Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Calorimetric Study of the Smectic-C to Smectic-F Transition in Terephtal-bis-(4n)- alkylanilines

K. J. Stine [a b] & C. W. Garland [a]

[a] Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139

[b] Department of Chemistry, University of California at Los Angeles, Los Angeles, CA, 90024

Version of record first published: 04 Oct 2006.

To cite this article: K. J. Stine & C. W. Garland (1990): Calorimetric Study of the Smectic-C to Smectic-F Transition in Terephtal-bis-(4n)- alkylanilines, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 188:1, 91-96

To link to this article: http://dx.doi.org/10.1080/00268949008047807

Mol. Cryst. Liq. Cryst., 1990, Vol. 188, pp. 91–96
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Calorimetric Study of the Smectic-C to Smectic-F Transition in Terephtal-bis-(4n)-alkylanilines

K. J. STINE† AND C. W. GARLAND

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(*Received April 4, 1990; in final form May 9, 1990*)

An ac calorimetric study of the fluid smectic-C to hexatic smectic-F transition is reported for the pentyl, hexyl and heptyl homologs of terephtal-bis-(4n)-alkylaniline. The heat capacity peaks, which are rounded over 2–3K, and the shifts in the phase angle ϕ indicate that the transition is first-order in all three compounds.

The 3-D bulk hexatic smectic-B phase[1] (SmB_H) has smectic-A (SmA) layering with long-range order in the direction of the local six-fold crystalline axes (bond orientational, or BO order) but short-range positional order within the layers.[2] The transition between the SmA and SmB_H phases should belong to the 3-D XY universality class, but heat capacity studies of numerous compounds give first-order behavior[3] or large values of the heat capacity critical exponent α (0.48 to 0.67)[4] which are far from the 3-D XY value of $\alpha = -0.007$. Such results suggest the influence of tricritical behavior since $\alpha = 0.5$ at a tricritical point. Hexatic structures have also been observed in tilted smectic-C (SmC) materials. BO order combined with long-range molecular tilt is found in the smectic-I (SmI) phase, where the tilt is towards a nearest neighbor, and in the smectic-F (SmF) phase, where the tilt is between two nearest neighbors.[5] In the case of the SmI and SmF phases, theory[6] predicts that due to coupling between tilt and BO order the tilt angle acts as an effective ordering "field" inducing small but finite BO order in the SmC phase, which then grows rapidly on cooling into the SmI or SmF phase. The coupling between tilt and BO order has been utilized to prepare single-domain freely suspended films of the SmI phase in a high-resolution x-ray study[7] of the SmC-SmI transformation in the liquid crystal methylbutylphenyloctyloxybiphenyl carboxylate (8OSI). Heat capacity data obtained near the SmC-SmI transition of 8OSI and

†Present address: Department of Chemistry, University of California at Los Angeles, Los Angeles, CA 90024.

analyzed using a parametric equation-of-state model suggest that α is close to 0.5 but that the hypothetical "zero tilt-field" transition would be weakly first order.[8] This idea is consistent with the anomalously small value of the order parameter exponent $\beta = 0.08$.[8,9]

Aharony, *et al.*[10] suggested a general phase diagram for hexatic/smectic systems. For SmA materials, the SmB_H to CrB (a 3-D plastic crystal) transition is required by symmetry to be first-order. Near the SmA/SmB_H/CrB triple point, coupling between the hexatic and crystal order parameters should drive the SmA-SmB_H transition first-order. Away from the triple point this transition could become second-order at a tricritical point along the SmA-SmB_H transition line. The tilted analog of this phase diagram would have a SmC/SmI/CrJ (or SmC/SmF/CrG) triple point and a SmC-SmI (or SmC-SmF) tricritical point, complicated by the non-zero tilt field. Coupling of the BO order to the herringbone order parameter[11] or to the fluctuations of the SmA layers[12] has also been proposed as a mechanism for producing the above general phase diagram.

