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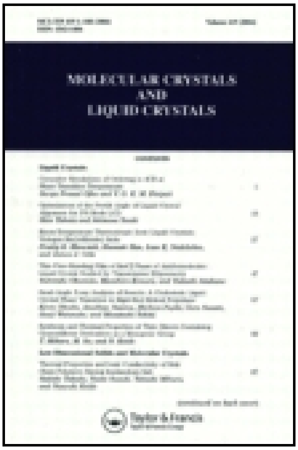

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Liquid Crystals in Cylindrical Pores: Effects on Transition Temperatures and Singularities

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(Received March 25, 1983)

Positive dielectric anisotropy liquid crystals are studied in cylindrical pores in a 10 μm thick polymer membrane of diameters 0.2–12 μm. Transition temperature depressions increase with decreasing pore size. Singularities of strength 1 are observed in the center of the pores, accompanied by some strength ½ singularities. By applying a voltage across the membrane, the $S = 1$ singularities are shown to be "escaped" singularities. $S = +½$ singularities show a critical destruction at a characteristic voltage.

INTRODUCTION

Porous media[1] and thin films[2,3] have provided convenient systems to measure the effect of surface interactions on the physical properties of liquid crystals. For example, for sufficiently small pore radius the isotropic-nematic transition temperature, T_{NI}, decreases while the width of the transition region increases.[1] In general, a rounding or weakening of thermodynamic singularities may occur in finite systems.[4] In thin films, T_{NI} is predicted to increase with decreasing film thickness,[5] ~.1°C for 10^3 Å. However, experimental investigations show either little effect[2] or a decrease[3] in T_{NI} for thin films.

A particularly appropriate porous membrane for investigation of these effects is the polycarbonate film "Nuclepore" which has been "drilled" by nuclear bombardment to create a series of cylindrical pores of quite uniform size (Figure 1). These pores are almost perfect cylinders with diameters ranging from 0.1 μm to 12 μm. Via optical microscopy, it is possible to observe these pores filled with liquid crystals in the size range 0.2 μm to

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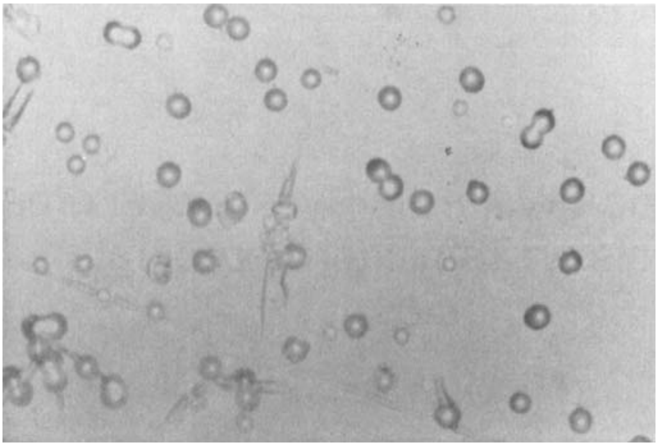

FIGURE 1 Photomicroscopic view perpendicular to microporous membrane. Unpolarized light, magnification ≃ 375 X.

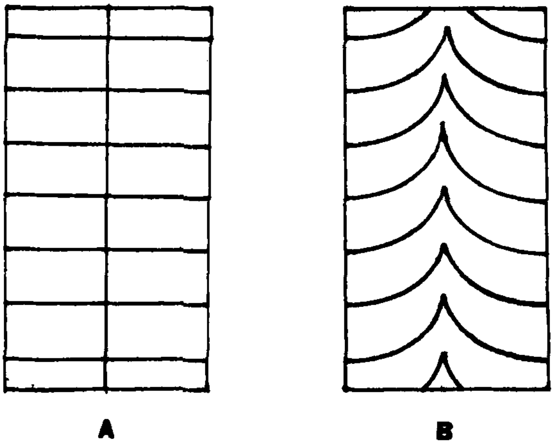

FIGURE 2 Side view of cylindrically symmetric director fields in capillary; (a) $S = +1$ singularity; the director field is in a radial direction everywhere except in a core region surrounding the center where the director field is not defined; (b) "escaped" $S = +1$ singularity with no core.

12 μm, and in this paper data are presented on transition temperature depressions, the behavior of singularities of strength 1 and ½ within the pores, and the effect of electric field on the strength 1 singularities. Studies of the stability of $S = +1$ singular lines[6] in cylindrical capillaries have indicated that deviations of the director field from a planar solution always occur for sufficiently large radius. In this case, the director field corresponds to that shown in Figure 2, and upon application of an electric field

parallel to the axis of the capillary, one might expect a continuously tunable birefringence for a positive dielectric anisotropy material.

