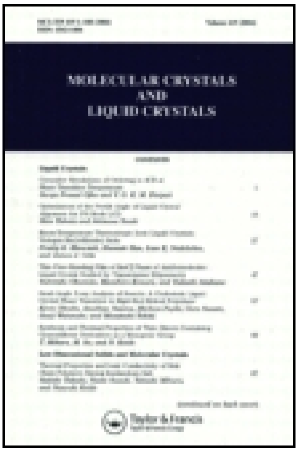

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SMECTIC ORDER IN A POROUS INTERCONNECTED SUBSTRATE

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Abstract Measurement of the specific heat and small angle neutron scattering studies for *n*CB liquid crystals confined to the 0.05 μm diameter pores of Millipore filters, a fibrous porous substrate, reveal that in spite of the interconnection and restrictive size, smectic layers are formed. The existence of this long range smectic order that increases with decreasing temperature is in contrast to findings in other porous geometries where a smectic phase is either absent or greatly suppressed by the confinement. For 9CB, we also study the possible effects of confinement on the critical behavior at the second order smectic-A to nematic phase transition.

INTRODUCTION

Since liquid crystal materials are strongly influenced by the presence of nearby surfaces, and surfaces may play an important role in the operation of liquid crystal displays, there has been a growing interest in studies of the physical properties of confined liquid crystals. Specific heat measurements at phase transitions for alkylcyanobiphenyl *n*CB liquid crystals (*n* the number of carbons in the liquid crystal) confined to the parallel, non-interconnected, 0.2 μm diameter cylindrical pores of aluminum oxide Anopore membranes, found considerable departures from bulk behavior.[1] These were manifest through transition temperature shifts and specific heat peak suppression that are strongly dependent on the director configuration within the pores and on the order of the phase transition. In particular, the smectic-A to nematic transition (AN) was greatly suppressed, nearly disappearing for a homeotropic (radial) alignment. Surprisingly, even though broadening and rounding of the transition caused by surface induced elastic constraints and a two-phase coexistence region were present, over a limited reduced temperature range a bulk-like critical behavior was retained.

When *n*CB liquid crystals were confined to the severely restrictive multiply connected pores of Vycor and Aerogel glasses, several features were unveiled. From X-ray scattering measurements for 8CB in the 175 Å pores of silica Aerogel,[2] the smectic order, although increasing with decreasing temperature, is found to be short ranged and retained to much lower temperatures than the bulk crystalline phase. Specific heat measurements found no clear evidence of a smectic-A to nematic transition that was either absent or greatly broadened.[3] The nematic to isotropic (NI) phase transition was shifted to lower temperatures while only somewhat suppressed. For 5CB in the 70 Å pores of Vycor glass,[4] the NI transition is replaced by a continuous evolution of orientational order. No specific heat signature at the transition was found for either 5CB or 8CB at either AN or NI transitions.[4,5] Similar confinement effects were also studied by confining a liquid crystal material (thermotropic as well as a lyotropic) to a polymeric network,[6,7] where, by changing the polymer concentration, the confining size is effectively changed.

Here, we describe specific heat studies at the smectic-A to nematic (AN) phase transition for 9CB confined to the 0.05 μm nominal size (~ 0.3 μm actual size) interconnected pores of Millipore fibrous filter paper. Despite the disorder introduced by the substrate, by comparison with bulk, a suppressed yet prominent specific heat peak at a slightly shifted AN transition temperature is found. The existence of smectic order that increases with decreasing temperature is shown from small angle neutron scattering measurements for 8CB, where a distinct peak in the neutron scattering intensity due to the presence of smectic layers is seen. Such a clear evidence for long range smectic order was not seen with other previously studied interconnected porous substrates.

EXPERIMENTAL DETAILS

A cellulose acetate fibrous filter paper, multiply connected Millipore is available as disks in several diameters and a variety of nominal pore sizes. For this work, the cyanobiphenyl liquid crystals were confined to 6 mm x 6 mm squares cut from a 115 μm thick, 4.7

cm diameter Millipore filter type VM, of nominal 500 Å pore size; the porosity as estimated from a mass measurement of the filter after liquid crystal filling is near 65 %. Scanning electron microscopy photographs[8] reveal a distribution of pore sizes with a typical pore size a factor of six larger than the manufacturer quoted size; similar order of magnitude discrepancies exist for other quoted nominal pore sizes that we have studied. Thus, the Millipore substrate allows studies in an interconnected geometry in some respects similar to that of the extensively studied porous glasses, but on length scales (pore sizes) which are closer to those in Anopore. Further motivation for these measurements stems from recent results that show a similar behavior in the localized and superfluid properties of helium films formed in both Millipore and Anopore substrates.[8,9]

Specific heat measurements were performed using an AC calorimetry technique[10] on bulk and on a single, squared Millipore filter filled with 2.2 mg of 9CB. For the small angle neutron scattering studies on Millipore confined 8CB, homologous liquid crystal used because of its availability at the time of the measurements, we used the Small Angle Diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. For the neutron scattering studies, used so that measurements would be characteristic of the bulk ordering in the sample rather than surface effects as with X-rays, about a dozen rectangular strips of Millipore, approximately 1 cm wide and 2 cm long, were tightly stacked above one another and snugly fitted inside a transparent plastic container. For purposes of these studies that concentrate on the smectic order and the AN transition, the two liquid crystals simply differ on the transition temperatures and the nematic range which for 9CB is 1.9 K as compared to 7 K for 8CB.

