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THE NEMATIC TO ISOTROPIC PHASE TRANSITION IN AN ORGANIC RANDOM NETWORK

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Abstract The 4'-n-pentyl-4-cyanobiphenyl (5CB) liquid crystal is confined to the random interconnected voids of fibrous Millipore filter paper. The nematic to isotropic (NI) transition is studied using an ac calorimetry technique on Millipore filters of various void sizes. Even though the nematic correlation length is much smaller than all of the Millipore void sizes employed, substantial differences from the bulk behavior occur at the NI transition.

INTRODUCTION

Studies of the properties of liquid crystals (LCs) under confinement are of broad appeal. Employing a variety of experimental techniques studies of confined liquid crystals have found phase transitions dominated by elastic distortions [1-3], configurational transitions and surface induced nematic ordering [4,5], surface induced discrete smectic order [6], replacement of nematic ordering with a continuous evolution of local orientational order, and a pore size limited correlation length [7-10]. Several physical systems like the superfluid transition have been probed in porous materials [11,12], thus, the experimental studies have attracted considerable theoretical attention [13,14].

In this work, 4'-n-pentyl-4-cyanobiphenyl (5CB) is confined to the interconnected voids of Millipore fibrous filter paper, as a function of void size (porosity). Since, the correlation length for nematic order is smaller than all void sizes employed, a bulk-like nematic to isotropic (NI) phase transition would be expected. However, as shown by the results presented below, the NI transition in Millipore is substantially affected: ac calorimetry shows broad and round specific heat peaks located at a depressed from bulk transition temperature.

EXPERIMENTAL DETAILS

Millipore [15, 16] are thin polymeric structures (~ 125 μm thick) with porosity's ranging from 50 to 75 %. They are composed of pure, biologically inert mixtures of cellulose acetate and cellulose nitrate, and are available in several void sizes. Specific heat work employed 0.025, 0.05, 0.1, 0.22 and 0.8 μm nominal (used hereafter) void sizes. Scanning electron microscopy (SEM) studies of Millipore show a broad void size distribution. From the SEM study, the average size is estimated at 0.2, 0.3, 0.3, 0.7 and 2.5 μm respectively, which is much larger than the manufacturer quoted size [16].

For the specific heat studies we used an *ac* calorimetry technique [17]. This technique measures the specific heat C_P (but not the enthalpy) and simultaneously determines the phase shift between the induced ac temperature oscillations and the applied power signal. The phase shift contains qualitative information about the order of the phase transition [18].

RESULTS AND DISCUSSION

The specific heat C_P exhibiting the NI transition for bulk and Millipore confined 5CB shown in Fig. 1 reveals substantial effects sensitive to the changing void size. The phase shift for all samples (not shown here) exhibits a peak mimicking that in the specific heat, as expected at a first order transition [1,18]. In Fig. 2, the bulk excess specific heat (solid line in Fig. 1) is subtracted from the 0.8 and 0.05 μm void size results to emphasize deviations from the bulk behavior. Clearly, there is a bulk-like nature and enhanced two-phase region in the larger void sizes while additional broadening and rounding is present in the smaller voids.

The *fwhm* (full width at half maximum) of the specific heat peak increases with decreasing void size from 50 mK for bulk to about 300 mK in the 0.025 μm voids. The specific heat maximum does not scale with L^3 (L being the confining length), a finite size scaling expectation for first order phase transitions [14]. The depressed confined transition temperatures do not exhibit a regular dependence on the confining void size.

