

Crystalline transitions in free-standing films of 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline

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(Received 30 November 1999; revised manuscript received 3 February 2000)

Free-standing films of 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline are known to exhibit multiple smectic-*I* surface layers in the presence of a smectic-*A* interior. The phase transitions leading to the crystallization of these films have been studied using electron diffraction. Our data are consistent with the scenario of the smectic-*I* surface layers first developing a crystal-*B* outermost layer before transforming entirely into the crystal-*B* phase, to be followed by the freezing of the smectic-*A* interior. The adjacent crystal-*B* and smectic-*I* layers show evidence of orientational epitaxy.

PACS number(s): 64.70.Md, 61.30.Eb

The compound 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline (7O.7) has been widely studied because of its rich liquid-crystal polymorphism. In the bulk, its phase properties are not unusual, showing the nematic, smectic-*A* (Sm-*A*), smectic-*C* (Sm-*C*), and crystal-*B* (Cry-*B*) phases upon cooling [1]. However, 7O.7 exhibits a variety of hexatic behavior in free-standing films. The tilted hexatic smectic-*F* (Sm-*F*) phase is found in films thinner than about 175 molecular layers, changing at higher temperatures to the smectic-*I* (Sm-*I*) phase in films thinner than about 25 layers [2]. Films of six layers or fewer in the Sm-*I* phase undergo two additional transitions upon further heating, first to films with Sm-*I* surfaces and a Sm-*C* interior and finally to the Sm-*C* phase [3,4]. We recently showed that free-standing 7O.7 films of up to 25 layers thick possess the unusual coexistence as a function of distance from the surface of three distinct phases: an outermost Sm-*I* layer, several layers of a middle phase, and a Sm-*A* interior [5]. The middle phase is a novel tilted liquid, with hexaticlike positional correlations but no long-range bond-orientational order, which transforms to the Sm-*I* at a lower temperature. We have extended these studies to lower temperatures using electron diffraction. In this paper, we report the multiple intermediate steps leading to the transformation of these films to the Cry-*B*, the unusual occurrence of the tilted Sm-*I* phase developing an orthogonal Cry-*B* layer either on the surface or in the interior, and the evidence for orientational epitaxy between adjacent layers of these two phases.

As reported previously [5], the electron-diffraction pattern for a 20-layer film of 7O.7 above 80.5 °C consists of a uniform diffuse ring characteristic of the Sm-*A* liquid. Between 80.5 and 77.7 °C, the diffuse ring is not uniform, but has a twofold intensity modulation indicative of the presence of surface Sm-*C* layers coexisting with a Sm-*A* interior. Between 77.7 and 69.0 °C, the diffraction pattern consists of a pair of short bright arcs and a pair of longer arcs in the presence of a uniform diffuse ring. This diffraction pattern has been interpreted as evidence for the existence of multiple layers of a novel phase, which we called smectic-*C'* (Sm-*C'*), sandwiched between a single Sm-*I* layer on either surface and a Sm-*A* interior which is estimated to be one-third the thickness of the entire film. The middle Sm-*C'* phase appears to be the tilted analog of the highly correlated

isotropic liquid phase observed in *n*-pentyl-4'-*n*-pentanoyloxybiphenyl-4-carboxylate (54COOBC) [6,7] and 4-*n*-butoxybenzylidene-4-*n*-octylaniline (4O.8) [8,9].

To examine the phase behavior at lower temperatures, we have conducted electron-diffraction studies with free-standing 7O.7 films of 8 to 25 molecular layers, using an electron microscope equipped with a pressurized, temperature-controlled sample chamber [10]. Figure 1 shows the typical diffraction patterns obtained with a 20-layer film. When the film is cooled below 69.0 °C, the diffraction pattern shown in Fig. 1(a) is obtained, with one pair of hexatic arcs in the presence of a uniform diffuse ring, signifying the presence of seven outermost Sm-*I* layers on either surface of the film, with the interior six layers remaining in the Sm-*A* phase. This interpretation is supported by the fact that the ratio of the integrated intensity of the Sm-*I* arcs below 69.0 °C to that above 69.0 °C is around 7. Thus at 69.0 °C, all the middle Sm-*C'* layers in the film have abruptly transformed to the Sm-*I* phase.

