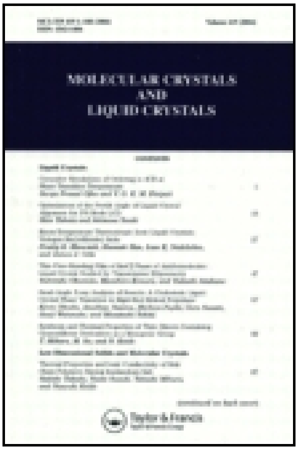

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Optical Textural Study of Surface Phase Transitions Involving Tilted Hexatic Phases in Free-Standing Liquid-Crystal Films

Chih-Yu Chao [a], Tung-Cheng Pan [a] & John Ho [b]
[a] Department of Physics, National Taiwan University, Taipei, Taiwan, ROC
[b] Department of Physics, University at Buffalo, The State University of New York, Buffalo, New York, USA

To cite this article: Chih-Yu Chao, Tung-Cheng Pan & John Ho (2004): Optical Textural Study of Surface Phase Transitions Involving Tilted Hexatic Phases in Free-Standing Liquid-Crystal Films, Molecular Crystals and Liquid Crystals, 412:1, 401-408

To link to this article: http://dx.doi.org/10.1080/15421400490440318

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 401/[2011]–408/[2018], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490440318

Taylor & Francis
Taylor & Francis Group

OPTICAL TEXTURAL STUDY OF SURFACE PHASE TRANSITIONS INVOLVING TILTED HEXATIC PHASES IN FREE-STANDING LIQUID-CRYSTAL FILMS

Chih-Yu Chao and Tung-Cheng Pan
Department of Physics, National Taiwan University,
Taipei 10617, Taiwan, ROC

John T. Ho
Department of Physics, University at Buffalo,
The State University of New York, Buffalo,
New York 14260, USA

Surface freezing transitions in free-standing films of achiral Schiff's-base liquid crystals 5O.6 and 7O.7 exhibiting tilted hexatic phases have been studied using optical textures. The evolution of textures with temperature in 5O.6 films is qualitatively similar to that reported earlier in FTE1, except that the stripe texture consists of alternating light and dark stripes of unequal widths. No stripe texture is observed in 7O.7.

Keywords: free-standing smectic films; stripe texture; surface freezing transition; tilted hexatic phases

Smectic liquid-crystal (LC) systems have a rich variety of phases with different types of in-plane two-dimensional (2D) order. Among the most interesting are the tilted hexatic phases, which can differ from each other in the relation between the in-plane bond directions and the tilt direction. In the smectic-*I* (Sm-*I*) phase, the tilt direction is along one of the local bonds, while in the smectic-*F* (Sm-*F*) phase, it is halfway between two local bonds. A direct Sm-*I* – Sm-*F* transition is typically observed experimentally

We are grateful to B. N. Chang and P. J. Wu for participation in the early phase of this work, to J. E. Maclennan for helpful discussions, and to W. B. Shu for technical assistance. This work was supported by the National Science Council, Taiwan, R.O.C. and Chunghwa Picture Tube Company.

Address correspondence to Chih-Yu Chao, Department of Physics, National Taiwan University, Taipei 10617, Taiwan, ROC.

[1,2]. Earlier studies on a lyotropic LC suggested that a new smectic-*L* (Sm-*L*) phase, in which the tilt direction lies along an intermediate angle between 0° and 30° from a local bond, may also exist [3–5], although it was unclear whether the phase is hexatic or multicrystalline. Theoretically, it has been shown that an intermediate Sm-*L* phase can indeed occur between the Sm-*I* and Sm-*F* phases [6,7]. The possible existence of the hexatic Sm-*L* phase in a thermotropic LC was first found in optical studies of free-standing films of the terphenyl ester FTE1, where the occurrence of a modulated stripe texture was interpreted as indicative of a surface Sm-*L* phase [8,9]. This structural interpretation was subsequently confirmed in FTE1 films by electron diffraction (ED) [10,11].

