

Surface-Induced Discrete Smectic Order in the Isotropic Phase of 12CB in Cylindrical Pores

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(Received 13 June 1994; revised manuscript received 2 September 1994)

Through specific-heat and x-ray scattering studies, we show the existence of surface-induced discrete smectic order in the isotropic phase for dodecylocyanobiphenyl (12CB) confined to Anopore membranes. A quantized smectic layer growth is promoted by the pore surface when treated with an aliphatic acid of varying chain length. No surface-induced smectic order develops in untreated or lecithin treated pores nor in liquid crystals that possess a nematic phase.

PACS numbers: 61.30.Eb, 64.70.Md, 68.35.Md, 82.60.Fa

Studies of the influence of surfaces on the phase behavior of liquid crystal (LC) materials have mostly focused on nematics because of their relative simplicity (only orientational order) and use in display devices where surfaces play a fundamental role. Surface effects also alter the physical behavior of other more complex LC phases. The increased complexity is introduced by additional ordering such as long-range orientational evolution of the local nematic director as in cholesterics and translational order as in smectics. The global structure imposes constraints at an interface besides those dictated by the surface. The LC molecules orient so as to minimize the surface energy, consisting of contributions due to structural modifications and molecular-substrate interactions [1].

Quantized layer growth was observed at smectic liquid crystal surfaces [2–8]. X-ray reflectivity measurements at the free surface of dodecylocyanobiphenyl (12CB) showed that at temperatures above the smectic-*A* to isotropic (*A*-*I*) transition, smectic-*A*-like ordering developed at the surface while the bulk phase remained isotropic [2]. The specular reflectivity was consistent with a sinusoidal smectic density profile starting at the surface and abruptly ending after an integral number of bilayers; the free surface partial wetting was discrete. In approaching the *A*-*I* transition, the number of layers increased in quantized steps from zero to five before the bulk underwent a transition to the smectic-*A* phase. Mean field theoretical work showed that for a weak strength of the substrate potential, a few first-order layer transitions occur with smectic-*A* incomplete wetting; for stronger potentials, the smectic grows through an infinite sequence of layer transitions [9].

Smectic layering transitions, fewer and more continuous at the planar solid substrate than at the free surfaces, were also found at the interface between isotropic *n*CB ($n = 11, 12$, the number of carbon atoms) and alkylsilane-coated (100) silicon surfaces [8]. However, because of its roughness, the substrate induced the smectic order to a lesser degree than the free surface [2].

Surface effects are enhanced by confining a LC material. This was shown in studies employing interconnected structures like Vycor [10] and silica aerogel [11] porous glasses, or the cylindrical pores of polycarbonate

Nuclepore and aluminum oxide Anopore membranes. In cylindrical cavities (as studied here), phenomena include the observation of surface-induced nematic order in the isotropic phase ($T - T_{NI} \cong 20$ K), director configurational transitions, and shifting, suppression, and rounding of phase transitions. These were unveiled by deuterium nuclear magnetic resonance ($^2\text{H-NMR}$) [12–14] and specific-heat [15] studies for *n*CB liquid crystals, $5 < n < 12$, in Anopore [16]. Recently [17], $^2\text{H-NMR}$ for 5CB in aliphatic acid ($\text{C}_m\text{H}_{2m+1}\text{-COOH}$) treated Anopore, found an orientational transition from partial to quasicomplete wetting as the length of the aliphatic chain m increased.

Using x-ray scattering and ac calorimetry, we studied 12CB confined to Anopore membranes treated with the aliphatic acid. The translational order shows a stepwise growth at temperatures well into the isotropic phase. In addition to a considerable broadening and rounding of the *A*-*I* transition, unmistakable specific-heat signatures (peaks) are observed which are related to this surface-induced smectic growth. The transition enthalpy is consistent with the growth of a single bilayer. Given the polar nature of 12CB and studies of LCs in a planar geometry [2–9], these results, found for the first time in a cylindrical geometry, agree with a bilayer smectic growth. This view is supported by parallel $^2\text{H-NMR}$ studies [18].