RESULTS AND DISCUSSION

Specific heat results as a function of temperature near the AN transition for bulk 9CB and Millipore confined 9CB are shown in Fig. 1; confinement effects at the weakly first order NI transition will be discussed in a future article. Evidently, in the confined case there is the unmistakable specific heat peak that is suppressed by 40 % compared to that of bulk, at a shifted AN transition temperature. The 0.23 K downward temperature shift can be attributed to disordering effects introduced by the surfaces. The symmetric nature of the specific heat peak is an indication of the second order of the AN transition.

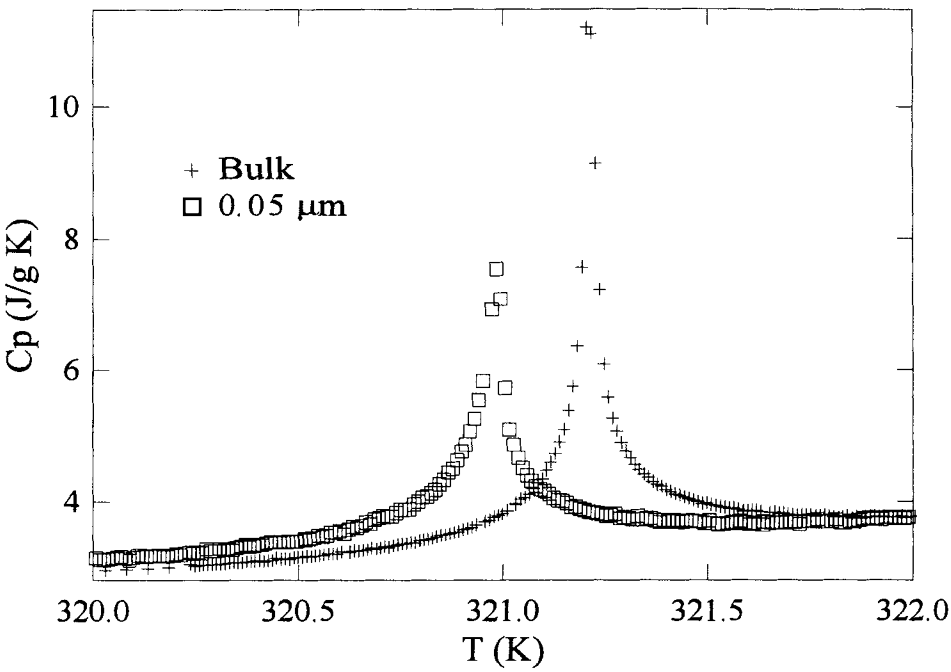

FIGURE 1 Specific heat as a function of temperature near the AN transition for bulk and Millipore confined 9CB. The transition temperatures are 321.21 and 320.98 K respectively.

The Millipore results are fully appreciated if contrasted with those previously found at the AN transition for 8CB confined to the 0.2 μm diameter cylindrical and parallel pores of 40 % porous Anopore membranes. These are shown in Fig. 2 together with bulk 8CB results.[1] Surprisingly, in spite of the well defined cylindrical geometry, the AN transition is greatly suppressed; the specific heat peak maximum is only 16 % that of bulk and is shifted to lower temperatures by ~ 0.8 K, i.e., four times more depressed than in Millipore. The smectic order in Anopore is short ranged (much smaller than the pore diameter) and a nematic phase is preferred.[1] The striking differences in behavior lie on the different morphology offered by the two substrates and the surface-liquid crystal interaction. In Anopore there exist an actual solid pore and a strong liquid crystal-surface coupling that introduces severe elastic constraints inhibiting the smectic growth; in Millipore, the fibers disturb the local order leaving unaffected the global smectic behavior.