We report here the results of optical studies of the textures in free-standing films of the Schiff's-base compounds 5O.6 and 7O.7. Earlier optical studies have reported stripe textures indicative of a Sm-*L* phase on the surface of a smectic-*C* (Sm-*C*) interior in both 5O.6 and 7O.7, similar to that in FTE1 [8,9]. However, subsequent experiments on these materials have raised questions about the nature of their surface-freezing behavior. First, in 5O.6, a more recent optical study has reported unusual sequences of textures and phases, some in the presence of the smectic-*A* (Sm-*A*) [12], which may not be totally consistent with the earlier observations [8,9]. Second, in 7O.7, recent detailed ED studies on the structure of free-standing films [13,14] have shown no evidence for the existence of a surface Sm-*L* phase that was suggested in the optical experiments [8,9]. Our current optical studies are aimed at clarifying these conflicting results.

Our Schiff's-base compounds 5O.6 and 7O.7 were recrystallized to achieve high chemical purity. Free-standing films of these materials were drawn in the Sm-*A* or Sm-*C* phase over a hole of 3 mm × 10 mm in a glass cover slip in a hot stage whose temperature was controlled with a resolution of 0.01°C, with the film spreader beneath the supporting glass slip. Images were recorded using a polarizing microscope in the reflection mode. Because of chemical instability of the hydrolysis-prone Schiff's-base compounds, the hot stage in our studies was specially designed to be in a closed, dry system, a precaution that was not taken in earlier optical experiments. We have made detailed studies of the textures of films from 4 to 20 molecular layers in 5O.6 and 8 to 20 layers in 7O.7 while cooling through the Sm-*C* – hexatic transition.

We first describe the results in 5O.6. In general, the phase transition temperatures decrease with increasing film thickness. The temperatures reported below are approximate values applicable to the thicker films of 15 to 20 molecular layers. The texture of the films in the Sm-*C* phase above 58°C is characterized by rapid fluctuations in the **c**-director field. Broad, fluctuating extinction brushes emanating from point defects represent typical features of the optical texture of this phase, as shown in Figure 1. Upon

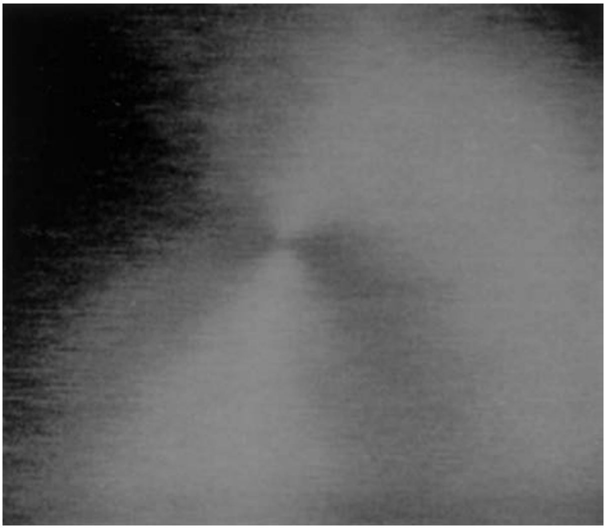

FIGURE 1 Broad, fluctuating extinction Sm-*C* brushes emanating from point defect in a 5O.6 film at 60°C. The horizontal dimension is about 250 µm.

cooling to just below 58°C, the **c**-director fluctuations are largely reduced, leaving a large-scale, frozen texture of fairly uniform domains separated by walls. The walls are similar to that observed in Refs. [8,9]. At slightly lower temperatures, the films display an array of thin disclination lines spaced 0.5 – 1 µm apart. The director orientation between each pair of lines is initially difficult to resolve but on lowering the temperature the lines move further apart and each band is seen to have an obvious gradation from dark to bright, implying that the director rotates continuously across each band. This line texture is thus composed of bands of continuous director splay, separated by splay disclinations, which is typically observed in the Sm-*I* or Sm-*F* phase. Meanwhile, some faint **c**-director fluctuations are still observable. Since a similar line texture was observed in FTE1 [8,9] in a temperature range where ED study has indicated the coexistence of Sm-*I* surfaces and a Sm-*C* interior [10], we suggest that the structure in 5O.6 at this temperature range is also similar. This texture is found to reappear with more clarity in 5O.6 below 51°, which is shown in Figure 2.

