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Layer-Dependent Surface-Induced Tilt, Hexatic, and Positional Orders in Free-Standing 7O.7 Films

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Electron diffraction in free-standing films of 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline of up to 25 molecular layers has revealed the coexistence, as a function of distance from the surface, of three distinct phases: an outermost smectic-*I* layer, several layers of a middle phase, and a smectic-*A* interior. The middle phase is an unusual highly-correlated tilted liquid, with hexaticlike positional correlations but no long-range bond-orientational order, which transforms to the smectic-*I* at a lower temperature. The discovery of this unusual middle phase also represents the possibility of a novel layer-dependent two-stage tilt-induced surface-freezing transition.

Keywords: highly-correlated tilted liquid; smectic-*C'* (Sm-*C'*) phase

INTRODUCTION

Liquid crystals are unusual examples of systems which can exhibit surface-induced order. Growth of a more ordered surface phase onto a less ordered interior has been reported for nematic order at the isotropic-solid interface [1] and for smectic-*A* (Sm-*A*) order at the nematic-vapor [2] or isotropic-vapor interface [3]. Among liquid

crystals that exhibit hexatic phases, which are expected to exist between the liquid and crystal phases in the theory of defect-mediated melting in two dimensions [4,5], various surface-freezing behavior has been observed in free-standing films, including complete layer-by-layer Sm-*A* to the tilted hexatic smectic-*I* (Sm-*I*) [6] and incomplete layer-by-layer Sm-*A* to hexatic-*B* (Hex-*B*) transitions [7]. All the above examples are characterized by the coexistence of two distinct phases, one on the surface and another in the interior of the films. In this paper, we report the results of structural measurements using electron diffraction on free-standing 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline (7O.7) films of up to 25 layers thick that reveal the unusual coexistence of three phases, with a middle phase a few layers thick sandwiched between the outermost layers and the interior, which is in sharp contrast to the traditional transitions observed in most other liquid crystal materials. The middle phase observed appears to be a novel tilted *liquid* with hexaticlike positional correlations but no long-range bond-orientational order.

Our electron-diffraction measurements were conducted with free-standing 7O.7 films of 8 to 25 molecular layers [8], with a typical electron beam diameter of 10 μm. The diffraction pattern for a 20-layer film above 80.5°C consists of a uniform diffuse ring characteristic of the Sm-*A* liquid, as shown in Fig. 1(a). On cooling, a diffraction pattern exemplified by Fig. 1(b), with the diffuse ring acquiring an additional twofold intensity modulation characteristic of the Sm-*C* phase, was observed between 80.5°C and 77.7°C. A detailed χ scan of the intensity around the ring reveals the presence of a significant uniform background, suggesting that the surface Sm-*C* layers coexisted with a Sm-*A* interior comprising about one-third of the total film thickness.

Between 77.7°C and 69.0°C, the film produced a diffraction pattern typified by Fig. 1(c), consisting of a pair of short bright arcs and a pair of longer arcs in the presence of a uniform Sm-*A* diffuse ring. The χ-scan intensity around the ring over a 180° range at several temperatures is shown in Fig. 2. It can be seen that both the intensity and angular width of the short arc are sensitive to temperature, while that

of the long arc is temperature independent. In addition, we find that the intensity $I(\chi)$ around the short arc can be fitted to the Eq.(1):

$$I(\chi) = I_0[1/2 + \sum C_{6n} \cos 6n(\chi - 30^o)] + I_{BG} \quad (1)$$

where C_{6n} are the $6n$-fold bond-orientational order parameters. This fact, together with the twofold symmetry of the short arcs, indicates the presence of a Sm-*I* phase, most likely on the surface. Figure 3 is the temperature dependence of the positional correlation lengths ξ_I and $\xi_{C'}$ of the Sm-*I* and Sm-*C'* phases, respectively. The values of ξ_I are typical of those found in a hexatic phase, and its discontinuities at 77.7°C and 69.0°C confirm the first-order nature of the both transitions.

