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NMR Studies of Surface Induced Ordering in Polymer Dispersed Liquid Crystals

by

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NMR STUDIES OF SURFACE INDUCED ORDERING IN POLYMER DISPERSED LIQUID CRYSTALS

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Introduction

NMR studies of nematic liquid crystals confined to micron and submicron-size cavities in a solid polymer are described. The high surface-to-volume ratio imposed by the cavities and the high density of cavities present in polymer dispersed liquid crystals (PDLCs) allow for NMR studies of unusual surface phenomena not possible before by this powerful experimental method. Unique measurements of surface anchoring energies and angles, and experiments on the surface layer transition predicted by theory are shown to be accessible by this technique. Nematic director configurations and modifications of the nematic-isotropic transition induced by the confinement of a nematic liquid crystal to a small and highly curved cavity are studied.

These basic studies are guided by applications of PDLCs in light shutters for displays and other electrooptic devices. When nematic liquid crystals are dispersed as submicron-size droplets in polymers, electrically switched light shutters with a wide range of applications extending beyond existing liquid crystal technology are possible.[1,2] These applications include large-scale flexible displays that do not require polarizers and are simple and cost effective to fabricate. Switchable coatings for windows to be used for controlling daylight or interior lighting, privacy, cosmetics, solar heat gains, security, etc., provide a totally new application of liquid crystal materials.

Director Configurations

A nematic liquid crystal confined to a small spherical volume exhibits a specific director configuration resulting from an interplay between elastic forces, a possible external field, and surface interactions. Using a constant order parameter approximation valid in larger droplets at temperatures far from the N-I transition, a rich variety of different configurations are found to be possible by minimization of the elastic, surface, and field parts of the droplet free energy.[3] In this case, the free energy of a nematic droplet can be written as:

$$F = \frac{1}{2}\int\left[K_{11}(\nabla\cdot\mathbf{n})^2 + K_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2 - \frac{\Delta\chi}{\mu_o}(\mathbf{B}\cdot\mathbf{n})^2\right]dV + \frac{1}{2}\int W_o(\theta-\theta_o)^2 dA \quad (1)$$

Here n is the director, and K_{11}, K_{22}, K_{33} are the elastic constants associated with splay, twist, and bend deformations. The relative diamagnetic susceptibility anisotropy $\Delta\chi$ is taken as positive. W_o is the anchoring energy and θ_o the preferred anchoring angle.

In the single elastic constant approximation ($K_{11}=K_{22}=K_{33}$) the minimization of Eq. (1) results in a partial differential equation which can be solved numerically to graph the configuration. Figures 1(a) and (c) show computer simulations of two of the most commonly observed director configurations from strong tangential and perpendicular anchoring (θ-$\theta_o=0$ or $\pi/2$) , respectively, in the absence of an applied field.[4] The effect of an electric or magnetic field on the bipolar configuration is to align the symmetry axis parallel to the field but cause little distortion of the director configuration in the droplet (Fig. 1b). In the case of the radial configuration for strong anchoring conditions a field strength of $B \simeq 4(\mu_o K/\Delta\chi)^{\frac{1}{2}}/R$ will cause a