In 5O.6 films below 55°C, this line texture transforms into that of parallel, uniform stripes of alternating brightness and darkness. The stripes are found to be parallel to the original line texture, each splay band typically evolving into precisely one light and one dark stripe with unequal widths, as shown in Figure 3. Upon cooling, the period of both types of stripes increases with decreasing temperature, with the width of the narrower

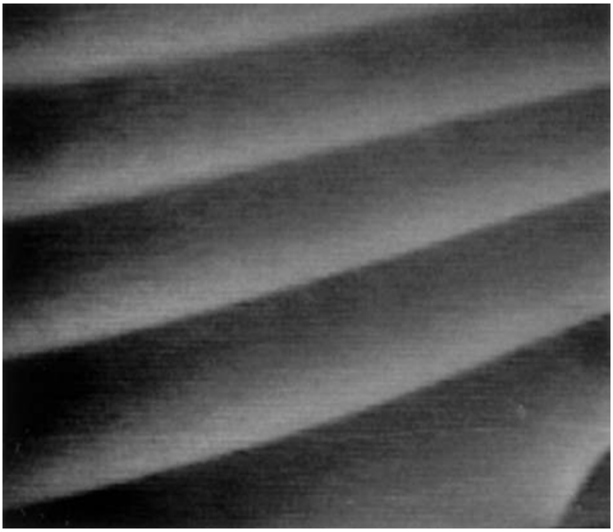

FIGURE 2 Line texture (splay texture) in a 5O.6 film at 50.8°C showing typical modulated sharp lines separating bands with continuously changing intensity. The horizontal dimension is about 150 μm.

stripe increasing at a faster rate than that of the wider stripe as the temperature is decreased. Between crossed polarizers, the alternating bright and dark stripes denote variations of the azimuthal orientations of the **c**-director. By slowly rotating the microscope hot stage, one may observe that the stripes become darkest when the **c**-director is either parallel or perpendicular to the polarizers, whereas the stripes become brightest when the **c**-director makes a 45° angle with the polarizers. The director orientation appears to be uniform within each stripe and jumps by about 30° when crossing a stripe boundary, which is a sharp, weakly undulating wall. The stripe texture observed here is qualitatively similar to that in Refs. [8,9], with the noted exception that the widths of the alternating light and dark stripes are equal in FTE1 but unequal in 5O.6. It should also be noted the typical stripe width in 5O.6 is about 1/4 that in FTE1. Interior **c**-director fluctuations are still observable in the background throughout the stripe phase in 5O.6, although they become less visible with decreasing temperature. Since the stripe texture in FTE1 has been identified as indicative of Sm-*L* surfaces coexisting with a Sm-*C* interior, we speculate that the structure of the 5O.6 films in this temperature range may also be similar. Additional ED studies will be needed to confirm this. At this point, the origin of the unequal widths of the alternating stripes is unclear. We can

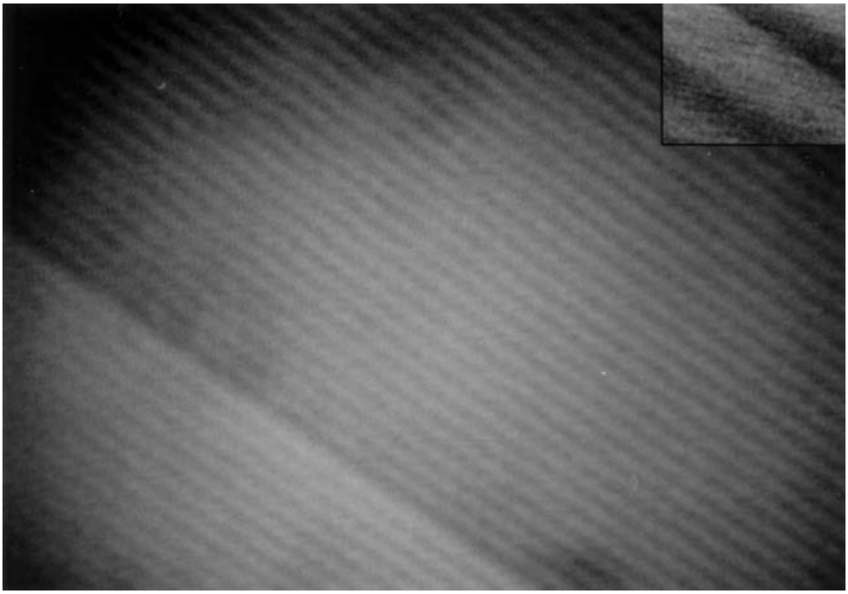

FIGURE 3 Stripe texture in a 5O.6 film at 54°C, showing alternating light and dark uniform bands of unequal widths. The horizontal dimension is about 200 μm. The inset shows details of the adjacent light and dark stripes.

speculate on the possible role of splay chirality [15] or tilt modulations [16] that have led to qualitatively similar textures in other phases.

