Molecular Crystals and Liquid Crystals

DCS Study of Smectic Phase Transitions

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DCS STUDY OF SMECTIC PHASE TRANSITIONS

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ABSTRACT: A previously described technique for measuring the order of phase transitions[1-3] using DSC has been applied to the liquid crystalline transitions found in TBBA. All of the values obtained were in agreement with those that have been measured by other techniques, and also with what would be anticipated from the nature of the transition. This study has shown that the technique is applicable to smectic-smectic transitions in liquid crystals.

A new method of quantitatively discriminating between first and second order transitions by DSC was recently proposed[1,2] and successfully applied to the smectic A-nematic transition.[3] Because this technique has not been applied to all of the more than 50 known liquid crystalline phase transitions,[4] we became interested in its application to some smectic-smectic transitions. One of the most completely studied materials exhibiting smectic phases is N,N-terephthalylidene bis 4-n-butylaniline (TBBA). This compound, on heating, exhibits crystalline (K), smectic G (G), smectic C (C), smectic A (A), nematic (N) and isotropic (I) phases, and the purpose of this study was to apply the technique described in reference 1 to these transitions.

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EXPERIMENTAL

TBBA was prepared by condensation of 2 moles of p-n-butylaniline with terephthaldehyde in ethanol at room temperature. After filtering the precipitate and washing it with ethanol, the yellow crystals were recrystallized from ethanol.

The DSC measurements were carried out using a Perkin-Elmer DSC2 controlled by a model 3600 data station. The measured enthalpies and transition temperatures of the TBBA agree with the DSC literature values.[5] The sample weight used for the DSC measurements was between 5 and 20 mg.

RESULTS AND DISCUSSION

The method used for determination of the order of the phase transitions requires the measurement of the ratio $N = h_2/h_1$, where h_1 is the height of the transition peak and h_2 is the height of the same peak taken at twice the heating rate.[1] N is 2 for a second order transition and is between 1 and $\sqrt{2}$ for an isothermal first order transition. As pointed out in reference 3, this technique is very convenient when applied to liquid crystals since at least two transitions, the crystal to liquid crystal and the nematic to isotropic, are always first order. One can then use these transitions as standards when determining the order of the other transitions in the liquid crystal. The value of N for the different phase transitions of TBBA is shown in Table 1.

TABLE 1. N Values of the Phase Transitions in TBBA

$K \rightarrow G$	$G \rightarrow C$	$C \rightarrow A$	$A \rightarrow N$	$N \rightarrow I$
1.4	1.4	1.8-2.3	1.3	1.4

The crystal to smectic G and the nematic to isotropic transitions are first order with $N \leq 1.4$, and the method can thus be applied with confidence to the other transitions. The smectic G to smectic C transition is first order with $N \leq 1.4$ as shown in Table 1. This is not surprising since its enthalpy is very large and the breaking of the quasi-crystalline order in the layer is reminiscence of a melting process. The smectic A to nematic transition is also found to be first order with $N \leq 1.4$. This follows the McMillan rule[6] that $(T_{A \rightarrow N}/T_{N \rightarrow I}) > 0.87$, thus denoting a first order smectic A to nematic transition in the case of TBBA where $T_{A \rightarrow N}/T_{N \rightarrow I} = 0.93$. It should be pointed out that while the McMillan rule does not always agree with experiment[7] a very recent report[8] has demonstrated, by