Anopore are produced through an electrochemical anodizing process [19]. Made from a high-purity alumina matrix, they possess $0.2 \mu\text{m}$ diam, parallel, cylindrical pores of high density 1.8×10^{10} pores/membrane (porosity $\sim 40\%$) [16,19]. The $60 \mu\text{m}$ thick Anopore are cut to 1 cm diam disks and immersed in the appropriate (2%) aliphatic acid previously dissolved in methanol. The treated disks are placed in a vacuum oven at 120°C to remove the water resulting from the bonding reaction. The coated disks are then dipped in a 12CB bath at $T > T_{AI}$ for several hours. A single (three) disk containing ~ 2.5 mg of 12CB is used for the specific-heat (x-ray) studies.

Translational order in a cylindrical geometry is probed using x-ray scattering from smectic layers parallel to the pore surface. This was previously demonstrated through studies of 8CB confined to larger pore ($25 \mu\text{m}$) glass

capillary arrays [20]. The measurements are performed using a Rigaku 18 kW rotating anode generator with a copper target [21]. The disks are sealed in a holder made of two thin aluminum plates with a 6 mm opening for x rays. The sample holder is mounted in a two-stage oven and the axes of the cylindrical pores aligned parallel to the incident beam. The sample is then heated to the isotropic phase and the intensity of the Bragg peak monitored as a function of temperature while cooling. Two types of scans are performed; q_{\parallel} scans, which probe the longitudinal smectic correlations and ω scans to determine the sample mosaicity.

X-ray scattering results for $m = 9, 12,$ and 15 treatments are shown in Fig. 1. Here, we plot the peak intensity at 0.16 \AA^{-1} (or 39.3 \AA layer spacing) versus temperature. An increase in peak intensity is definite evidence for the development of translational order. With decreasing temperature and $m = 9$, the peak intensity increases monotonically starting at $T - T_{AI} = 1 \text{ K}$; for a longer aliphatic chain length, discrete steps (as many as eight for $m = 15$) are clearly visible. The intensity nearly saturates at T_{AI} , constant for remaining $T < T_{AI}$. Corresponding discrete increases are found in the parallel correlation length (see inset to Fig. 2) which directly yields the number of smectic bilayers as a function of temperature.

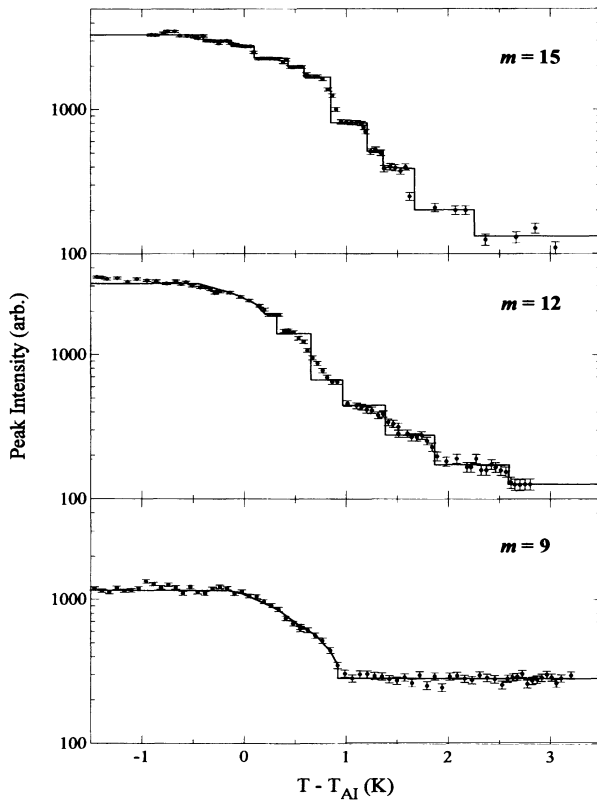


FIG. 1. X-ray scattering peak intensity as a function of $T - T_{AI}$ for $m = 9, 12,$ and 15 aliphatic acid treatments of the Anopore $0.2 \mu\text{m}$ pore. Solid lines are guides to the eye.