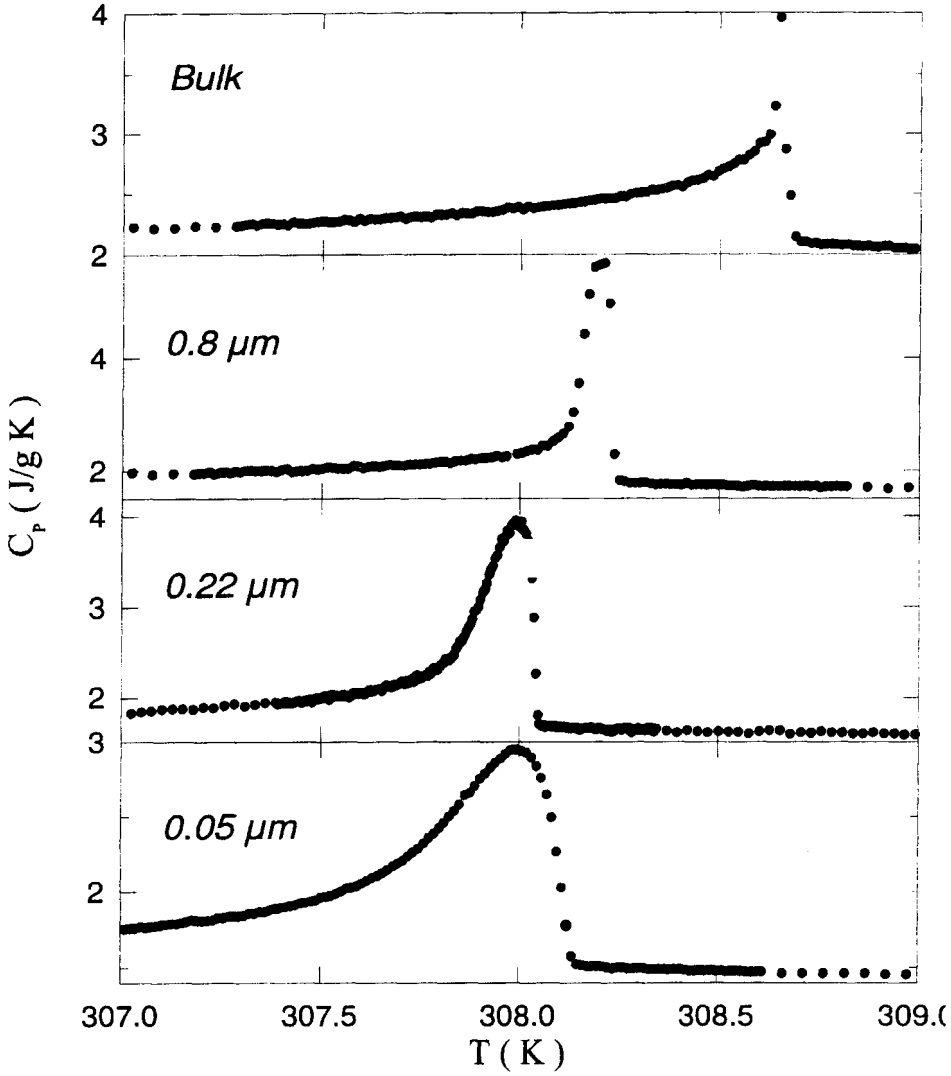

FIGURE 1 Specific heat for bulk and for some selected Millipore confined samples.

The temperature shift cannot be attributed to finite size effects since even the smallest void size is much larger than the thermal correlation length near T_{NI}. Surface tension effects and elastic constraint arguments also yield temperature depression that should be proportional to either the void size or its square [19]. These data does not follow either relationship. A more likely scenario for the temperature shift is that it is due to surface disorder or impurity-like effects which are intrinsic to all Millipore filters.

