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ELECTRON-DIFFRACTION STUDIES OF PHASE TRANSITIONS IN 4O.8 FREE-STANDING THIN FILMS

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Abstract The structural phase transitions of free-standing thin films of N-(4-n-butyloxybenzylidene)-4-n-octylaniline (4O.8), which exhibits smectic-*A* and crystal-*B* phases in the bulk, have been studied in detail using electron diffraction. When a smectic-*A* film is cooled, the outermost layer transforms initially to the hexatic-*B* phase and subsequently to the crystal-*B* phase at a lower temperature. The first transition is consistent with the thermal anomaly in the heat capacity and the second transition coincides with the shear response observed in mechanical measurements. Upon further cooling, the film undergoes additional layer-by-layer smectic-*A*-hexatic-*B*-crystal-*B* transitions in its interior.

INTRODUCTION

In bulk 4O.8, it has been well established that the smectic-*A* (Sm-*A*) phase, which is composed of stacked liquid layers, transforms at 49°C to the crystal-*B* (Cry-*B*) phase, which exhibits long-range positional order [1,2]. Free-standing 4O.8 films are therefore expected to provide useful information about the melting process in reduced dimensions. It is thus surprising that, despite the simplicity of the phase behavior of bulk 4O.8, thermal and mechanical experiments on its free-standing films have produced unexpected and apparently contradictory results. For example, upon cooling from the Sm-*A* phase, heat-capacity and optical-reflectivity measurements on an 8-layer film revealed successive phase transitions occurring at 62°C, 51°C, 50°C, and 49°C, as

shown in Fig. 1(a) [3,4]. On the other hand, mechanical measurements using a torsional oscillator in contact with 4O.8 films of similar thickness suggested that a Sm-*A* film first develops a solidlike shear modulus at around 55°C, and then undergoes another sharp change in the shear response at around 49°C, as shown schematically in Fig. 1(b) [5-6]. While both sets of experimental data are believed to reveal some kind of surface and/or interior transition behavior that is prevalent in liquid-crystal films, they present an outstanding puzzle that has yet to be resolved. In this paper, we report the results of a detailed electron-diffraction experiment on free-standing 4O.8 films which not only answer the puzzling question, but also reveal a novel layer-by-layer freezing behavior involving the hexatic-*B* (Hex-*B*) phase that has not been observed previously.

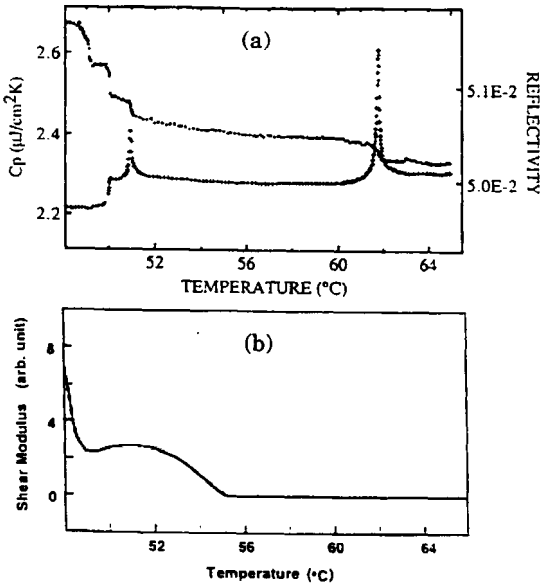

FIGURE 1 (a) Temperature dependence of heat capacity (crosses) and optical reflectivity (solid squares) measured simultaneously in an 8-layer 4O.8 film. (b) Schematic representation of the temperature dependence of the shear modulus in an 8-layer 4O.8 film reported in Refs. 5 and 6.

Electron-diffraction measurements were performed in an electron microscope equipped with a pressurized and temperature-controlled sample chamber [7,8]. We have studied in detail the structural transitions of free-standing films of 4O.8 with thickness

between 6 and 12 molecular layers and found similar behavior among these films. Upon cooling from the Sm-*A* phase, the typical variety of diffraction patterns observed is summarized as follows and illustrated in Fig. 2 for a 10-layer film:

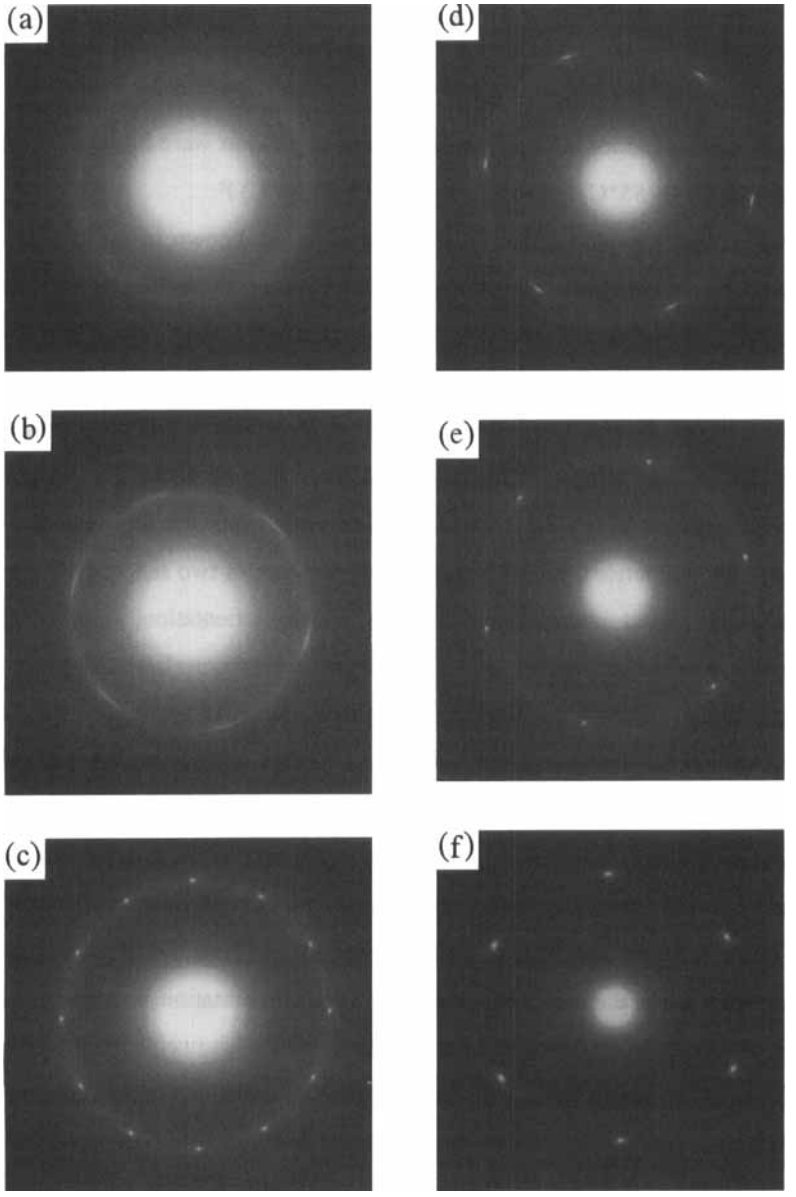

FIGURE 2 Electron-diffraction pattern obtained from a 10-layer 4O.8 film at (a) 63.5°C, (b) 58.5°C, (c) 51.5°C, (d) 50.5°C, (e) 50.2°C, (f) 48°C.

Pattern A: a diffuse ring [Fig. 2(a)]

Pattern B: 6 arcs on top of a diffuse ring [Fig. 2(b)]

Pattern C: 12 spots on top of a diffuse ring [Fig. 2(c)]

Pattern D: 6 spots and 6 arcs on top of a diffuse ring [Fig. 2(d)]

Pattern E: 6 spots on top of a diffuse ring [Fig. 2(e)]

Pattern F: 6 spots [Fig. 2(f)].

The temperature sequence in which these diffraction patterns were found to occur is:

A (62°C) B (55°C) C (51°C) D (50.4°C) E (49°C) F.