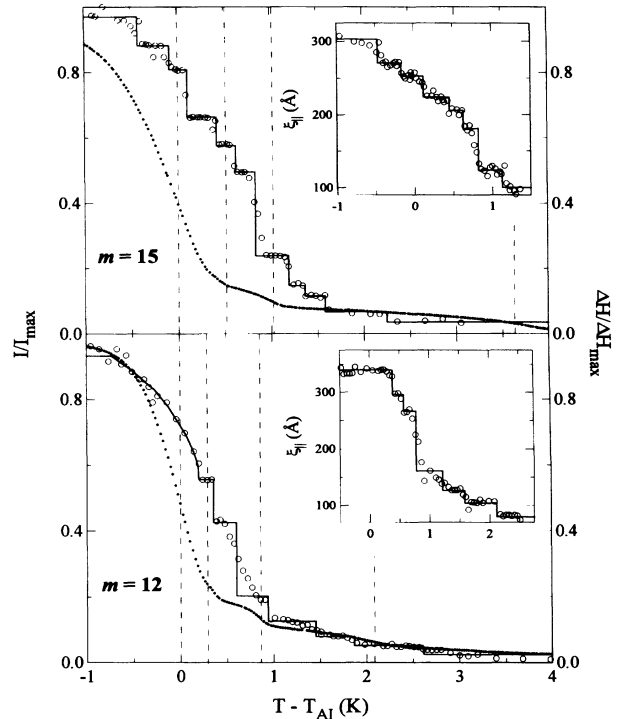


FIG. 2. X-ray peak intensity (open circles) and total enthalpy (dotted line), normalized by their respective values at low temperature, as a function of $T - T_{AI}$, for $m = 12$ and 15 treatments. Dashed lines indicate the temperature of the specific heat peaks. Inset: Parallel correlation length against temperature.

The treated surface induces a stepwise smectic growth in the isotropic phase; the effect is enhanced by the longer aliphatic chain.

These results are consistent with the stepwise (quantized) formation of approximately nine bilayers. Assuming a bilayer thickness of $\sim 40 \text{ \AA}$, and beginning at the pore wall, there is a 350 \AA thick smectic shell of homeotropically aligned bilayers at the lowest temperature, as calculated from the line-shape analysis. The core of the pore contains smectic layers highly misoriented or oriented in a direction not perpendicular to the x-ray scattering vector of our experimental setup. From this and volume considerations, it is estimated that 58% of the molecules form the smectic bilayer shell. The overall configuration is difficult to ascertain from these measurements, but it is probably of the planar radial type [18].

To thermodynamically characterize the system, an ac specific-heat study is undertaken [22]. A comparison of heating and cooling scans shows that the specific heat exhibits some hysteresis that manifests in a difference of $\sim 10\%$ in the peak maximum and 0.2 K shift in peak temperature [23]. This behavior does not affect our conclusions.

Several features are evident from the specific heat (cooling) plotted in Fig. 3 against temperature difference from $T_{AI} \equiv T_P$, the largest peak temperature, for several