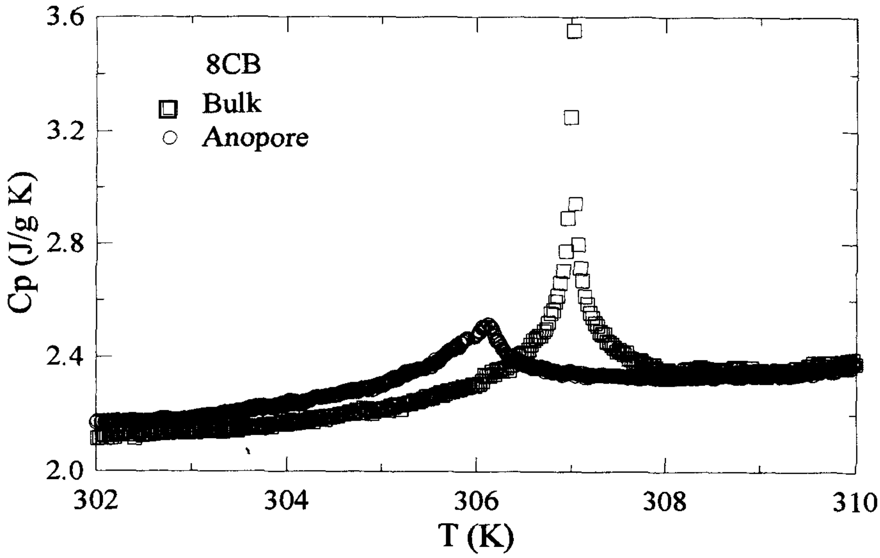

FIGURE 2 8CB specific heat as a function of temperature near the AN transition for bulk and confined to the 0.2 μm parallel pores of Anopore membranes. Note the large suppression of the AN confined peak.

The AN transition belongs to the 3D-XY universality class that predicts a specific heat power law exponent α = - 0.007. Such a transition is however strongly influenced by the proximity of the nematic to isotropic phase transition. Due to the 9CB narrow nematic range (range that is unaffected by the Millipore confinement), values for α are expected to be non-universal. Accordingly, the critical behavior for bulk and Millipore confined 9CB was tested by fitting the excess specific heat with the expression:[11-13]

$$\Delta C_P = B_C + A_{\pm} |t|^{-\alpha} \{1 + E_{\pm} |t|^{1/2}\}, \qquad (1)$$

after a regular background subtraction that includes contributions from the nearby NI transition. B_C is a small remnant nonsingular background, $t = T/T_{AN}-1$, is the reduced temperature, while the quantity in the bracket represents a first order correction-to-scaling term with its XY exponent set to 0.5.[14]

Since 9CB is close to the tricritical point[14,15] and in addition, due to the proximity of the NI transition, fits to Eq. (1) for the AN transition are quite sensitive to the background subtraction. The bulk 9CB McMillan ratio is T_{AN}/T_{NI} = 321.21/323.09 = 0.994.

For bulk in the reduced temperature range $2\times10^{-5} < t < 4\times10^{-3}$, mostly limited on the high temperature side, the best fit shown in Fig. 3, is obtained with $\alpha = 0.703$ and an amplitudes ratio $A_-/A_+ = 1.1$, compared with $\alpha = 0.5$ from previous studies.[15] Considering that from X-ray scattering results[16] the correlation length exponents for bulk 9CB are $\nu_{\|} = 0.57$ and $\nu_{\perp} = 0.37$, our result for α is consistent with the scaling relation prediction[14] $\alpha = 2 - (\nu_{\|} + 2\nu_{\perp}) = 0.69$. For the confined system, due to the more rounded and broader nature of the NI transition, no stable specific heat exponent could be determined. Over the slightly narrower reduced temperature regime $5\times10^{-5} < t < 6\times10^{-3}$, reasonable fits are achieved with α ranging from 0.3 to 0.7 (the fixed $\alpha = 0.7$ fit is shown in Fig. 3) and A_-/A_+ between 1.5 and 3. To establish confining effects for the AN critical behavior, wider nematic range liquid crystal materials need to be studied.