EXPERIMENTAL

The liquid crystals employed are p-cyano-p′-*n*-nonylbiphenyl (K27, T_{NI} 50.3°C) and p-cyano-p′-*n*-pentylbiphenyl (K15, T_{NI} 35.3°C) obtained from EM Chemicals, both having a positive dielectric anisotropy. The Nuclepore membranes are 10 μm thick and the pores are essentially perpendicular to the film. Pore density increases with decreasing pore size, *e.g.* 1 μm, density $\cong 5 \times 10^6$ cm^{-2}; 0.2 μm, density $\cong 5 \times 10^7$ cm^{-2}.

A sample is prepared by allowing a small amount of isotropic liquid crystal to wet the membrane. They are quickly adsorbed indicating a good mutual attraction between the liquid crystal and the membrane. The membrane is then pressed between a clean glass slide and coverslip and placed in a Mettler hot stage. The sample is allowed to sit in the isotropic phase for approximately ½ hour. Uncovered samples left overnight exposed to air showed no measurable shift in transition temperature, either in bulk or confined to the membrane pores. The Nuclepore membrane was used as obtained. No observable change occurred in transition temperatures of liquid crystals when either new membrane material or membrane material exposed to the atmosphere (T = 22°C) for 24–48 hours are used.

Figure 3 gives the transition temperature depression determined on both cooling and heating the samples as follows. In the isotropic phase, with the sample between crossed polars, the membrane could be oriented so that an

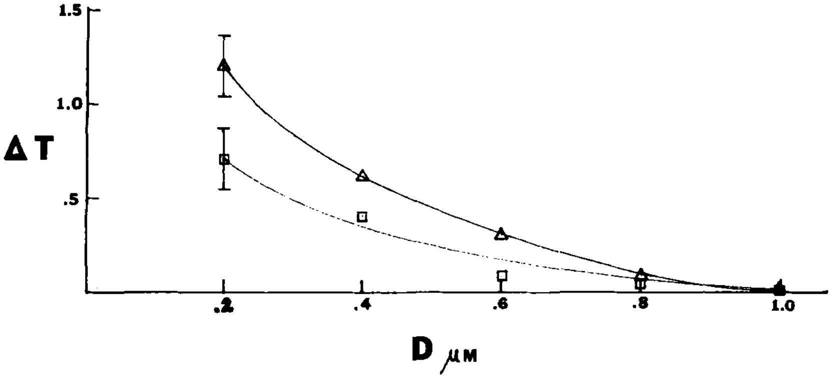

FIGURE 3 Nematic-isotropic transition temperature depression ($\Delta T = T_{\text{bulk}} - T_{\text{observed}}$) *vs* pore diameter.
△ *K*27, T_{NI} = 50.3°C (bulk)
□ *K*15, T_{NI} = 35.3°C (bulk).

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almost complete extinction of light could be obtained. The polymer membrane in an oriented birefringent material, presumably because of stretching during manufacture. On decreasing temperature, the isotropic-nematic transition in the smaller pores (<1 μm) is observed as a sudden non-uniform increase in the birefringence (Δn) over the whole field of the microscope. The non-uniformity in Δn is due to both a spatial distribution in pore sizes and to incomplete filling of the pores by liquid crystal. It is possible, however, to select a relatively uniform area for observation. Material on the surface of the membrane also underwent an isotropic-nematic transition which could be distinguished from the pore transition in two ways: (1) it generally occurred at the same temperature for different pore size; (2) a nucleation front could be observed continuously sweeping across the microscope field. Portions of the sample were chosen for observation in which these effects were minimized.

RESULTS AND DISCUSSION

In the 12 μm diameter pores we first observed, upon decreasing T, an increase in Δn on the perimeter of a pore where nucleation of a nematic phase by the pore surface began.[7] As T is lowered to just below T_{NI}, a texture corresponding to Figure 4 resulted. Figure 2 is a rationalization of the occurrence of "escaped" $S = 1$ singular lines[8] for the director field in the pores.

