Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Calorimetric and Optical-Reflectivity Study of Thin Free-Standing 64COOBC Liquid-Crystal Films

C. Y. Chao [a], C. R. Lo [a], Y. H. Liu [a], M. Veum [b], C. C. Huang [c], V. Surendranath [d] & J. T. Ho [e]

[a] Department of Physics, National Central University, Chung-Li, Taiwan, 32054, ROC

[b] Department of Physics, Millsaps College, Jackson, Mississippi, 39210, USA

[c] School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota, 55455, USA

[d] Department of Physics, Kent State University, Kent, Ohio, 44242, USA

[e] Department of Physics, State University of New York at Buffalo, Buffalo, New York, 14260, USA

Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 499-506
Reprints available directly from the publisher
Photocopying permitted by license only

Calorimetric and Optical-Reflectivity Study of Thin Free-Standing 64COOBC Liquid-Crystal Films

C.Y. CHAO[a], C.R. LO[a], Y.H. LIU[a], M. VEUM[b], C.C. HUANG[c], V. SURENDRANATH[d] and J. T. HO[e]

[a]*Department of Physics, National Central University, Chung-Li, Taiwan 32054, ROC,* [b]*Department of Physics, Millsaps College, Jackson, Mississippi 39210, USA,* [c]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA,* [d]*Department of Physics, Kent State University, Kent, Ohio 44242, USA and* [e]*Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260, USA*

High-resolution heat-capacity and optical-reflectivity measurements have been conducted on thin free-standing films of *n*-hexyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (64COOBC). The data suggest incomplete layer-by-layer liquid-hexatic transitions. The transition in extremely thin films shows a diverging heat-capacity anomaly. The results are compared with those reported in other compounds, and discussed in the context of the theory of two-dimensional melting.

Keywords: liquid-crystal thin films; 2D melting theory

Theories of two-dimensional (2D) melting [1-3] suggest a mechanism in which a 2D solid could melt, via two KT-type transitions, through an

intermediate hexatic phase, into the isotropic liquid. While much experimental effort has been undertaken to test these theoretical predictions, studies on several liquid-crystal systems have proven to be among the most fruitful [4], notably in the homologous series *n*-alkyl-4'-*n*-alkyloxybiphenyl-4-carboxylate (*nm*OBC). In fact, pioneering x-ray measurements provided the first indication of the existence of the three-dimensional analog of the 2D hexatic phase in 65OBC films [5], in which herringbone ordering was also observed. The heat-capacity measurements from two-layer 3(10)OBC films revealed a diverging heat-capacity anomaly [6] near the continuous smectic-*A* (Sm-*A*) - hexatic-*B* (Hex-*B*) transition, which is in disagreement with the predictions of 2D melting theory [7]. The observed diverging heat-capacity anomaly can be well fitted by a power-law expression with the critical exponent $\alpha = 0.31 \pm 0.03$ [8]. Subsequently, overexposed electron-diffraction (ED) studies on 3(10)OBC films revealed weak herringbone order in the Hex-*B* phase [9]. Thus it was suggested that the discrepancy between the heat-capacity data and theoretical prediction might be due to the presence of herringbone order in these compounds. Surendranath *et al.* [10] have identified the Hex-*B* and crystal-*B* (Cry-*B*) phases in some members of the *n*-alkyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (*n*4COOBC) homologs. In addition, ED measurements have revealed no discernible herringbone spots in the overexposed diffraction pattern from 54COOBC Hex-*B* thin films, which suggests that the herringbone order in these films is either not present or significantly weaker than that in *nm*OBC compounds [11]. Nevertheless, the Sm-*A* - Hex-*B* transition in 54COOBC thin films has also been found to show a pronounced pretransitional heat-capacity anomaly, with the critical exponent $\alpha = 0.30 \pm 0.07$ [11], which is still in sharp contrast to the theoretical prediction [7]. Although many previous experimental results

indicate that the 2D melting theory in its present form does not describe in detail the liquid-hexatic transition in liquid-crystal thin films, it remains an important experimental task to look for some other compounds similar to 54COOBC exhibiting the liquid-hexatic-crystal phase sequence in the absence of herringbone order and to investigate the thermal properties of their thin films.