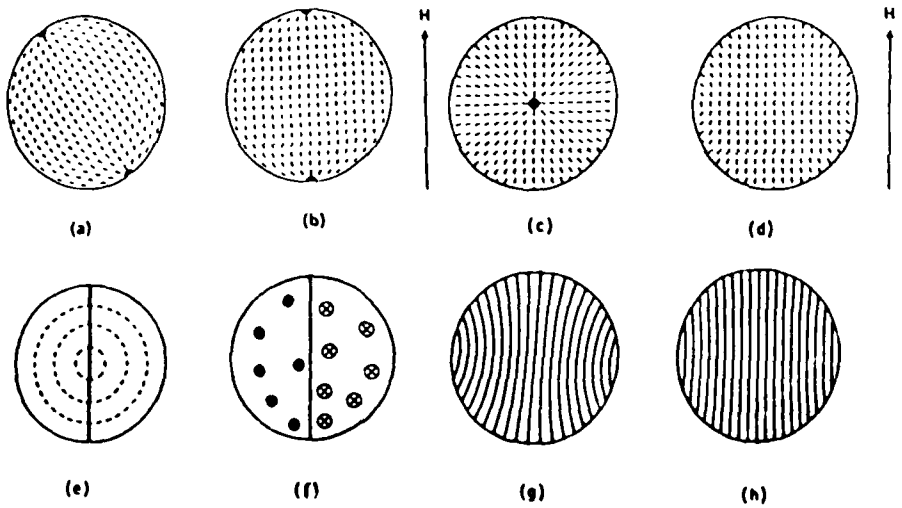

Fig. 1. Simulated director configurations illustrating: The bipolar configuration from strong tangential anchoring in a spherical cavity, (a); bipolar configurations in the presence of field, (b); radial or star configuration with a central point defect from strong perpendicular anchoring, (c); configuration from strong perpendicular anchoring in the presence of an applied field, (d); θ configuration resulting from strong tangential anchoring with a central line defect, (e); $\hat{\phi}$ configuration (director pointing in and out of plane of paper) resulting from strong tangential anchoring with a central line defect, (f); resulting configurations from weak perpendicular anchoring as the droplet size becomes progressively smaller or strength of anchoring becomes progressively weaker or applied field is increased, (g) and (h).

transition to the axial configuration of Fig. 1(d).[5] Figures 1(e) and (f) show other possible configurations which can result from strong tangential anchoring depending upon the ratios of deformation constants. Even in the absence of a field, a cross-over between (e), (f), or (a) can occur as a function of the ratio K_{11}/K_{33}.[3,6] For weak perpendicular anchoring ($\theta \neq \theta_o$), a cross-over between Fig. 1(c) and (g) or (h) can occur depending upon the anchoring strength, W_o, the droplet size, R, the

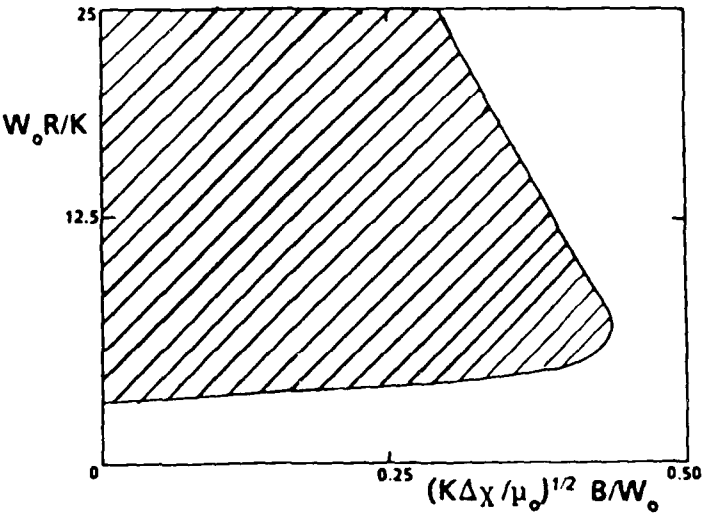

Fig 2. Calculated estimate of the allowed values of W_o, R, and B for a radial configured droplet (shaded area). Droplets with axial structures similar to those of Fig. a(g) and (h) are simulated for the unshaded area.

strength of an applied field, B. Figure 2 shows a theoretical estimate of the allowed values of W_o, R, and B for a radial droplet. Using deuterium NMR one can determine the droplet configuration[5] for specific droplet sizes to determine values for W_o. Deuterium NMR is one of the most sensitive methods to examine the director configuration as illustrated in Fig. 3.

Effects on the N-I Transition

A major feature of PDLC materials is that they provide a high surface-to-volume ratio allowing the use of NMR to study a variety of surface effects not possible before. The effect of a restricted geometry on a nematic has been a topic of high interest.[7] Pioneered by Sheng, [8] theory predicts that a nematic phase confined to a small cavity will have its N-I transition shifted in temperature. More interestingly, it was further predicted that there exists a first order surface layer transition at the walls at a temperature above but near the bulk isotropic-nematic transition. As the