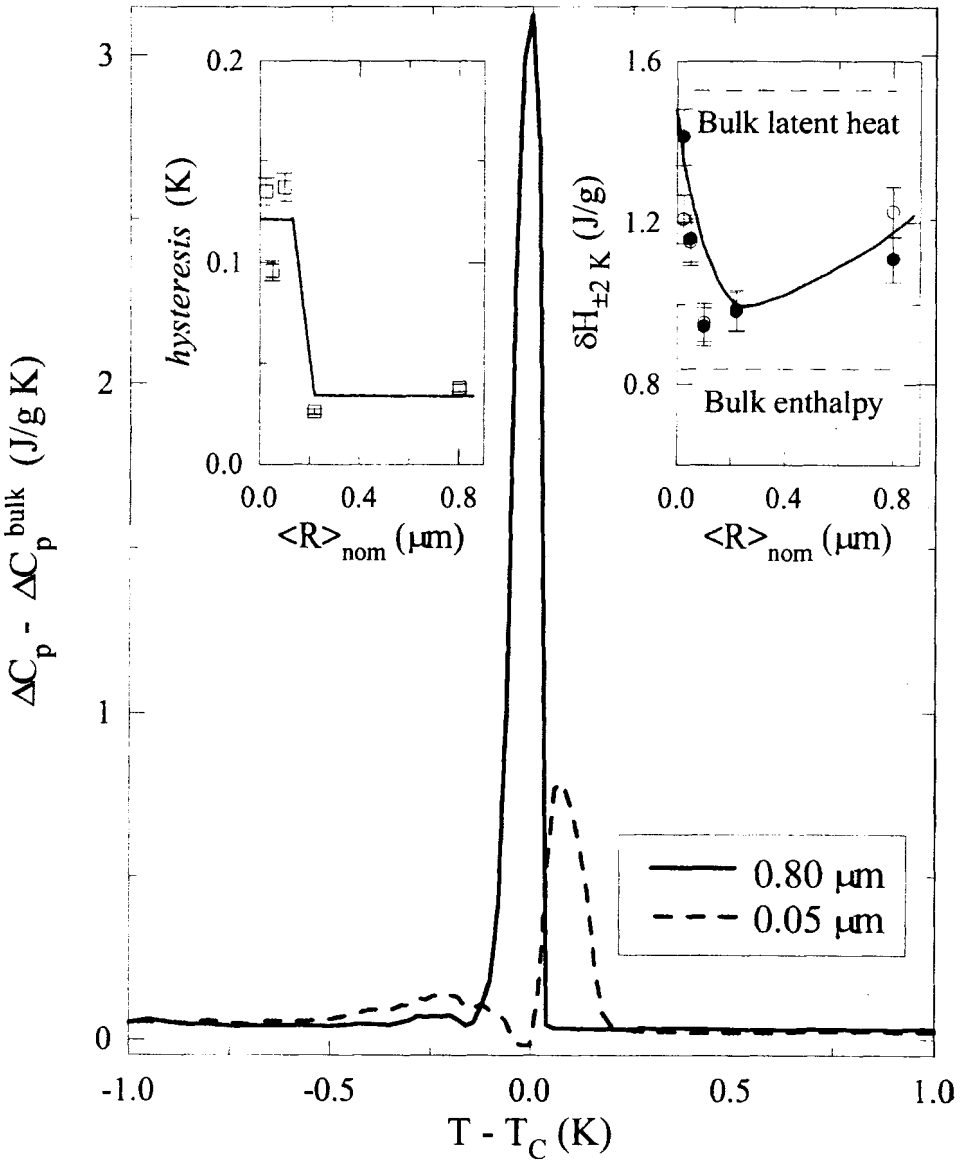

FIGURE 2 Excess specific heat for the 0.8 and 0.05 μm confined 5CB samples after subtraction of the bulk excess specific heat. Right inset: hysteresis of T_c between heating and cooling as a function of nominal void size. Left inset: area under excess specific heat (δH), ± 2 K about T_c for heating (.) and cooling (o) scans as a function of nominal void size.

When combining results from cooling and heating runs, there is an overall trend of lowering T_c with decreasing void size : a downward shift from bulk by 0.3 K for the

V_8 = 0.8 μm and 0.5 K for the V_{25} = 0.025 μm samples. In addition, comparing the hysteresis in T_C (difference in T_C position between heating and cooling runs) we find a crossover behavior (see also below) at $V_C \sim 0.1$ μm void size. This is clearly shown in the left inset of Fig. 2.

Using a "single-pore" model [9], the disordering energy due to topological constraints that would be introduced as hQ^2 in a Landau free energy expansion, can be roughly estimated from the shifts of T_C from bulk by $\Delta T = 2h/a$, where a is the coefficient of the bulk Q^2 term. Using an average $\Delta T \cong 0.5$ K, we find $h \cong 3.3\times10^4$ J/m^3 compared to 1.4×10^6 J/m^3 found for Vycor porous glass [9]. This is a crude estimate that may at best be applicable only to the smallest Millipore void size studied but it is probably significant of the considerable surface influence.

Another feature of these results, is the NI transition enthalpy which is calculated from $\delta H = \int \Delta C_p dT$ integrated over the temperature range $T_C \pm 2$ K, and it is shown in the right inset of Fig. 2. For bulk, l_{5CB} = 1.56 J/g is the latent heat [20] and δH_{5CB}= 0.85 J/g over the same temperature range. In the confined cases, δH is 1.2 J/g for the largest voids decreasing to 0.95 J/g at ~ 0.1 μm void; for smaller void sizes, δH increases sharply to ~ 1.4 J/g a value comparable to the bulk's latent heat. As before, a crossover behavior appears to set in at ~ 0.1 μm void size. Under more restrictive confinement conditions, the enthalpy would necessarily decrease as seen in silica Aerogel [3]. With further increase in confinement to sizes smaller than the nematic correlation length, the NI transition would be completely suppressed and replaced by a continuous evolution of orientational order [9]. Therefore, in Millipore, where the enthalpy is larger than bulk's for all samples studied, it is believed that the enhancement in enthalpy for $V > V_C$ is solely due to the enhanced two-phase coexistence region, while for $V < V_C$, it arises from the overall broadening of the transition and smearing out of the latent heat which might be converted or behave like pretransitional heat capacity thus contributing to the measured *ac* signal. This behavior suggests that the void spaces become increasingly isolated from one another with decreasing mean void size.

To conclude, despite the large confining void sizes, the bulk NI transition is substantially affected by the random nature of organic Millipore filters. Results indicate a

possible crossover behavior as a function of void size. This agrees with recent results from studies of the smectic-A to nematic transition of 8CB and 9CB in Millipore [21] that showed that the confined critical behavior is different from bulk at a liquid crystal dependent confining size.

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