Studies of several other compounds exhibiting the Sm-*A* - Hex-*B* - Cry-*B* sequence have been limited only to thick films [12]. Applying a relatively small modification to the *nm*OBC structure, Surendranath *et al.* have synthesized some members of the *n*4COOBC homologs which are very rich in hexatic behavior [10]. Subsequent bulk heat-capacity results from 64COOBC and 34COOBC show weakly first-order Sm-*A* - Hex-*B* transitions [13]. Utilizing our high-resolution free-standing film calorimeter [14] and optical-reflectivity system [6], we have conducted an experimental investigation of the phase-transitional behavior in thin free-standing films of 64COOBC. This compound exhibits the following bulk transition sequence [10]: isotropic (68.5 °C) Sm-*A* (56.7 °C) Hex-*B* (49 °C) Cry-*B*. The existence of the Cry-*B* phase below the Hex-*B* phase is similar to that of 54COOBC, but different from the typical *nm*OBC sequence, where the Hex-*B* phase is generally followed by the crystal-*E* phase.

Employing our free-standing film ac calorimeter, we have measured the temperature dependence of the heat capacity for various 64COOBC film thickness. Figure 1 displays the heat-capacity data from ten-, six-, and two-layer films. Associated with the Sm-*A* - Hex-*B* transition, three well-separated and sharp heat-capacity peaks can be seen in the ten- and six-layer films, which clearly demonstrates the existence of layer-by-layer transitions. The two-layer film displays a single sharp and nearly symmetric heat-capacity peak. With a temperature ramping rate of about

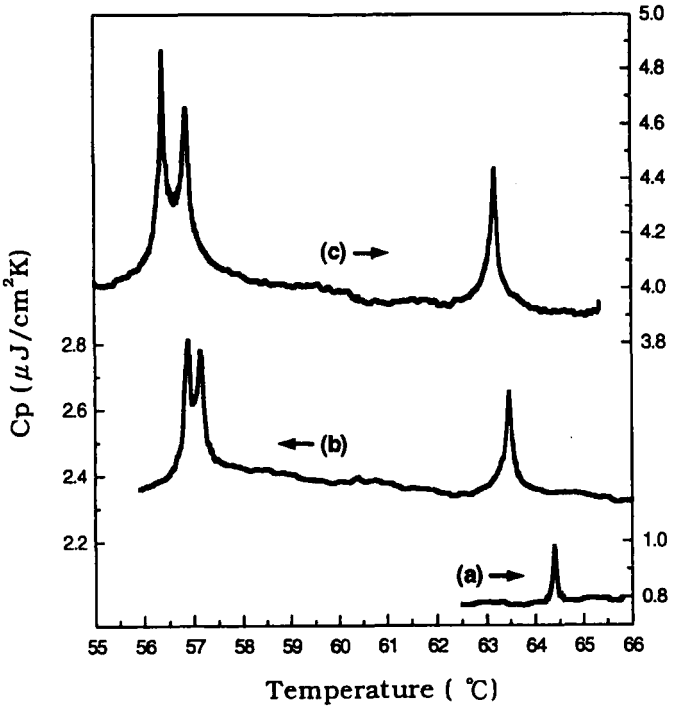

FIG. 1 Heat-capacity data in ten-, six-, and two-layer 64COOBC films.

10 mK/min near the first heat-capacity peaks upon cooling, detailed thermal hysteresis studies have been carried out on the surface transitions of ten- and six-layer films. We have obtained thermal hysteresis of 30 and 40 mK (with resolution of 50 mK) for the surface transitions of ten- and six-layer films, respectively. Thus the surface-layer transitions of these two 64COOBC films are essentially continuous to within our resolution. For the two-layer film, the thermal hysteresis is found to be 70 $\pm$ 50 mK, with the magnitudes of the heat-capacity peak differing by less than 7% between the heating and cooling runs, suggesting that this transition is only weakly first order.