Below around 53°C, the widths of both the light and dark stripes increase with decreasing temperature, but at different rates, until they eventually become equal. Subsequently, a brick wall pattern is observed, as shown in Figure 4(a). Through relative elongation and contraction of successive bend wall segments, the brick wall pattern gradually transforms into a dirk-like texture, and then into a honeycomb texture on cooling, as shown in Figure 4(b). At 51°C, the director fluctuations and domain wall undulations are quenched and the stripes slowly lose their modulated texture and gradually expand to much broader splay bands, producing a texture similar to that seen between 58°C and 55°C, as shown in Figure 2. Based on a similar texture observed in FTE1 [8,9] and its structural identification using ED [10], we suggest that the 5O.6 films are in the Sm-*F* phase below 51°C.

In 7O.7 films above 77.7°C, the texture shows rapid fluctuations in the **c**-director field, consistent with earlier ED results showing Sm-*C* surfaces coexisting with a Sm-*A* interior [13]. At 77.7°C, the director fluctuations are quenched, leaving a frozen texture of fairly uniform splay domains

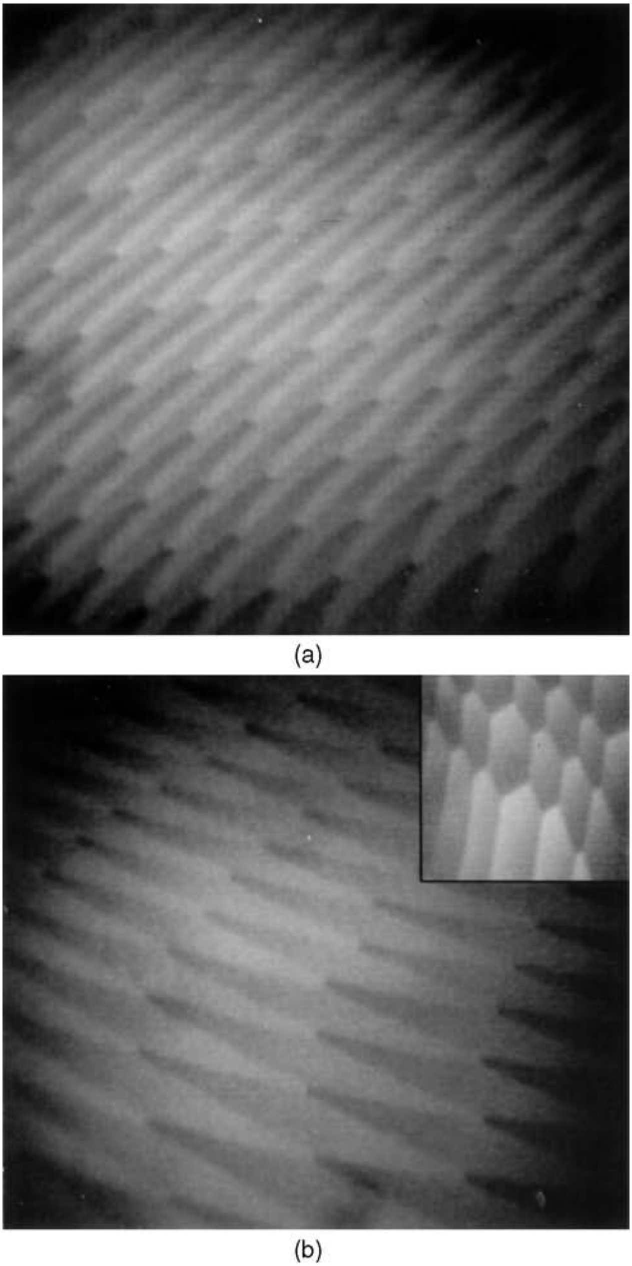

FIGURE 4 (a) Upper: Brick wall texture in a 5O.6 film at 52°C. (b) Bottom: Dirk-like texture at about 51.8°C. The inset shows a honeycomb texture at about 51.5°C. The horizontal dimensions are about 250 μm for (a) 200 μm for (b) and 100 μm for the inset in (b).