Recently Noh, *et al.*[13] carried out a high-resolution x-ray study of the SmC-SmF transformation in the pentyl, hexyl and heptyl homologs of single-domain freely suspended films of the terephtal-bis-(4n)-alkylaniline series (TB5A, TB6A, and TB7A). The shorter butyl homolog TBBA or TB4A has a first-order SmC-CrG transition; thus a triple point will occur in mixtures of TB4A and TB5A. Low-resolution x-ray data on the layer spacing variation across the SmC-SmF transformation and DSC measurement of the entropy changes were reported previously by Kumar.[14] These data show a discontinuous jump in the smectic layer spacing of ~0.5Å for TB5A, ~0.6Å for TB6A, and ~1.0Å for TB7A. The reported entropy changes are 0.954R for TB5A, 0.820R for TB6A and 1.436 R for TB7A. Noh, *et al.*[13] present the temperature dependence of the first three harmonics (C_6, C_{12} and C_{18}) of the BO order for TB5A, TB6A and TB7A. The BO order induced in the SmC phase is immeasurably small in the TBnA compounds, in contrast to the noticeable pretransitional BO order in the SmC phase of 8OSI. This indicates that the coupling between BO order and tilt order is weaker in the TBnA compounds than in 8OSI. The temperature dependence of the harmonics shows that the transition is clearly first-order in TB5A, possibly continuous in TB6A, and probably first-order in TB7A.

In this paper, we report heat capacity data for the SmC-SmF transition of TB5A, TB6A and TB7A obtained using an automated high-resolution ac calorimeter described elsewhere.[15] The measured heat capacity C_p and the phase angle ϕ between the sample temperature oscillation and the ac power input indicate that the SmC-SmF transition is ultimately first-order for all three homologs with large two-phase coexistence regions.

The temperature variation C_p obtained on heating through the SmF to SmC transition is shown in Figure 1 for the three TBnA homologs. These C_p peaks are severely rounded over a region of 2.5–3 K. This rounding is much larger than the ~0.3 K rounding observed for the SmC-SmI transition of 8OSI. Since the effect of the tilt-field is expected to be smaller in the TBnA compounds than in 8OSI, the heat capacity peaks should be less smeared out due to finite field coupling terms.[8] As discussed below, we believe that the rounding of the C_p peaks is due

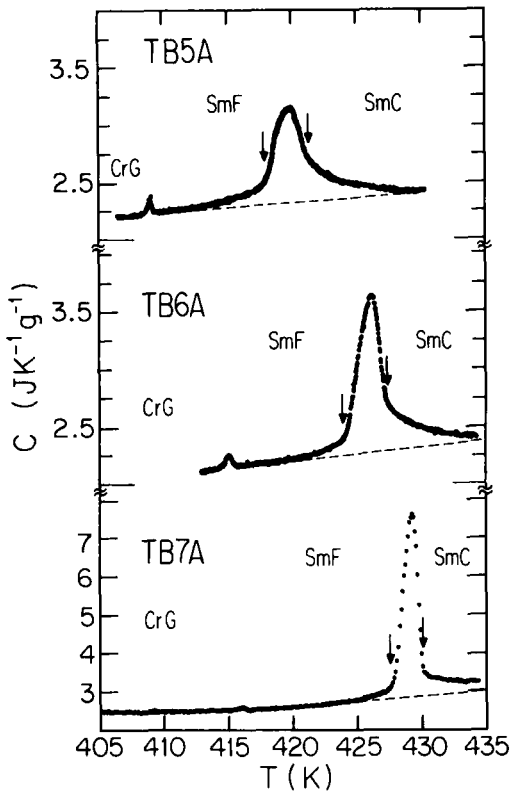

FIGURE 1 Heat capacity of three homologs of the TBnA series. The SmC-SmF peak between the arrows corresponds to apparent C_p values in a two-phase coexistence region.