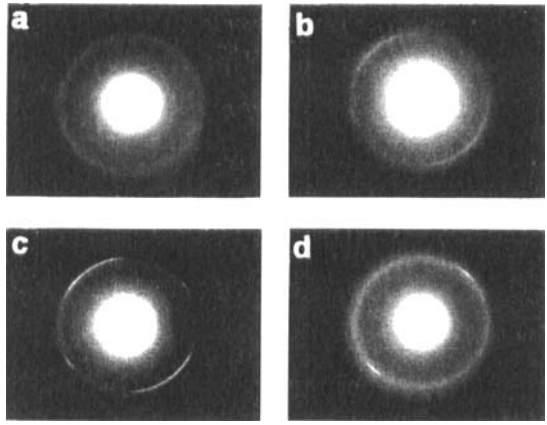

FIGURE 1 Electron-diffraction pattern from a 20-layer 7O.7 film at (a) 81.0°C, (b) 77.9°C, (c) 74.0°C, and (d) 68.8°C.

The long arcs are quite unusual. The magnitude and temperature dependence of the positional correlation length $\xi_{C'}$ are similar to those of ξ_I, as shown also in Fig. 3. However, it is clear from Fig. 2 that, unlike the Sm-*I* short arc, neither the amplitude nor the angular width of the long arc shows a strong temperature dependence. Furthermore, its χ-scan intensity cannot be fitted to Eq.(1). A strong

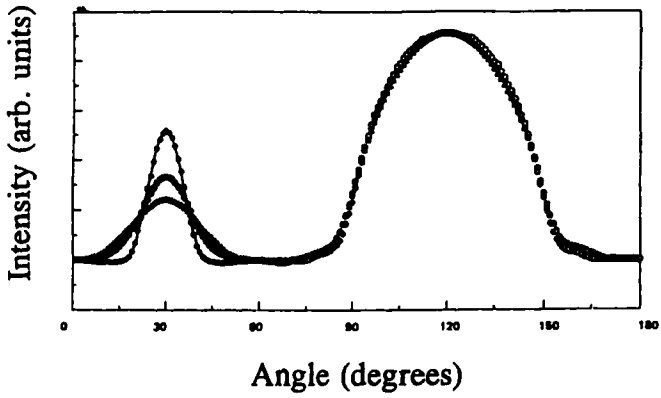

FIGURE 2 Diffraction intensity from a 20-layer film along a χ scan at 77.6°C (open triangles), 76.1°C (open circles), and 69.1°C (solid circles). The lines are fits to Eq.(1).

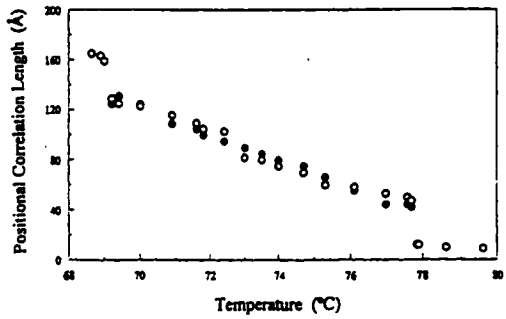

FIGURE 3 Temperature dependence of the positional correlation lengths ξ_I (open circles) of the surface Sm-*I* phase and $\xi_{C'}$ (soild circles) of the middle Sm-*C'* phase in a 20-layer film.

hint of the origin of the long arc can be found in Fig. 4, in which we compare its χ-scan intensity profile with that due to the several Sm-*C* surface layers at higher temperatures. It can be seen that the two profiles are almost identical. Since the Sm-*C* diffraction pattern is the projection on the detection plane of a tilted uniform Sm-*A* diffuse ring, Fig. 4 suggests that the long arc is the projection of a tilted uni-

form sharp ring. It is interesting to note that such a sharp ring has been observed previously as a possible new liquid phase between the Sm-*A* and the Hex-*B* in *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC) [9] and 4-n-butoxybenzylidene-4-n-octylaniline (4O.8) [10], with hexaticlike positional correlations but no long-range bond-orientational order. The long arcs observed here in 7O.7 thus appear to indicate the presence of a novel phase, which we call the smectic-*C'* (Sm-*C'*), this is the tilted analog of the highly correlated isotropic liquid phase observed in 54COOBC and 4O.8.