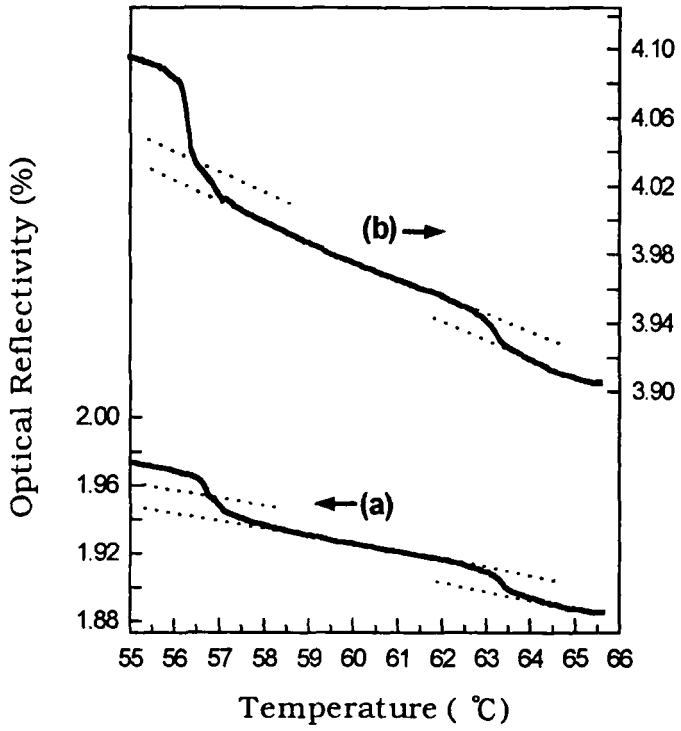

FIG. 2 Optical-reflectivity data in ten- and six-layer 64COOBC films.

In addition to the heat-capacity measurements, the in-plane density changes determined by the optical-reflectivity experiments in these layer-by-layer transitions can help us understand how many smectic layers are involved in each step. Optical-reflectivity data from the ten- and six-layer films are shown in Fig. 2, where three anomalies are clearly seen in these two films, reinforcing the existence of layer-by-layer transitions. It is worth noting that the three density changes observed in six-layer film are almost the same, which indicates that each phase transition involves a pair of smectic layer undergoing the Sm-A - Hex-*B*

transition inwardly with decreasing temperature. For the ten-layer film, the density changes of the surface and next-to-surface transitions are nearly the same, and are both equal to that of the surface transition of the six-layer film. This result provides strong evidence that the second transition in the ten-layer film upon cooling involves only two smectic layers transforming from the Sm-*A* to Hex-*B* phase, while the third transition corresponds to the remaining six interior smectic layers undergoing the same transition. Thus the surface-freezing behavior in these thin films belongs to the case of incomplete layer-by-layer transitions.

It is instructive to examine in detail the nature of the Sm-*A* - Hex-*B* transition of the two-layer 64COOBC film. The fact that the two-layer film exhibits a single heat-capacity anomaly indicates that it possesses 2D thermal behavior. Although the transition is weakly first order, the pronounced pretransitional heat capacity and divergent character are in

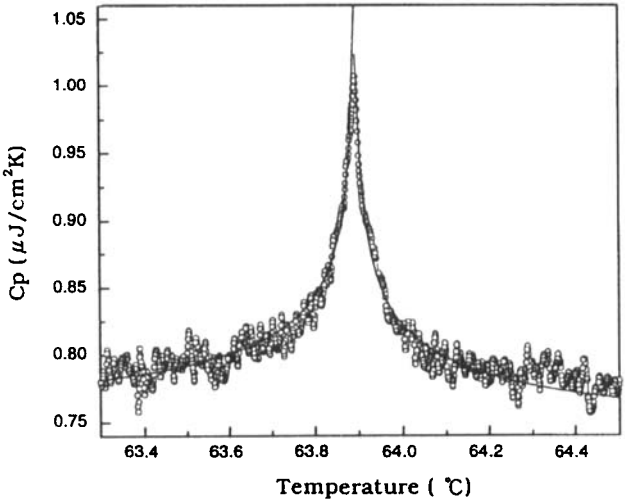

FIG. 3 Detailed heat-capacity data in a two-layer 64COOBC film. The line is a power-law fit with a critical exponent of $\alpha = 0.39 \pm 0.03$.