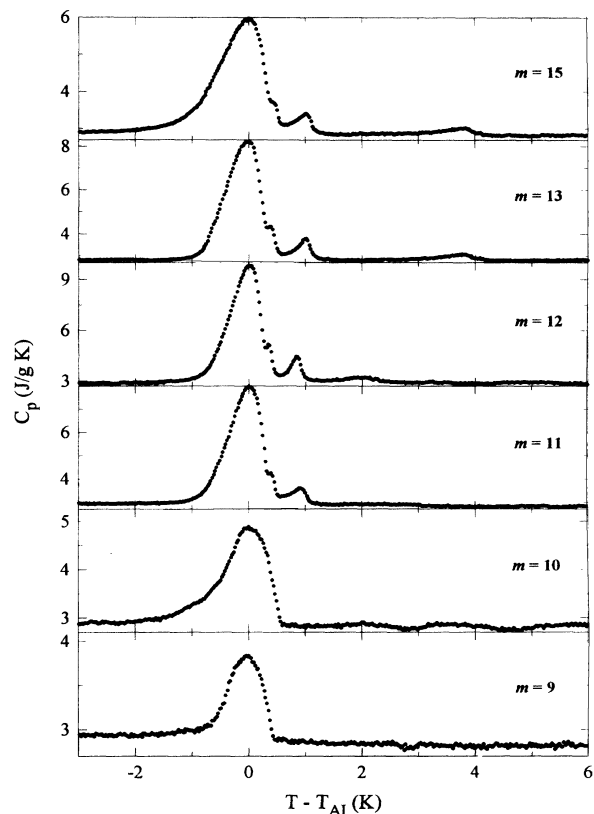


FIG. 3. Specific heat (cooling) as a function of reduced temperature for several aliphatic acid treatments.

aliphatic acid treatments of the pores. For all chain lengths, the large low temperature specific-heat peak is identified with the *A-I* transition. The typical full width at half maximum (FWHM) of this *A-I* peak is ~ 0.5 K, which is comparable to widths reported in previous studies with 10CB and 12CB in untreated and lecithin treated Anopore [15,22]. Here, the FWHM slightly increases with m . Since the imposed temperature oscillations (ac technique) are ~ 3 mK, such broadening is a reflection of surface heterogeneities, a possible temperature dependent anchoring energy [24], and is partly due to the smectic layering transitions occurring near T_{AI} .

As seen in Fig. 4, the temperature of the *A-I* peaks are within 0.3 K of the average (from all chain lengths) $T_{AI} = 330.25$ K. Both T_{AI} and the specific-peak height C_m increase up to $m = 12$, decreasing afterward. The peak height is at least a factor of 2 larger than that for $m = 9$ which is comparable to that measured in lecithin treated Anopore [15]. The same trend is seen in the *A-I* transition enthalpy (Fig. 4), which has a maximum of 4.6 J/g for $m = 12$ [25]. This suggests that the strength of the surface-LC interaction is optimum for $m = 12$. Surface ordering extending through the core of the pore is dominant for $m \leq 12$; disordering effects play an increasingly important role for $m > 12$, curiously, the same number of carbon atoms as in the 12CB molecule.

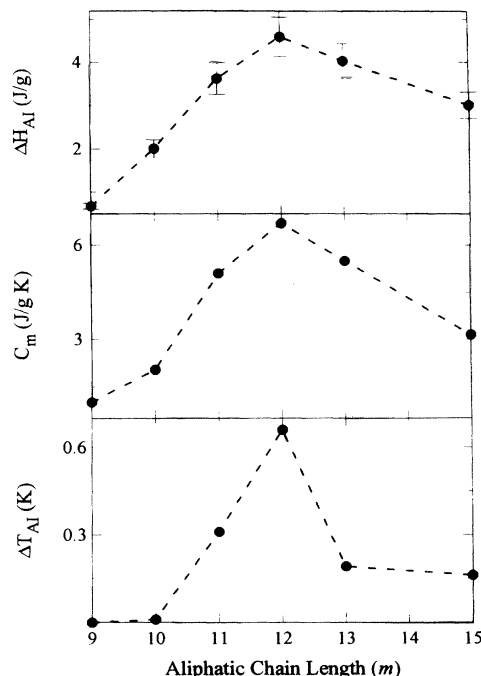


FIG. 4. Transition temperature shift ΔT_{AI} , *A-I* specific heat peak height C_m , and *A-I* transition enthalpy ΔH_{AI} , as a function of aliphatic acid chain length m . Note the reversal in trends at $m = 12$. The error bars in ΔH_{AI} are best estimates. Dashed lines are guides to the eye.

Alternatively, a different surface-LC interaction may take place in systems with different m due to changes in the director configuration. For 5CB in aliphatic treated Anopore [17], a configurational transition occurred at $m = 7$, suggesting that the interaction between the long alkyl chain and the LC molecules is mostly sterical, while for shorter chains, strong interactions between the alumina surface and the rigid core of LC molecules dominate. This would be manifest in a specific heat measurement, which in Anopore [15], was strongly dependent on the director configuration within the pores.