At 68.7 °C, there is a transition to the unusual diffraction

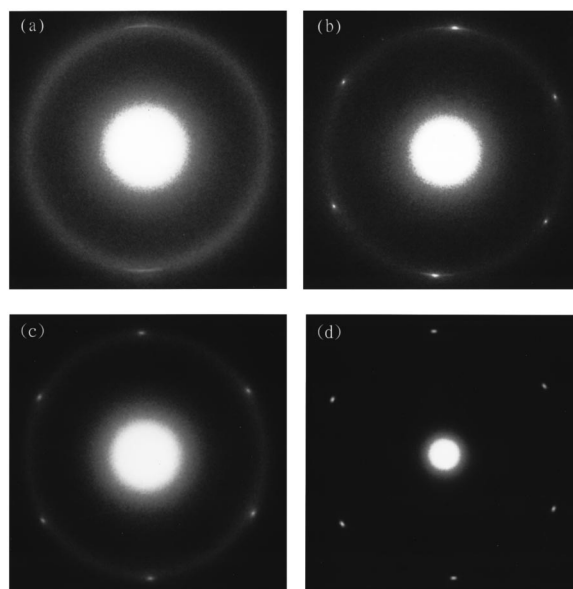


FIG. 1. Electron-diffraction pattern from a 20-layer 7O.7 film at (a) 68.8 °C, (b) 68.6 °C, (c) 68.0 °C, and (d) 67.0 °C.