separated by thin disclination lines. This splay texture, which persists down to 69°C, is similar to that in Figure 2. It is composed of bands of continuous director splay, which is characteristic of the Sm-*I* phase [2], and is again consistent with ED observations [13]. More importantly, we observe no stripe texture between 77.7°C and 69°C in 7O.7 films, in contrast to earlier optical studies [8,9]. In this temperature range, we also do not observe **c**-director fluctuations, which is consistent with our previous ED results indicating that the interior layers are in the Sm-*C'* and Sm-A phases [13], but not the Sm-*C* phase as suggested by earlier x-ray experiments [17]. Since the Sm-*C'* phase is more strongly correlated than the Sm-*C* phase [13], it is reasonable to expect **c**-director fluctuations to be suppressed.

Our results in 5O.6 do not agree in significant ways with those in Ref. [12], which described sequences of phases and textures that are quite different from ours. However, in view of the fact that Ref. [12] mentioned no special effort to prevent sample hydrolysis and reported transition temperatures that are typically 8°C lower than ours, we suspect that sample degradation may be the cause of the discrepancy.

In summary, our optical results in 7O.7 films are consistent with earlier ED structural data on the surface freezing of these films [13]. However, our results differ from earlier optical studies [8,9] in that we do not observe any stripe texture in 7O.7 films. Our results in 5O.6 films are qualitatively similar to those seen earlier in FTE1 [8,9] and suggest that the surface freezing behavior of 5O.6 may also involve the Sm-*L* phase just as in FTE1 [10]. Additional ED studies on 5O.6 films to confirm the structure are warranted. Unexpectedly and perhaps significantly, the stripe texture we observe in 5O.6 films consists of alternating light and dark stripes of unequal widths, which evolve to be equal at lower temperatures.

REFERENCES

[1] Dierker, S. B., Pindak, R., & Meyer, R. B. (1986). *Phys. Rev. Lett.*, *56*, 1819.

[2] Sirota, E. B., Pershan, P. S., Sorensen, L. B., & Collett, J. (1987). *Phys. Rev A*, *36*, 2890.

[3] Smith, G. S., Sirota, E. B., Safinya, C. R., & Clark, N. A. (1988). *Phys. Rev. Lett.*, *60*, 813.

[4] Sirota, E. B., Smith, G. S., Safinya, C. R., Plano, R. J., & Clark, N. A. (1988). *Science*, *242*, 1406.

[5] Smith, G. S., Sirota, E. B., Safinya, C. R., Plano, R. J., & Clark, N. A. (1990). *J. Chem. Phys.*, *92*, 4519.

[6] Selinger, J. V. & Nelson, D. R. (1988). *Phys. Rev. Lett.*, *61*, 416.

[7] Selinger J. V. & Nelson, D. R. (1989). *Phys. Rev. A*, *39*, 3135.

[8] Maclennan, J. E. & Seul, M. (1992). *Phys. Rev. Lett.*, *69*, 2082.

[9] Maclennan, J. E., Sohling, U., Clark, N. A., & Seul, M. (1994). *Phys. Rev. E*, *49*, 3207.

[10] Chao, C. Y., Hui, S. W., Maclennan, J. E., Chou, C. F., & Ho, J. T. (1997). *Phys. Rev. Lett.*, *78*, 2581.

[11] Chao, C. Y., Maclennan, J. E., Pang, J. Z., Hui, S. W., & Ho, J. T. (1998). *Phys. Rev. E*, *57*, 6757.

[12] Demikhov, E. I. & Dolganov, V. K. (1996). *JETP Lett.*, *64*, 32.
[13] Chao, C. Y., Hui, S. W., & Ho, J. T. (1997). *Phys. Rev. Lett.*, *78*, 4962.
[14] Chao, C. Y., Lo, C. R., & Ho, J. T. (2000). *Phys. Rev. E*, *61*, 5407.
[15] Najjar R. & Galerne, Y. (2001). *Mol. Cryst. Liq. Cryst.*, *367*, 395.
[16] Yabe, Y., Shen, N., Mazur, E., & Yokoyama, H. (1999). *Phys. Rev. Lett.*, *82*, 759.
[17] Sirota, E. B., Pershan, P. S., Amador, S., & Sorensen, L. B. (1987). *Phys. Rev. A*, *35*, 2283.