Smaller specific-heat peaks, more noticeable for the longer aliphatic chains (as in the x-ray data) are seen at temperatures as high as 4 K above T_{AI} (see Fig. 3). These peaks become sharper and larger closer to T_{AI} and appear to correspond to larger increases in the x-ray peak intensity. As the surface influence weakens with increasing temperature, they are broad and small, consistent with the somewhat smeared step nature and smaller increases in x-ray peak intensity. No isotropic phase peaks are detected for $m < 11$ (consistent with the absence of steps in the x-ray data for $m = 9$), while two distinct peaks plus a half peak that is too close to and is swamped by the large *A-I* peak, are evident for $m \geq 11$. With larger m and thus stronger surface-LC interaction at the pore wall (but weaker through the core), peaks are seen farther from T_{AI} .

These features appear to be unique to n CB LCs lacking a nematic phase ($n \geq 10$) and result from the aliphatic acid treatment of the pore surface. No specific heat peaks in the isotropic phase are found for 12CB (and 10CB) in either untreated or egg yolk lecithin-treated Anopore [15,23]. Also, there are no isotropic phase (small) peaks for 8CB or 9CB (which have a nematic phase) in aliphatic acid treated Anopore [23].

Allowing for small discrepancies in the absolute temperature due to the different thermometers used in the two experiments, the small peaks' temperature positions are consistent and can be identified with the location where the x-ray data show discrete increases in translational order correlations. This is presented in Fig. 2, where we plot the x-ray peak intensity normalized by its maximum value at low T , together with the total enthalpy (sum of areas under all peaks), also normalized by its maximum low T value. In both cases, plateaus followed by sharp increases are seen at nearly coinciding temperatures. The dashed lines of Fig. 2, representing the temperature of each specific-heat peak, coincide with the middle of an x-ray constant peak intensity region.

While many x-ray features are reproduced by the enthalpy, there are some minor differences. Not all x-ray plateaus are reproduced in the enthalpy as layers form too closely spaced in temperature. Because of its width, a small specific heat peak arising from a layer formed near T_{AI} could not be separated with the present resolution; it would simply contribute to the broad $A-I$ peak and a monotonic increase in enthalpy. This is demonstrated by the "half" peak seen on the high temperature side near the $A-I$ peak. For $m = 15$, we presently lack an explanation for the absence of specific heat peaks between 1 and 3 K above T_{AI} . A simultaneous x-ray and specific-heat study is needed for a closer correlation.

By recognizing that the total enthalpy is a measure of the smectic volume within a 1000 Å pore radius, the 350 Å thick smectic shell contributes 58% to this total. For $m = 15$, this corresponds to an enthalpy of 2.01 ± 0.15 J/g. Remarkably, the enthalpy associated with the small specific heat peaks, 0.18 ± 0.02 and 0.2 ± 0.02 J/g, is consistent with the formation of a single smectic bilayer, 35 ± 5 Å layer spacing (compared to 39.3 Å from x ray). Identical results are obtained when the calculation is repeated for $m = 13$.

In summary, we have presented concrete evidence for the development of discrete smectic order in the isotropic phase of 12CB confined to submicron size cylindrical pores. The surface-induced smectic order is associated with changes in the chemical nature of the pore's surface. The strength and extent of the surface interactions changes with the length of the aliphatic acid. No smectic growth was found with other surface treatments nor in LCs with a nematic phase. High resolution x-ray scattering provides clear evidence of discrete smectic layer growth in the isotropic phase accompanied by distinct specific-

heat peaks of transition enthalpy consistent with the formation of a smectic bilayer.

We thank Greg Crawford for preparing the early samples and useful discussions. This work was supported by the NSF ALCOM Grant No. DMR 89-20147. Two of us (S. K. and D. F.) thank the Research Council of Kent State University for its support through an Academic Year Research and Creative Activity Appointment.

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