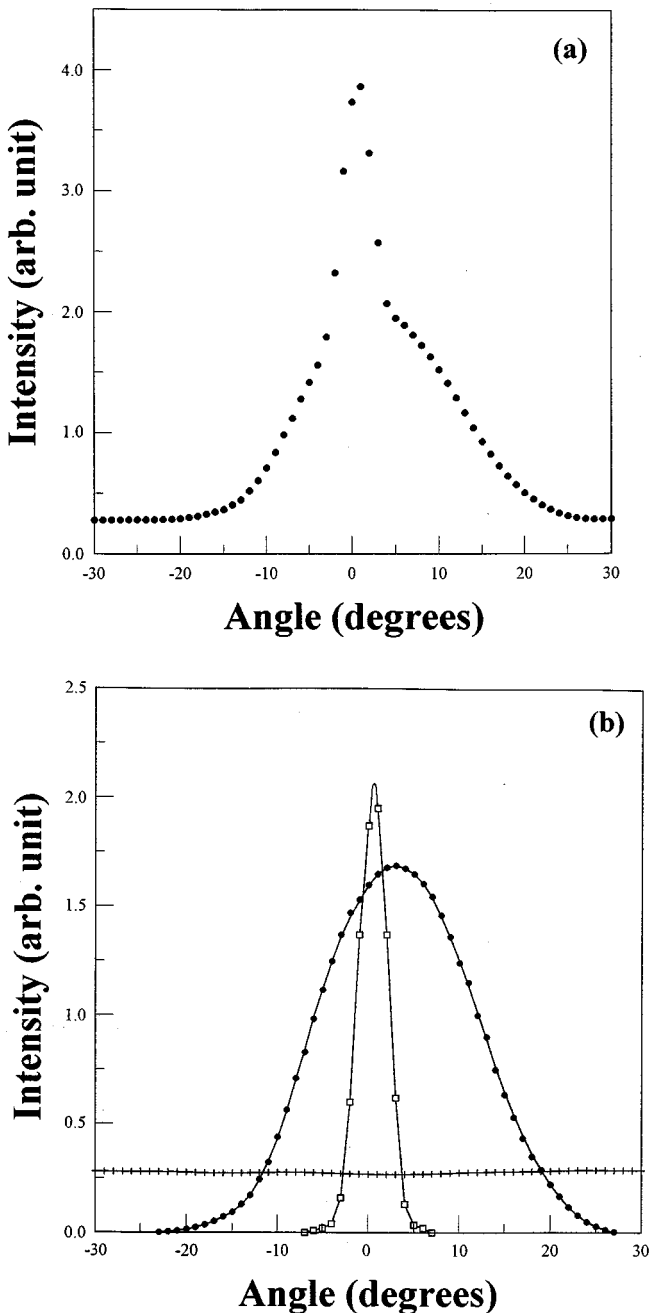


FIG. 2. (a) Diffraction intensity from a 20-layer film along a χ scan at 68.6 °C. (b) Separation of the diffraction intensity in (a) into the Sm-A (crosses), Sm-I (solid circles), and Cry-B (open squares) contributions. The line through the solid circles is a fit to Eq. (1).

pattern shown in Fig. 1(b). It shows the coexistence of a pair of bright arcs, six sharp spots, and a diffuse ring. The intensity $I(\chi)$ around the ring as a function of the angle χ in the neighborhood where all three features are present is plotted in Fig. 2(a). The superposition of a sharp spot, a bright arc, and a uniform ring is clearly discernible, and is confirmed by the fact that the diffraction intensity can be shown to be the sum of these three separate features, as illustrated in Fig. 2(b). The six bright spots of equal intensity suggest diffraction from the Cry-B phase. Since liquid crystals are known to exhibit surface freezing, we will assume for the moment that the Cry-B phase resides on the surface of the film. Other possibilities will be discussed at the end of this paper. The

intensity of the bright arc can be fitted to the equation traditionally used for diffraction due to bond-orientational order:

$$I(\chi) = I_o \left(1/2 + \sum_{n=1}^{\infty} C_{6n} \cos 6n(\chi - 30^\circ) \right) + I_{BG}, \quad (1)$$

where C_{6n} are the $6n$ -fold bond-orientational order parameters [11]. This fact, together with the twofold symmetry of the short arcs, indicates that the layers immediately beneath the Cry-B surfaces are still in the Sm-I phase. Finally, the diffuse ring provides evidence that the interior layers remain in the Sm-A phase. Our previous knowledge of the structure of the film immediately above 68.7 °C suggests that the film immediately below 68.7 °C most likely consists of a Cry-B layer on each outermost surface, six Sm-I layers immediately next to the Cry-B surfaces, and an interior composed of six Sm-A layers. A direct verification of this structural description using the integrated intensity of the various diffraction features is complicated by our low instrumental resolution of the Cry-B spots and the need to make delicate background intensity subtraction. However, a relatively crude analysis of the data yields the values 1, 4.3 ± 1 , and 2.0 ± 1 for the relative integrated intensity of the Cry-B, Sm-I, and Sm-A signals, respectively. This result is at least qualitatively consistent with our thickness assignment of the three phases.

The fact that there is only one set of Cry-B spots in Fig. 1(b) indicates that the two outermost Cry-B layers are in perfect registry with each other. This occurrence despite the relatively large distance between these two outermost layers illustrates the importance of the influence of the intervening Sm-I and Sm-A layers. Figure 1(b) also suggests that the Cry-B spots are in close alignment with the Sm-I arcs. However, a closer examination of the separate intensities in Fig. 2(b) reveals that the peak positions of the Cry-B spot and the Sm-I arc are not perfectly aligned, but have a small angular separation of about 2°. This result may be another manifestation of the interesting phenomenon of orientational epitaxy, similar to that reported earlier in the case of crystal-E (Cry-E) surfaces on top of a hexatic-B (Hex-B) interior [12,13]. Such a small rotation of the two lattices might be necessary to minimize the energy of the strain between the two adjacent layers, which are slightly incommensurate in their lattice parameters. That fact that a similar behavior was observed also with adjacent surface Cry-B and next-to-surface Hex-B layers in 40.8 [8] suggests that this phenomenon might be ubiquitous.