sharp contrast to the theoretical prediction [7] of the 2D melting theory, which suggests that the KT-like liquid-hexatic transition should exhibit only an essential singularity. The fitting of the heat-capacity anomaly of the two-layer film to a simple power-law expression yields $\alpha = 0.39 \pm 0.03$, which is similar to the α value previously reported in the Sm-*A* - Hex-*B* transition of two-layer 54COOBC films, [11] but somewhat larger than that in 3(10)OBC [8]. It may be interesting to note that the value is close to the prediction of $\alpha = 0.36 \pm 0.05$ in a coupled *XY* model in appropriate parameter spaces [15]. The fitting of the two-layer 64COOBC data is shown in Fig. 3.

According to the prediction of the 2D melting theory [1-3], the behavior of the heat capacity near the Sm-*A* - Hex-*B* and the Hex-*B* - Cry-*B* transitions should both be of the KT-type [7]. We do not as yet have a definite explanation for the unexpected critical anomaly in the heat capacity near the Sm-*A* - Hex-*B* transition seen here in the 2D 64COOBC film. The possible connection between the thermal anomaly and the presence of herringbone order in 2D *nm*OBC films is probably not relevant in 64COOBC. We have obtained a preliminary overexposed ED pattern from a 64COOBC Hex-*B* thin film which did not show any weak satellite spots, indicating no discernible herringbone order. The heat-capacity anomaly in a 2D 64COOBC film is quite similar to that in 54COOBC, with the possible difference being that the experimental peak is sharper in the former. In the case of 54COOBC, it has been suggested that a highly-correlated isotropic phase, called the smectic-*A*' (Sm-*A*'), exists between the Sm-*A* and Hex-*B* phases, and that the heat-capacity anomaly actually corresponds to the Sm-*A* – Sm-*A*' transition [16]. Whether this explanation applies to 64COOBC is unclear, since the ED experiment to show the possible existence of the Sm-*A*' phase in 64COOBC has not been performed.

Acknowledgments

One of us (C. Y. C.) acknowledges support from National Science Council, Taiwan, Republic of China, under Grant No. NSC 87-2112-M-008-035.

References

[1] J.M. Kosterlitz and D.J. Thouless, J. Phys. **C6,** 1181, 1973.
[2] D.R. Nelson and B.I. Halperin, Phys. Rev. B **19,** 2457, 1979.
[3] A.P. Young, Phys. Rev. B **19,** 1855, 1979.
[4] C.C. Huang and T. Stoebe, Adv. Phys. **42,** 343, 1993.
[5] R. Pindak, D.E. Moncton, S.C. Davey, and J.W. Goodby, Phys. Rev. Lett. **46,** 1135, 1981.
[6] T. Stoebe, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. **68,** 2944, 1992.
[7] A.N. Berker and D.R. Nelson, Phys. Rev. B **19,** 2488, 1979; S. A. Solla and E. K. Reidel, *ibid.* **23,** 6008, 1981.
[8] T.Stoebe *et al.,* Physica (Amsterdam) **205A,** 108, 1994.
[9] T.Stoebe, J. T. Ho, and C. C. Huang, Int. J. Thermophys. **15,** 1189, 1994.
[10] V. Surendranath *et al.,* Mol. Cryst. Liq. Cryst. **131,** 1, 1985.
[11] A.J. Jin *et al.,* Phys. Rev. Lett. **74,** 4863, 1995.
[12] E. Gorecka, L. Chen, W. Pyzuk, A. Krowczynski, and S. Kumar, Phys. Rev. E **50,** 2863, 1994.
[13] R. Mahmood *et al.,* Phys. Rev. A **38,** 4299, 1988.
[14] R. Geer, T. Stoebe, T. Pitchford, and C. C. Huang, Rev. Sci. Instrum. **62,** 415, 1991.
[15] I.M. Jiang *et al.,* Phys. Rev. E **48,** 3240, 1993.
[16] C.F. Chou, A.J. Jin, S.W. Hui, C.C. Huang, and J.T. Ho, Science **280,** 1424, 1998.