Since mesomorphic orders in liquid crystals are known to occur first at the surface and then develop inwardly, the above diffraction patterns lead to the following most plausible interpretation. Above 62°C, the film is in the Sm-*A* phase. At 62°C, the outermost layers undergo a transition to the Hex-*B* phase while the interior layers remain in the Sm-*A* phase. It should be noted that the Hex-*B* surfaces initially exhibit powder-averaged diffraction before yielding a single-domain hexatic diffraction pattern upon further cooling. At 55°C, the outermost layers freeze into the Cry-*B* phase in the presence of Sm-*A* interior layers. The ubiquitous presence of two sets of 6 Bragg spots, with invariably equal intensity but arbitrary relative orientation, implies that the crystalline axes of the top and bottom surface layers are not correlated, probably due to the much longer relaxation time in the Cry-*B* phase compared to the Hex-*B* phase. At 51°C, the second-outermost layers transform into the Hex-*B* phase, which is sandwiched between the Cry-*B* surface layers and the Sm-*A* interior. The fact that the 12 diffraction spots have now collapsed into 6 suggests that the existence of the interior Hex-*B* layers serves to lock-in the crystalline axes in the top and bottom surface layers. At 50.4°C, the second-outmost layers also freeze into the Cry-*B* phase. Thus the film has two Cry-*B* layers on each surface and a Sm-*A* interior. This interpretation is supported by our quantitative analysis of the diffraction patterns, which showed that the integrated intensity of the diffraction spots in Pattern E is roughly twice that in Pattern C. Finally, after additional layer-by-layer transitions that might be taking place in films thicker than 6 molecular layers but are not resolvable by electron diffraction, the entire film transforms into the Cry-*B* phase at 49°C. These unusual layer-by-layer transitions are depicted schematically in Fig. 3 for a 6-layer film.

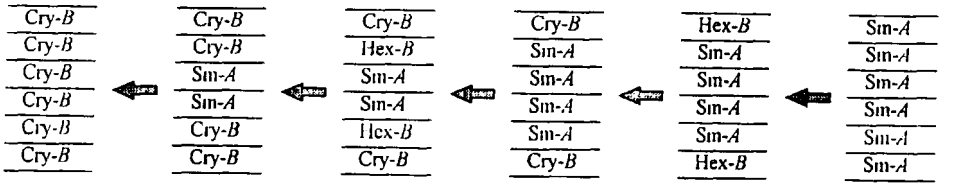

FIGURE 3 Layer-by-Layer transition sequence upon cooling observed in 6-layer films of 4O.8.

Our data lead to several important observations. This represents the first reported occurrence of an orthogonal hexatic phase near the surface of a material that is not known to exhibit the hexatic phase in the bulk [9]. Our data also resolve several apparent inconsistencies among published heat-capacity, optical-reflectivity and mechanical measurements on 4O.8 films. First, at 62°C, both heat capacity and optical reflectivity showed a distinct phase transition [3,4], but no shear response was detected [5,6]. These results are all consistent with our discovery that the phase transition at 62°C, which has hitherto been interpreted as a surface Sm-*A*-Cry-*B* transition, is actually a Sm-*A*-Hex-*B* transition of the outermost layers. Such a transition is not expected to be detectable in a mechanical measurement, since a hexatic phase does not have an in-plane shear modulus [10]. It should be pointed out that, theoretically, the heat capacity near a Sm-*A*-Hex-*B* transition in two dimensions should exhibit only a broad hump above the transition [11,12]. However, the experimental observation of a sharp heat-capacity anomaly at the surface Sm-*A*-Hex-*B* transition in 4O.8 films is consistent with similar observations reported in other liquid-crystal materials [13]. Second, at 55°C, mechanical measurements detected a phase transition characterized by the onset of shear response of the film [5,6]. This is consistent with our observation of a Hex-*B*-Cry-*B* transition of the outermost layers at 55°C, since the torsional-oscillator experiments should be particularly responsive to the existence of a crystalline phase on the surface [14]. The fact that no detectable change in the heat capacity was observed at this transition [3,4] suggests that a major entropy change occurs at the Sm-*A*-Hex-*B* transition but not at the

Hex-*B*-Cry-*B* transition. Third, at 51°C, the second anomaly observed in heat capacity and optical reflectivity [3,4] coincides with our discovery of the Sm-*A*-Hex-*B* transition of the second outermost layers. This transition is not expected to be accompanied by any abrupt change in the shear response, as was indeed the case experimentally [5,6]. Finally, at 49°C, the changes seen in the heat capacity, optical reflectivity, and shear modulus are all consistent with our observation that the entire film now freezes into the Cry-*B* phase.

This also represents the first report of a novel layer-by-layer freezing sequence mediated by the hexatic phase. In 4O.8 films, the outermost layers undergo the two-step Sm-*A*-Hex-*B*-Cry-*B* freezing before the second outermost layers commence their own Sm-*A*-Hex-*B*-Cry-*B* transitions, as shown in Fig. 3.

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