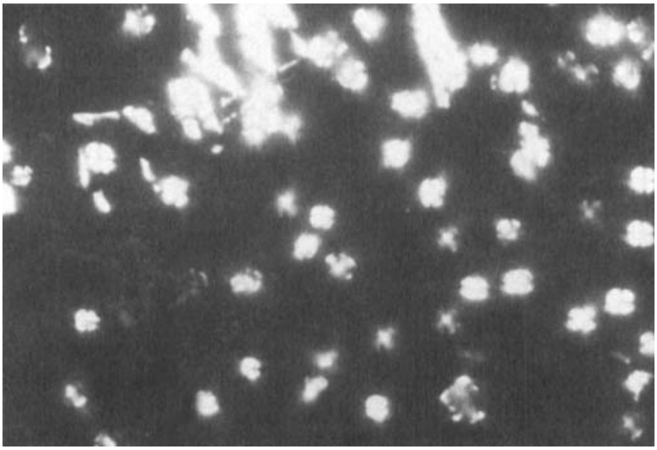

FIGURE 4 Membrane with 12 μm pores filled with $K27$. $T = 50.2°C$, magnification $\simeq 375\ X$, crossed polars. Note singularities in pores at extreme right of picture.

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Some time ago Meyer[9] and Cladis and Kleman[6] had demonstrated that a lower free energy is attained by a three dimensional cylindrical system if a coreless solution to the elastic equations is selected. Such a solution applies strictly to an infinite cylinder; however, the coreless solution will still appear in two dimensions as long as the director is not constrained to a plane.[10] Surface tension effects at the ends of a short cylinder should be taken into account for a proper determination of the director field.

That the observed $S = 1$ singularities are "escaped" singularities can be demonstrated by a method suggested by Meyer.[9] Electro-optic cells were prepared of 36 μm thickness and a 10 Kc voltage was applied across the cell. Upon application of 30 V parallel to a pore axis, the birefringence is observed to slightly decrease in the center of a pore (Figure 5). With continuously increasing electric field (up to 100 V) the decrease in birefringence continuously spreads to the perimeter of the pore.

We also observe $S = +\frac{1}{2}$ singularities in the pores under increasing electric field. Above a critical voltage, the director field discontinuously "snaps" to a lower energy configuration to accommodate the electric field. Upon lowering the electric field below a critical value, the director field in many pores relaxed back to the original configuration ($S = \pm\frac{1}{2}$).

The proximity of the smectic A phase in K27 ($T_{N\to SA} = 48.8°$, bulk value) rendered the escaped structure unstable with decreasing temperature, due to anomalous increase in the bend and twist elastic constants K_{33} and K_{22}. In a few pores, true $S = 1$ singularities were observed in the smectic A

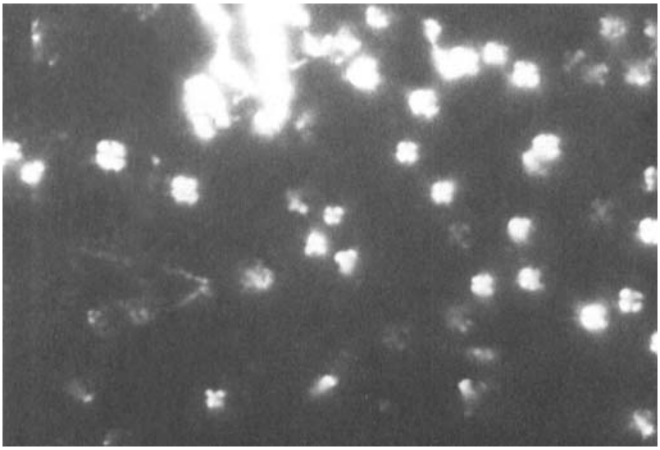

FIGURE 5 12 μm porous membrane in Figure 4 under the influence of an applied voltage (30 volts at 10 kilocycles). The electric field is perpendicular to the membrane. Membrane thickness $\simeq$ 10 μm.

phase. In the A phase, the fan texture aligned with the stretching direction of the membrane (Figure 6).

The temperature depression (Figure 3) is likely due to finite size effects (barring impurity effects). Two of the possible mechanisms involved are: (1) The assumed well aligned nematic material on the surface of the cylinder acts as an imposed deformation. The nematic material in the interior of the cylinder must arrange to minimize the elastic energy in accordance with this distortion. (2) Surface tension effects may cause temperature depression.