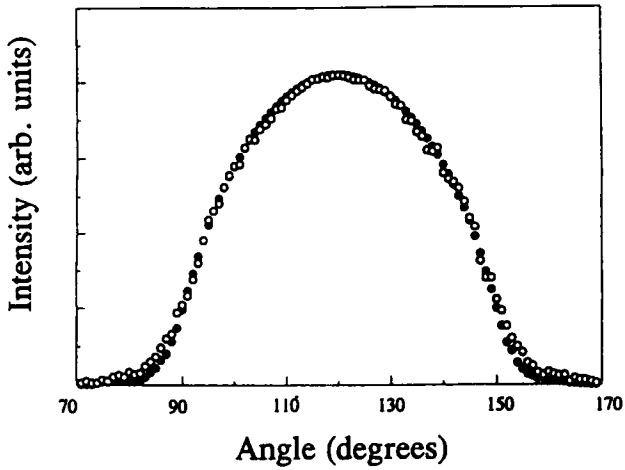

FIGURE 4 Intensity from a 20-layer film along a χ scan for the diffraction from the Sm-*C* surface layers at 77.9°C (open circles), and the Sm-*C'* phase at 74.7°C (solid circles). The amplitudes have been adjusted for comparison.

A revealing feature of the long arcs is the temperature dependence of the ratio of the integrated intensity of the long arc to that of the short arc for films of different thickness, shown in Fig. 5. It can be seen that this intensity ratio is essentially temperature independent between 77.7 and 69.0°C, and has an average value of 6.1, 4.2, and 3.1 for films of 20, 14, and 10 layers, respectively. The fact

that the ratio is a constant for a particular film thickness, independent of temperature and location on the film, eliminates the likelihood that the long and short arcs are due to diffraction from coexisting phases distributed laterally on the plane of the film. Because it is known that the molecular order in a liquid-crystal film generally decreases from the outermost to the interior layers, our results suggest that the highly correlated Sm-C' layers occurred between the surface Sm-I layers and the Sm-A interior. From the values of the intensity ratio reported above, we can deduce that, in the 20-layer film starting from either surface, one finds a single Sm-I outermost layer, followed by six layers of the Sm-C' correlated liquid, and finally an interior composed of six layers of the Sm-A ordinary liquid. Thus the total numbers of Sm-I, Sm-C', and Sm-A layers are 2, 12, and 6, respectively, for the 20-layer film. The corresponding numbers are 2, 8, and 4 for the 14-layer film, and 2, 6, and 2 for the 10-layer film. This trend of decreasing thickness of the interior phases is also consistent with our observation that an eight-layer film has no Sm-A interior, and suggests that the surface-induced orders extend into at least four molecular layers.

At 69.0°C, all the Sm-C' layers in the 20-layer film abruptly transformed to the Sm-I phase, giving the diffraction pattern shown in Fig. 1(d), with one pair of hexatic arcs in the presence of a uniform diffuse ring, signifying that the seven outermost layers were in the Sm-I phase while the interior remained in the Sm-A phase. This interpretation is supported by our quantitative analysis, also included in Fig. 5, showing that the ratio of the integrated intensity of the Sm-I arc below 69.0°C to that above 69.0°C is around 6.9. The two discontinuities in the intensity ratio in Fig. 5 and those in the positional correlation length ξ_l in Fig. 3 both suggest that the transitions at 77.7°C and 69.0°C are first order.