Below 68.4 °C, the diffraction pattern shown in Fig. 1(c) is obtained. It consists of six bright spots coexisting with a diffuse ring. This indicates that all the remaining Sm-I layers have now frozen into the Cry-B phase, resulting in multiple (most likely 7) Cry-B layers on either surface and a Sm-A interior, probably of six layers. Below 67.4 °C, the diffraction pattern consists only of six sharp spots, as shown in Fig. 1(d), demonstrating that the entire film has finally frozen into the Cry-B phase. There is a possibility that transformation of the interior from the Sm-A to the Cry-B phase is not a direct one, but might involve a hexatic phase as an intermediate step. During the cooling runs, we observed visually that the diffraction immediately above 67.4 °C often consisted in part of rapidly rotating hexaticlike arcs. However, since the motion of the arcs was fast compared to the typical exposure

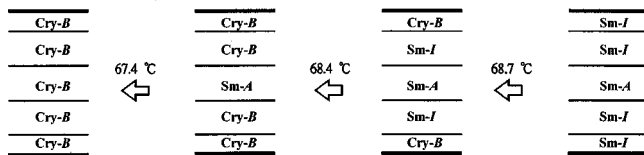


FIG. 3. Possible phase sequence in a 20-layer 70.7 film below 69 °C upon cooling.

time of several seconds, we were unable to record equilibrium diffraction patterns showing evidence for the intermediate hexatic phase.

A possible multiple-step phase sequence in 70.7 that is consistent with our data is summarized in Fig. 3. This behavior can be compared to that observed in other materials that exhibit hexatic phases. Surface freezing has been seen in *n*-heptyl-4'-*n*-pentyloxybiphenyl-4-carboxylate (75OBC) (Cry-*E* surface layer on Hex-*B* interior) [12], in 40.8 (Cry-*B* surface layer on Hex-*B* interior) [8], and in 5-(4''-hexyl,3'-fluoro-*p*-terphenyl-4-oxy)-pentanoic acid ethyl ester (FTE1) (crystal-*H* surface layer on Sm-*F* interior and crystal-*N* surface layer on smectic-*L* interior) [14]. In these examples, an orthogonal hexatic phase develops an orthogonal crystal surface, while a tilted hexatic phase develops a tilted crystal surface. In 70.7, we find the unusual possibility in which a tilted hexatic phase (Sm-*I*) develops an orthogonal crystal surface (Cry-*B*).

Finally, we would like to discuss other possible locations of the Cry-*B* layers between 68.7 and 68.4 °C. We have assumed in our data analysis that the Cry-*B* layers occur in the outermost surfaces of the film. This assumption is based on the observation that, in almost all of the studies on phase transitions in liquid-crystal films, the surface layers are found to be more ordered than the interior. In other words, the surface favors a hexatic phase over a liquid phase, and a crystalline phase over a hexatic phase. In 75OBC, for example, where there is coexistence between Cry-*E* and Hex-*B* phases, x-ray scattering along the thickness of the film suggests that the Cry-*E* layers are on the surfaces [12]. The application of this general rule to our data in 70.7 would suggest that the crystalline Cry-*B* layer with its higher positional order would lie outside of the hexatic Sm-*I* interior. However, in 70.7, there is a competing order that also may affect the phase of the surface layer, namely, tilt. It is known that 70.7 prefers a tilted surface over an orthogonal one [2]. Between the choices of an orthogonal Cry-*B* surface or a tilted Sm-*I* surface, we cannot totally rule out the latter in 70.7. If that is the case, the Cry-*B* layer will be interior to the Sm-*I* surface, which represents yet another unusual and interesting scenario.

One of us (C.Y.C.) acknowledges support from the National Science Council, Taiwan, Republic of China, under Grant Nos. NSC 88-2112-M-008-029 and NSC 89-2112-M-008-004.

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