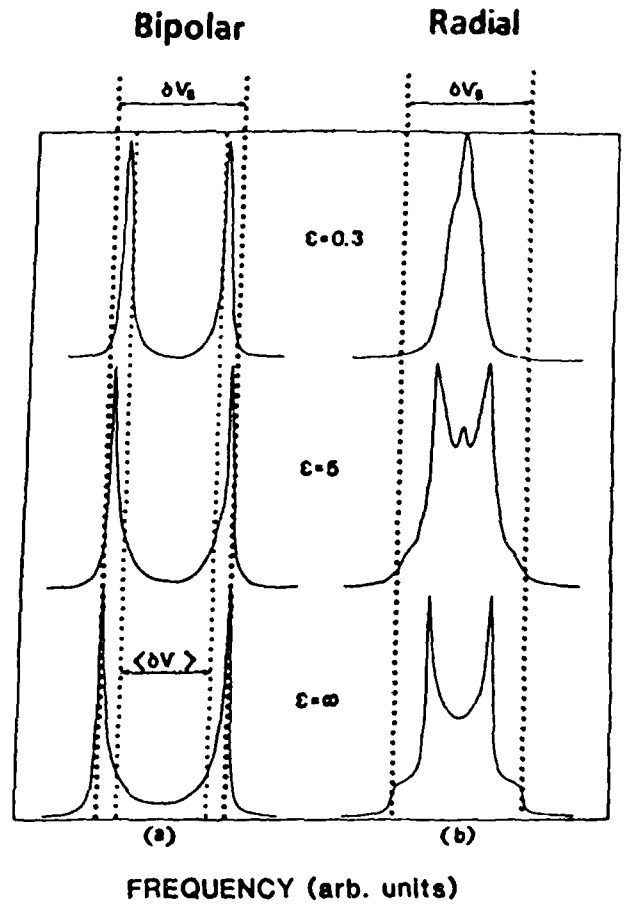

Fig 3. Simulated ^{2}H-NMR spectral patterns for aligned nematic droplets with the bipolar and radial configurations. The effect of self-diffusion on the patterns becomes more important as the droplet radius, R becomes smaller and is indicated by the parameter $\varepsilon = \delta\nu_B R^2/12D$ where D is the diffusion constant and $\delta\nu_B$ the quadrupolar splitting in a bulk nematic. Spectral patterns for droplets of Fig. 1(d) and (g) are not shown but have patterns similar to the bipolar structure.

thickness of the film decreases the surface layer transition is predicted to vanish; furthermore, the isotropic-nematic coexistence curve is expected to terminate in a critical point at a critical film thickness. In this case, the isotropic phase is replaced by a paranematic phase where a small but finite orientational order exists and the first order I-N transition is replaced by a continuous evolvement of order.

Allender and Žumer[9] applied the theory to spherical droplets which is based on the Landau-de Gennes approach. In the case of droplets where strong normal anchoring of the molecules enforce the radial configuration, the free energy is expressed as:[9]

$$F = \int \left[\frac{A}{2} S^2 - \frac{B}{3} S^3 + \frac{C}{4} S^4 + \frac{L}{2} \left(\frac{\partial S}{\partial r} \right)^2 + E \frac{S}{r} \left(\frac{\partial S}{\partial r} \right) + \frac{2KS^2}{r^2} \right] dV \qquad (2)$$

where $L=3L_1/2+L_2$, $E=3L_2$, $K=9/2\ (L_1+L_2/2)$, S is the orientational order parameter and the coefficients B and C in the expansion are temperature independent while A is linear in temperature. The effect of the external field is not considered.