In most of the examples reported to date, a particular order (either tilt, hexatic, or crystalline) is developed on the surface, which then propagates into the interior, sometimes in a layer-by-layer manner. In contrast, we have found in these

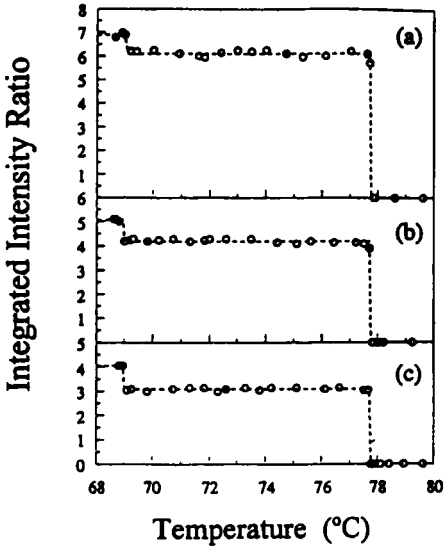

FIGURE 5 Ratio of the integrated intensity among various diffraction signals in a (a) 20-layer, (b) 14-layer, and (c) 10-layer film. The open circles denote the ratio of the intensity of the Sm-*C'* long arc to that of the Sm-*I* short arc at the same temperature, while the solid circles denote the ratio of the intensity of the Sm-*I* arc at that temperature to the average normalized intensity of the Sm-*I* arc between 77.7°C and 69.0°C.

7O.7 films that the tilt-induced hexaticlike positional correlations can be first developed deep into the film interior while the bond-orientational order is limited to the outermost layer, resulting in a distinct tilted middle Sm-*C'* phase sandwiched between a Sm-*I* surface layer and an orthogonal liquid interior. Tilt-induced bond-orientational order is developed in the interior only at a lower temperature at 69.0°C. Theoretically, the tilt of the interior Sm-*C* phase is predicted to induce hexatic order in the Sm-*C* phase in the presence of the surface Sm-*I* layers [11], changing it from a tilted liquid directly to an induced hexatic. Therefore, the important discovery of this middle intermediate Sm-*C'* phase could modify our the-

oretical understanding [11], and represents the possibility of a two-stage tilt-induced surface-freezing transition, which has never been observed previously. Furthermore, the fact that the middle Sm-C' phase appears to be the tilted analog of a possible new phase previously reported between the Sm-A and the Hex-B in orthogonal smectics provides an important additional indication for the existence of this unusual highly correlated liquid, which could significantly modify our understanding of two-dimensional melting.

Acknowledgments

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References

[1] W. Chen, L.J. Martinez-Miranda, H. Hsiung, and Y.R. Shen, *Phys. Rev. Lett.*, **62**, 1860 (1989).
[2] J. Als-Nielsen, F. Christensen, and P.S. Pershen, *Phys. Rev. Lett.*, **48**, 1107 (1982); P. S. Pershan and Als-Nielsen, *Phys. Rev. Lett.*, **52**, 759 (1984).
[3] B.M. Ocko, A. Braslau, P.S. Pershan, J. Als-Nielsen, and M. Deutsch, *Phys. Rev. Lett.*, **57**, 94 (1986).
[4] B.I. Halperin and D.R. Nelson, *Phys. Rev. B*, **19**, 2457 (1979).
[5] A.P. Young, *Phys. Rev. B*, **19**, 1855 (1979).
[6] B.D. Swanson, H. Stragier, D.J. Tweet, and L.B. Sorensen, *Phys. Rev. Lett.*, **62**, 909 (1989).
[7] R. Geer, T. Stoebe, C.C. Huang, R. Pindak, J.W. Goodby, M. Cheng, J.T. Ho, and S.W. Hui, *Nature (London)*, **355**, 152 (1992); A.J. Jin, M. Veum, T. Stoebe, C.F. Chou, J.T. Ho, S.W. Hui, V. Surendranath, and C.C. Huang, *Phys. Rev. Lett.*, **74**, 4863 (1995).
[8] C.Y. Chao, S.W. Hui, and J.T. Ho, *Phys. Rev. Lett.*, **78**, 4962 (1997).
[9] C.F. Chou, A.J. Jin, S.W. Hui, C.C. Hunag, and J.T. Ho, *Science*, **280**, 1424 (1998).
[10] C.Y. Chao, C.F. Chou, J.T. Ho, S.W. Hui, A.J. Jin, and C.C. Huang, *Phys. Rev. Lett.*, **77**, 2750 (1996).
[11] D.R. Nelson and B.I. Halperin, *Phys. Rev. B*, **21**, 5312 (1980).