We may simplify mechanism (1) by considering only fluctuations in S, the nematic order parameter, to arrive at a formula for ΔT, the temperature depression. The free energy density for $T > T_{NI}$ is[10]

$$g = a_2 S^2 + a_3 S^3 + a_4 S^4 + \frac{\kappa_o}{2} (\nabla S)^2 + \cdots \qquad (1)$$

where $a_2 = a_{20}(T - T^*)$, T^* is the lower temperature boundary of the N–I two phase region (supercooling temperature), a_{20}, a_3, a_4, and κ_o are constants. The nematic-isotropic transition temperature is defined as $T_{NI} = T^* + a_3/4a_{20}a_4$. For $T > T_{NI}$ keeping only quadratic terms in g, we find the correlation function for fluctuations in S of wave number q is[11]

$$G(q) \sim \left(a_2 + \frac{\kappa_o}{2} q^2\right)^{-1}.$$

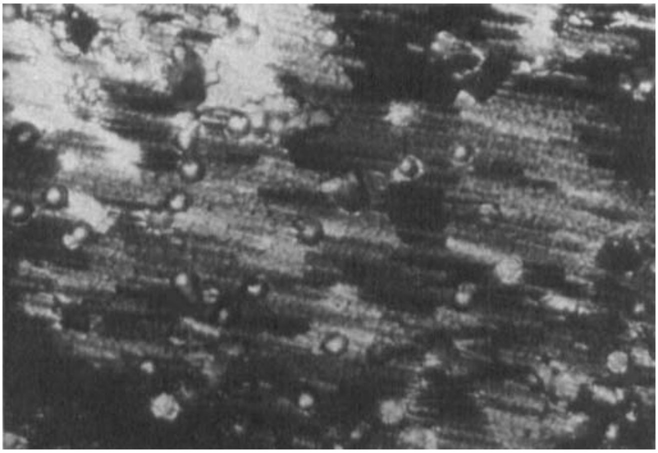

FIGURE 6 Smectic A phase of surface film. Pore diameter 12 μm, T = 48.5°C, magnification ≃ 375 X. Note alignment of the fan texture.

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In an infinite system we let $q \rightarrow 0$ and identify[11] the susceptibility $\chi \sim G(0)$. χ has a singularity at $T = T^*$. In a finite system, however, $q \rightarrow q_o = 2\pi/R$, where R is now the pore radius. Thus we can write

$$\chi \sim (T - T_R)^{-1}$$

where $T_R = T^* - \Delta T$ and

$$\Delta T = \frac{\kappa_o}{2a_{20}}\left(\frac{2\pi}{R}\right)^2 = 4\pi^2 T^*\left(\frac{\xi_o}{R}\right)^2 \tag{2}$$

where $\xi_o^2 = \kappa_o/2a_{20}T^*$.

Assuming $\kappa \simeq \kappa_o S^2$ where κ is a Frank elastic constant, we estimate a value for κ_o using $\kappa(T \lessdot T_{NI}) \simeq .5 \times 10^{-6}$ dyne and $S \simeq .3$ as appropriate values for cyanobiphenyls;[12] thus, $\kappa_o \simeq 5.5 \times 10^{-6}$ dyne. Also $a_{20} \simeq 9.0 \times 10^5$ erg/cm^{3}K,[13] so that $\xi_o \simeq 10$ Å. Substituting $R \simeq 10^3$ Å, $T^* \simeq 310$ K, we obtain $\Delta T \simeq 1.2$ K. Thus the temperature scale is shifted downwards by $\approx .4\%$.

The crude method used to derive Eq. 2 ignores interaction of fluctuations and overestimates the effect of boundary conditions treating the imposed deformation as a body force, not a surface force. Eq. 2 represents the temperature shift in a free energy per unit volume for an infinite system with an imposed deformation of wavelength R. This estimate is therefore to be used with caution.

For the second mechanism involving surface tension effects the formula[14]

$$\Delta T = \frac{\Delta\sigma T_{NI}}{R\Delta H n} \tag{3}$$

may be useful. Here $\Delta\sigma$ is the difference in surface tension between the nematic and isotropic phases, ΔH is the N–I transition enthalpy, and n is the number density of liquid crystal. We take $\Delta\sigma \simeq .026$ dyne/cm, $\Delta H \simeq .3$ kcal/mole,[15] $R = 10^{-5}$ cm, $T = 310$ K, and $n \simeq .5 \times 10^{22}$ cm^{-3} and arrive at

$$\Delta T \simeq 8 \times 10^{-3}\ \mathrm{K} \sim .01\ \mathrm{K}.$$

We conclude distortion effects are dominant in lowering T_{NI} for nematic materials in cylindrical pores with strong surface alignment. However, the data are insufficient to confirm this mechanism.

Porous membranes allow easy investigation of singularities in cylinders and also of the effect of finite size on transition temperature. An interesting possibility also exists that, with increased surface density of pores, a matrix for a nematic phase may be obtained for which the relaxation time of molecular reorientation, $\tau_R \cong (\gamma/\kappa)(R/\pi)^2$ (γ = effective viscosity,

κ = elastic constant, R = radius of pore), can be varied at constant electric field without changing the thickness of the cell. This may be interesting with respect to display applications.

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