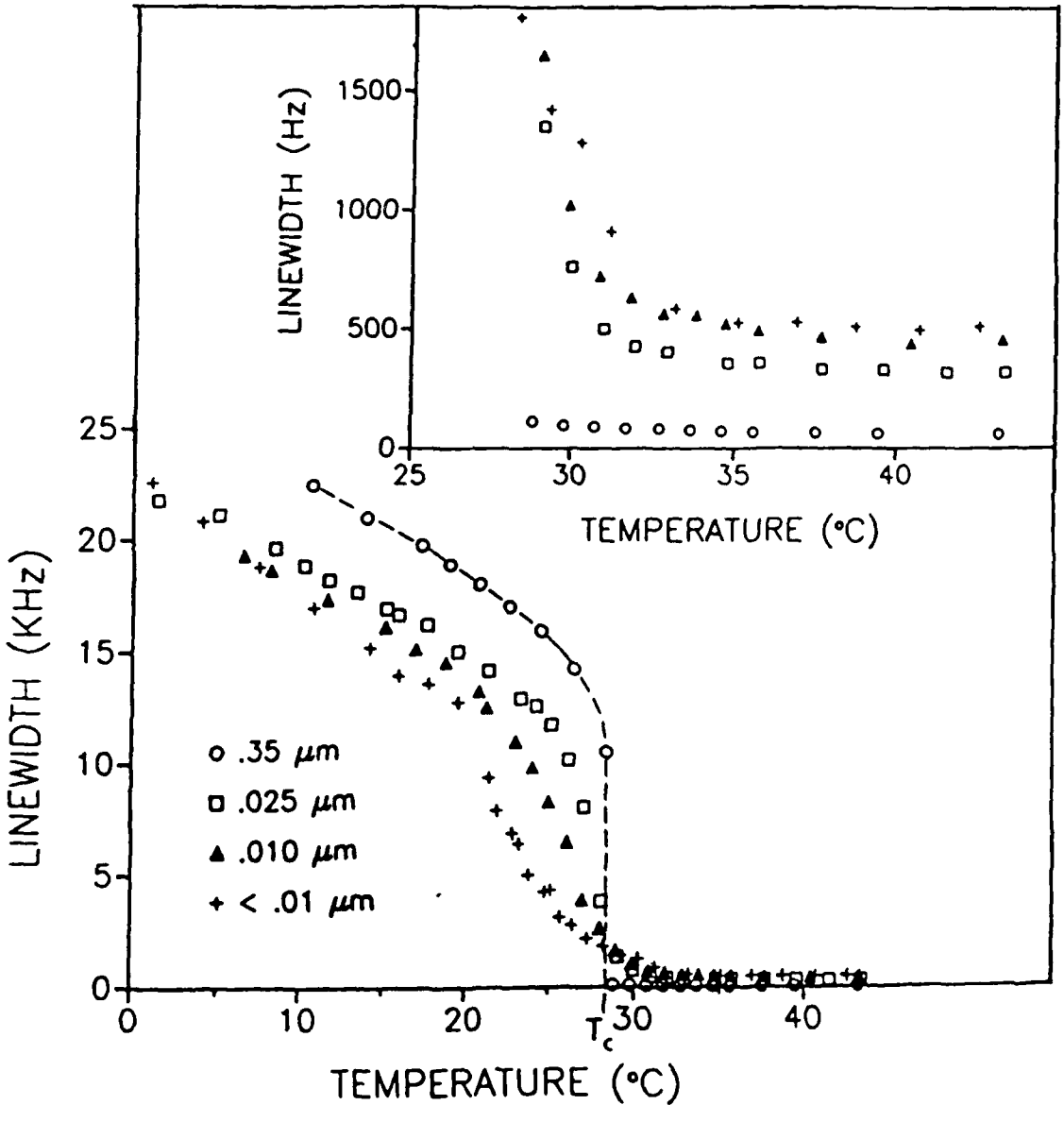

Fig 4. ^{2}H-NMR linewidth (directly proportional to the degree of order) versus temperature for nematic droplets of different diameters in a polymer matrix. Paranematic order above T_c is clearly evident in the inset. A continuous evolvement from paranematic to nematic order is demonstrated in the smaller droplets.

The minimization of Eq. (2) has been performed by Allender and Žumer. For nominal values of the material constants (typical of the compound 4'-pentyl-4-cyanobiphenyl, 5CB) it was found that there was a critical droplet radius, $R_c \approx 0.16$ μm, where the N-I transition becomes second order. Below this radius the transition completely vanishes and is replaced by a continual evolvement of order.

Using deuterium NMR we have verified that these effects do indeed occur.[10] Figure 4 shows a plot of the ^{2}H-NMR linewidth (directly proportional to the spatial average degree of order S over the droplet) for deuterated 5CB in an epoxy polymer binder. Paranematic order is clearly evident in small droplets (see inset) and the first order transition is replaced by a continual evolvement of order as the droplets become smaller. The value of the order parameter for smaller droplets when compared with the large droplet or bulk value implies that the configuration in these droplets is bipolar.

Efforts to search for the surface transition predicted by Sheng will be discussed in the presentation as will NMR methods to study phase separation methods used to make PDLC materials. Studies of nematic-nematic phase separation to make new types of PDLC materials will be described.

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