). When the size of the bipolar droplet is $\lesssim 0.5$ $\mu$m, their symmetry axes are randomly ordered in the field of the NMR magnet in which case the spectral lines are distributed into a Pake-type powder pattern.[16] Translational diffusion causes $\mathbf{r}$ in Eq. (2) to be time dependent. The angular frequency $\omega_q$ is therefore modulated by diffusion and depends upon the director configuration in the droplet. This effect becomes significant when the quantity $\epsilon = \delta v R^2/12 D < 1$, where $D$ is the molecular self-diffusion coefficient.[5] Typical values of $D \sim 10^{-11}$ m$^2$/sec for a nematic yield $\epsilon \ll 1$ for droplet radii $R \sim 0.01$ $\mu$m and $\delta v \approx 50$ kHz are used in this work.

The samples of dispersed nematic droplets were made from the liquid-crystal compound 4'-pentyl-4-cyanobiphenyl, 5CB-$\beta d_2$, deuterated in the $\beta$ position of the hydrocarbon chain. The polymer was a standard off-the-shelf epoxy (Bostik brand). The samples were prepared by mixing 5CB-$\beta d_2$ with the epoxide and the polyamine curing agent, which went completely into solution. The sample was then thoroughly mixed and lightly centrifuged to remove air bubbles and allowed to cure 3 h at
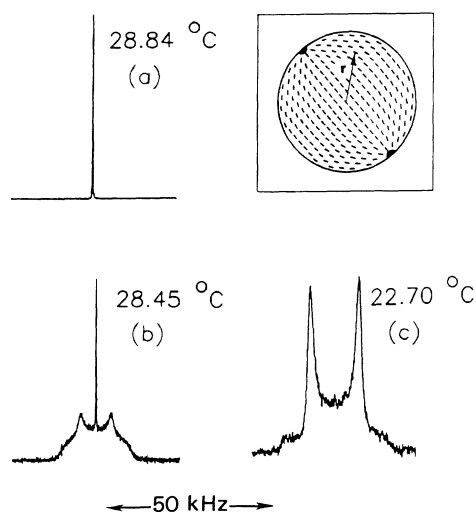
TABLE I. Droplet size vs weight percent liquid crystal relative to the epoxy polymer with the polymer consisting of equal amounts of epoxy resin and curing agent.

| Concentration of 5CB-$\beta d_2$ (wt.%) | Droplet diameter ($\mu$m) | Method of measurement |
|---|---|---|
| greater than 40 | greater than 3 | optical microscopy |
| 38 | 1.8 | SEM[a] |
| 33 | 0.35 ± 0.05 | SEM |
| 21 | 0.035 ± 0.01 | TEM[b] |
| 19 | 0.020 ± 0.005 | TEM |
| 17 | less than 0.02 | unobserved |

[a]SEM denotes scanning electron microscopy.
[b]TEM denotes transmission electron microscopy.

40 °C. Phase separation during the curing process yielded droplets of uniform size. The samples were then allowed to further cure at room temperature for several weeks with the effect of further purification of the nematic droplets and stabilization of the $I$-$N$ transition. The size of the droplets could be adjusted by varying the relative amounts of liquid crystal to epoxy. Less liquid crystal in solution leads to more rapid polymerization which reduces the droplet size.[17] The density of droplets is also reduced. The size of the droplets were measured by electron microscopy, and the data are shown in Table I.

Optical microscopy under crossed polarizers indicated that the director configuration was of the bipolar type.[5] Self-diffusion in the bipolar structure does not alter the



FIG. 1. Deuterium NMR spectra of 0.35-$\mu$m-diameter nematic droplets of 5CB-$\beta d_2$ recorded in the (a) isotropic phase at $T = 28.84$ °C; (b) biphasic region at $T = 28.45$ °C; and (c) nematic phase at $T = 22.70$ °C. Inset: Computer simulation of the bipolar configuration.
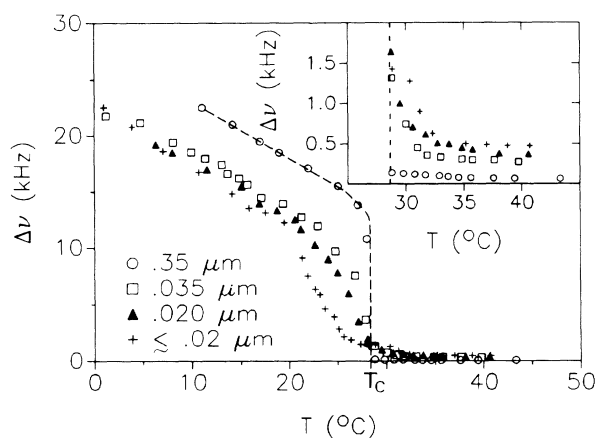