to coexistence of the SmC and SmF phases. The dashed lines in Figure 1 represent the regular background contribution C_p (background) to the total heat capacity. The vertical arrows mark estimates of the coexistence region based on the C_p variation and the phase shift data discussed below. Note that there is a noticeable pretransitional excess heat capacity contribution above and below the coexistence region, which is larger in the SmC phase than in the SmF phase. Within the coexistence region, ac calorimetry yields apparent C_p values, which are difficult to interpret quantitatively. Integration of the excess heat capacity $\Delta C_p = C_p - C_p$ (background) over the range $T_m - 10$ K to $T_m + 10$ K, where T_m is the temperature where the SmC-SmF C_p peak exhibits its maximum, yields *apparent* entropy values $\int(\Delta C_p/T)dT = 0.42R$ for TB5A, 0.48R for TB6A, and 0.82R for TB7A. These values are substantially smaller than the DSC entropy values quoted above, as expected since first-order latent heats are not quantitatively detected by the ac method.[15]

The temperature variation of the phase angle ϕ between the applied ac power and the sample temperature oscillation is shown in Figure 2 for the three TBnA homologs. Note that in each case there is a peak in ϕ in the vicinity of the SmC

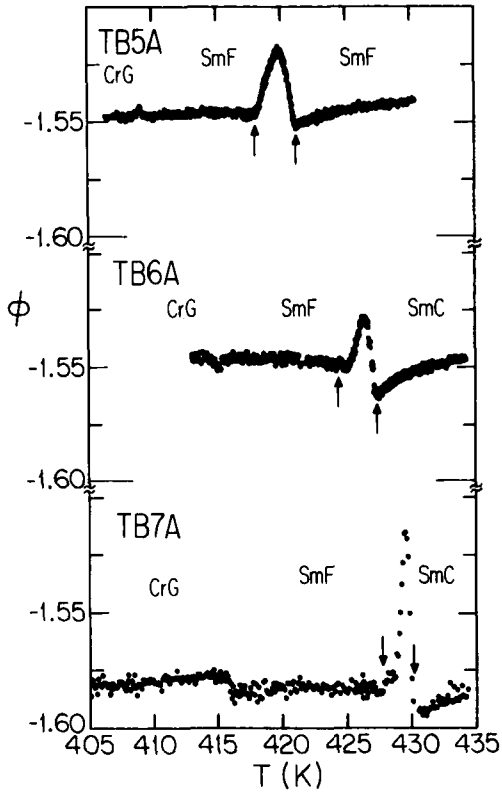

FIGURE 2 The phase shift ϕ in radians. The peak between the arrows is an indication of two phase coexistence (see text).

to SmF transition. In an ac calorimetry experiment, the phase angle ϕ is given by

$$\tan \phi = -\omega C_p^T / K_B \tag{1}$$

where ω ($= 0.196$ rad s^{-1} in the present experiment) is the operating frequency, K_B is the thermal conductance between the sample and the bath (measured to be 0.008 W K^{-1}), and C_p^T is the total heat capacity of the filled sample cell.[15] In obtaining this result, it is assumed that C_p^T is the static response function and that the thermal conductances between the heater and sample cell and between the sample cell and thermistor are infinite. Experimentally, it is found that far from a phase transition ϕ has a temperature-independent value which can vary slightly with the amount of GE varnish used to attach the strain gauge heater and thermistor to the sample cell. Equation (1) predicts that larger values of C_p^T will lead to smaller values of ϕ, so that a second-order peak in C_p^T should correspond to a dip in ϕ. However, peaks in ϕ are observed ubiquitously in coexistence regions such as those found at melting transitions, the N-I transition, and other first-order liquid crystal transitions.[15,16] This phase effect and the anomalously large C_p values are due to

imperfect conversion between two coexisting phases undergoing ac temperature oscillations.

The shape of the C_p peaks and the presence of peaks in ϕ indicate extensive coexistence of the SmC and SmF phases. Thus the SmC to SmF transition is first order even in the presence of the "tilt field." The width of the coexistence region, estimated from the ϕ peak width and the abrupt changes in dC_p/dT marked by arrows, is ~3.2 K for TB5A, ~3.1 K for TB6A, and ~2.4 K for TB7A. In addition to this first-order coexistence, the heat capacity data show pretransitional fluctuation effects that are comparable in all three homologs.