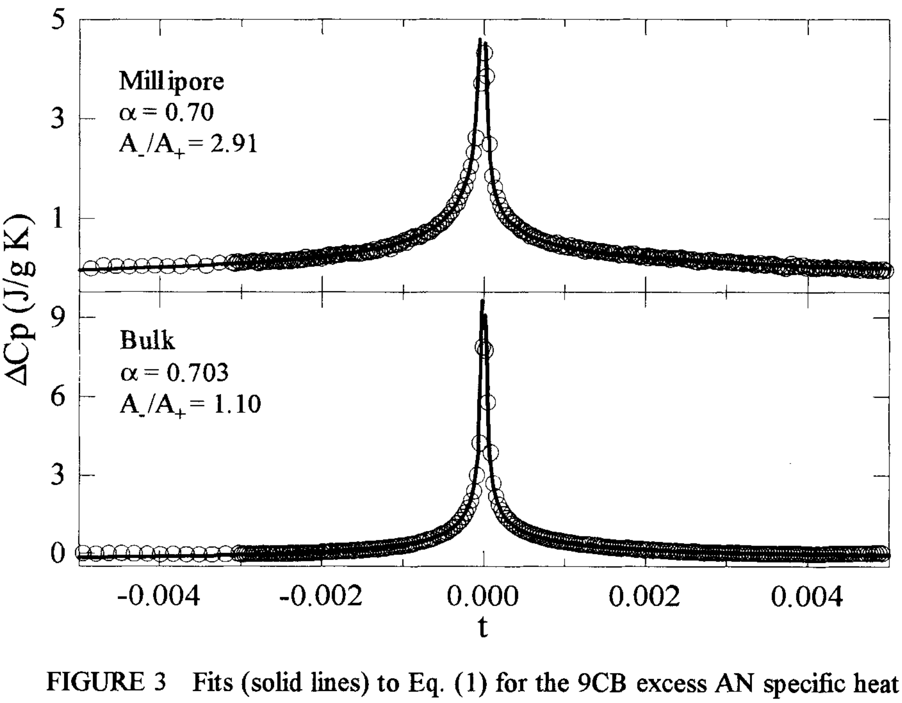

FIGURE 3 Fits (solid lines) to Eq. (1) for the 9CB excess AN specific heat as a function of reduced temperature for bulk and Millipore confinement.

The presence of long range smectic order within the Millipore substrate is established through small angle neutron scattering measurements. The neutron scattering intensity S(Q) as function of momentum transfer Q at temperatures in the smectic phase of 8CB are shown in Fig. 4. At both temperatures a distinct peak at Q ≅ 0.2 $Å^{-1}$ is evident; the peak intensity increases by about 30 % at the lower temperature indicating an enhancement in the smectic ordering. No scattering peak would be seen at higher temperatures in the nematic phase as it arises solely from the existence of translational order in the confined system. From the position of the peak maximum, the smectic layer spacing can be roughly estimated to be 6.28 / 0.2 $Å^{-1}$ = 31.4 Å. This is suggestive of the existence of a bilayer structure given the 8CB molecular length of ~ 16 Å. The broadness of the scattering peak is primarily due to the instrumental resolution of the diffractometer used in these measurements. However, additional broadening, above that due to the instrumental resolution, can be attributed to limitations on the correlation length due to the finite pore size, pore size distribution, and distortions introduced by the Millipore fibers in both the smectic layers and their spacing.

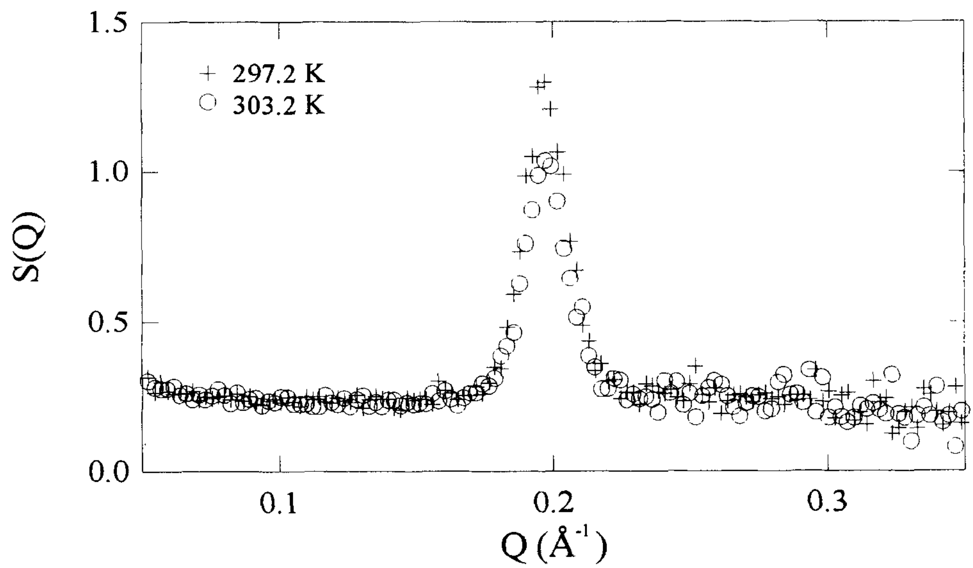

FIGURE 4 Small angle neutron scattering intensity as a function of momentum transfer for 8CB in Millipore at temperatures corresponding to the bulk smectic phase. Note the increase in peak size at the lower temperature.

In summary, we presented specific heat studies for 9CB and small angle neutron scattering measurements for 8CB confined to the nominal 0.05 μm interconnected Millipore filter paper. In contrast to findings with other porous substrates, and unexpectedly given its not well defined geometry, the Millipore results are consistent with the presence of long range smectic order. Studies with different Millipore pore sizes are in progress.

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