FIG. 2. Molecular orientational order vs temperature as measured by the linewidth, $\Delta v$, for nematic droplets of various sizes. The first-order isotropic-nematic phase transition is only observed in the 0.35-$\mu$m-diameter droplets. Inset: Expanded plot above $T_c$ illustrating paranematic ordering in all droplet sizes recorded.

shape of the Pake powder pattern but only reduces its width by $\approx 30\%$ in the small drop limit of $\epsilon \ll 1$.[5] This is in contrast to the radial configuration where the line substantially alters its shape and narrows to its isotropic width.

Selected deuterium spectra for 0.35-$\mu$m droplets of 5CB-$\beta d_2$ are shown in Fig. 1, where Fig. 1(a) shows a signal in the isotropic phase, and Fig. 1(c) shows the Pake pattern at a temperature well into the nematic phase. Figure 1(b) shows a small biphasic region recorded 400 mdeg K below the pure isotropic line. The relative area under the peaks in Fig. 1(b) shows that only a small part of the sample is in the isotropic phase.

Figure 2 shows the linewidth at half maximum intensity, $\Delta \nu$, of the Pake doublet versus temperature. The data in the isotropic phase (inset) are the width at half the maximum intensity of the isotropic line. The plot for 0.35-$\mu$m droplets is typical of the $N$-$I$ transition in a bulk nematic and shows a first-order transition. The spectra at the $N$-$I$ transition are clearly different for smaller droplets. Figure 3 shows the evolution of the deuterium NMR spectral pattern for 0.02-$\mu$m droplets as the temperature of the sample is shifted from the isotropic into the nematic. At temperatures well into the isotropic region the NMR line has noticeable width, indicating a paranematic order. As the temperature is lowered the line gradually broadens and evolves into the Pake pattern, in contrast to tha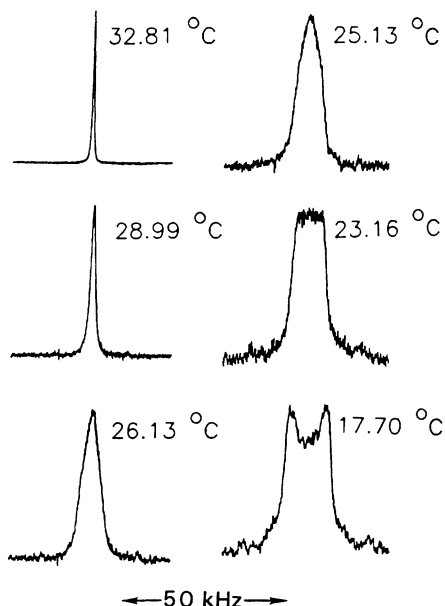t of the sample with larger drop-lets. The biphasic character of the line in Fig. 1(b) is not observed in the 0.02-$\mu$m droplets. A shift in the $N$-$I$ transition is evident for smaller droplets, and it is also apparent from Fig. 2 that at low temperatures, well into the nematic phase, the width of the Pake doublet is reduced by $\sim 30\%$ of the bulk spectrum, suggesting that the bipolar configuration is preserved even in very small droplets.

The ordering in small droplets generally follows the predictions by the Landau–de Gennes theory. The theory has only been applied to radial structure,[12,13] and has yet to be completed for a bipolar configured droplet. It is believed, however, that the general features of the phase transition for the bipolar droplet will not be significantly altered from that of the radial case.

The surface transition predicted by Sheng was not observed, although it could be that either the strength of the surface interaction or the droplet size was not in the right range,[4] or perhaps the surface transition is too near the bulk $N$-$I$ transition to be resolved in the NMR experiment. More work on this aspect is in progress.

Finally, we report that an interesting spin off of this work is that we were unable to make submicron droplets with the radial configuration even though larger droplets with this configuration were possible in some materials. We believe that radial droplets of radius less than 0.1 $\mu$m may not be possible at all on account of finite anchoring energies which become overwhelmed by elastic energies in small radial droplets.[14]

FIG. 3. Deuterium NMR spectra of 0.02-$\mu$m-diameter nematic droplets of 5CB-$\beta d_2$ recorded at various temperatures. The recordings illustrate the continual evolution of paranematic ordering at $T = 32.81\,°C$ into nematic ordering clearly apparent at $T = 17.70\,°C$.

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