It should also be noted that small C_p anomalies were observed at the SmF-CrG transition. The very small magnitude of these peaks is in agreement with the SmI-CrJ data for 8OSI.[8]

In conclusion, we have found that the SmC to SmF transitions in TB5A, TB6A and TB7A are first-order. This conclusion does not contradict the interpretation of the x-ray data of Noh, *et al.*[13] using harmonic scaling theory. The harmonic scaling analysis gives information on the nature of the critical fluctuations at temperatures low enough so that several harmonics can be reliably extracted from the modulation of the scattering. Such information cannot be obtained from the heat capacity. We do not find evidence for the transition being near tricritical in TB6A or more continuous for TB6A than for TB5A or TB7A, as suggested in Reference 13. The presently available calorimetric data for smectic to hexatic transitions[3,4,8] suggest that these transitions are either first-order or near tricritical but probably weakly first-order. There is clearly a need for more experimental data on smectic to hexatic smectic transitions to resolve the differences between the thermal behavior close to the transition and the x-ray scaling behavior in the hexatic phase.

Acknowledgments

We wish to thank D. Y. Noh for providing the TB5A, TB6A and TB7A samples and R. J. Birgeneau for helpful discussions. This work was supported by National Science Foundation grant DMR 87-19217.

References

1. R. J. Birgeneau and J. D. Litster, *J. Phys.* (*Paris*), **39**, L-399 (1978).
2. R. Pindak, D. E. Moncton, S. C. Davey and J. W. Goodby, *Phys. Rev. Lett.*, **46**, 1135 (1981).
3. C. C. Huang, G. Nounesis and D. Guillon, *Phys. Rev.*, A**33**, 2602 (1986); R. Mahmood, M. Lewis, D. Johnson and V. Surrendranath, *Phys. Rev.*, A**38**, 4299 (1988).
4. T. Pitchford, G. Nounesis, S. Dumrongratta, J. M. Viner, C. C. Huang and J. W. Goody, *Phys. Rev.*, A**32**, 1938 (1985).
5. P. S. Pershan, *Structure of Liquid Crystal Phases*, (World Scientific, Teaneck, N.J.), 1988.
6. D. R. Nelson and B. I. Halperin, *Phys. Rev.*, B**21**, 5312 (1980); R. Bruinsma and D. R. Nelson, *Phys. Rev.*, B**23**, 402 (1981).
7. J. D. Brock, A. Aharony, R. J. Birgeneau, K. W. Evans-Lutterodt, J. D. Litster, P. M. Horn, G. B. Stephenson and A. R. Tajbaksh, *Phys. Rev. Lett.*, **57**, 98 (1986).
8. C. W. Garland, J. D. Litster and K. J. Stine, *Mol. Cryst. Liq. Cryst.*, **170**, 71 (1989).
9. K. J. Lushington and C. W. Garland, **72**, 5752 (1980).
10. A. Aharony, R. J. Birgeneau, J. D. Brock and J. D. Litster, *Phys. Rev. Lett.*, **57**, 1012 (1986).
11. R. Bruinsma and G. Aeppli, *Phys. Rev. Lett.*, **48**, 1625 (1982).

12. J. V. Selinger, *J. Phys.* (*Paris*), **49**, 1387 (1988).
13. D. Y. Noh, J. D. Brock, J. D. Litster and R. J. Birgeneau, *Phys. Rev.*, B**40**, 4920 (1989).
14. S. Kumar, *Phys. Rev.*, A**23**, 3207 (1981).
15. C. W. Garland, *Thermochimica Acta*, **88**, 127 (1985).
16. K. J. Lushington, G. B. Kasting and C. W. Garland, *J. Phys. Lett.* (*Paris*), **41**, L419 (1980); Y. H. Jeong, G. Nounesis, C. W. Garland and R. Shashidhar, *Phys. Rev.*, A**40**, 4022 (1989).