measuring specific volumes, the first order character of the smectic A to nematic transition in TBBA in excellent agreement with our determination of N. In this study, we were most interested in the smectic C to smectic A transition, since both theoretically[9-11] and experimentally,[8,12-15] it has been found to be second order. That this is so can be readily understood, as the only difference between smectic C and smectic A is the tilt of the molecule with respect to the layer normal. This tilt angle decreases continuously with increasing temperature starting from the smectic C and becoming zero at the beginning of the smectic A phase, and is therefore a good example of a second order transition. To illustrate this, we plotted in Fig. 1, together with the DSC traces of the smectic C to smectic A transitions at 5 and 10K mn^{-1}, the values for the rate of variation of the tilt angle as a function of temperature as found in Fig. 7 of Ref. 16. This readily illustrates that the DSC peak becomes detectable at the point where $d\alpha/dt$ increases, and shows that the departure from the baseline expresses the energy needed to bring the tilt to zero. This continuous process ends at the transition point, where the measurement of N was performed. As expected for a second order transition, N was found to be close to 2. The large variation in the measurement (1.8-2.3) reflects the difficulty of properly determining the baseline, and a large sample (20 mg.) was necessary in order to detect this smectic C to smectic A transition. In order to ensure the validity of the measurement at this large loading, the values for the other transitions were confirmed as remaining at $N \le 1.4$.
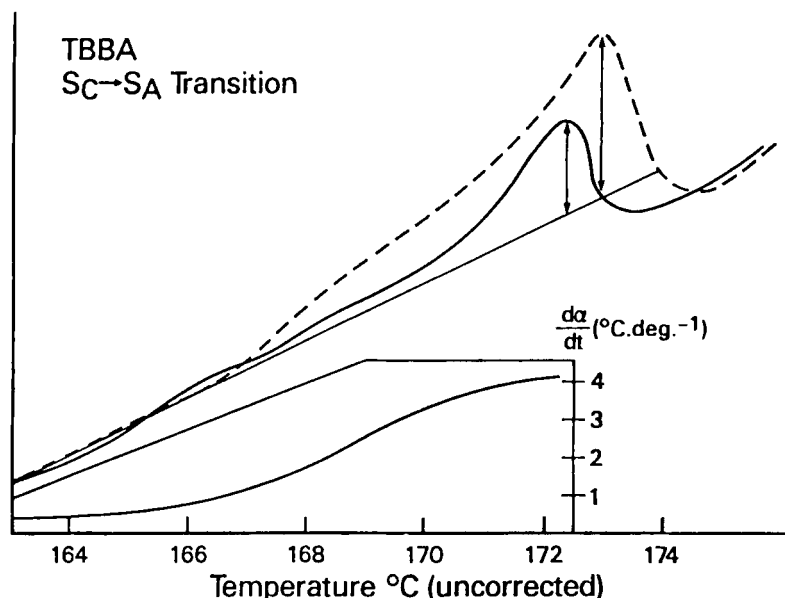
FIGURE 1   DSC trace of the smectic C to smectic A transition for TBBA at two heating rates. 5K mn^{-1} and 10K mn^{-1}. The lower plot is the rate of increase dα/dt, of the tilt angle α, *versus* temperature T.

The determination of the second order nature of a transition brings up an interesting question concerning the measurement and meaning of transition enthalpy. There is no latent heat associated with the smectic C to smectic A transition, and any arbitrary drawing of a baseline under the peak in order to measure a latent heat is thus incorrect. An interesting value which one can measure, however, is the enthalpy associated with a given change of tilt angle, which can be expressed by $\Delta H = (H_{T_2} - H_{T_1})/\alpha_{T_2} - \alpha_{T_1}$ with $H_{(T)}$ and $\alpha_{(T)}$ being, respectively, the enthalpy and the tilt angle at the temperature T. In the last 6°C below the smectic C to smectic A transition, the tilt angle change is 16° and the measurement of the area under the peak for this temperature range gives the value for ΔH as 5J/mole deg. Whether ΔH was independent of the tilt angle could not be determined.

Values for N, having been checked for six different transitions, are in very good agreement with other techniques used to measure the order of phase transition, and are what one would expect for transitions such as smectic C to smectic A. N can be readily

determined and gives valuable information concerning the nature of phase transitions being studied.

REFERENCES

1. P. Navard and J. M. Haudin, *J. Therm. Anal.* **29**, 405 (1984).
2. P. Navard and J. M. Haudin, *J. Therm. Anal.* **29**, 415 (1984).
3. P. Navard and R. Cox, *Mol. Cryst. Liq. Cryst. Lett.,* to appear.
4. D. Demus, S. Diele, S. Grande and H. Sackmann, in Advances in Liquid Crystals, Vol. 6, Academic Press, N.Y., p. 1 (1983).
5. J. R. Flick, A. S. Marshall and S. E. B. Petrie, in Liquid Crystals and Ordered Fluids, Vol. 2, J. Johnson and R. S. Porter, eds., Plenum Press, N.Y., p. 97 (1973).
6. W. L. McMillan, *Phys. Rev.* **A4**, 1238 (1971).
7. J. Thoen, H. Marynissen and W. Van Dael, *Phys. Rev. Lett.* **52**, 204 (1984).
8. N. V. S. Rao and V. G. K. M. Pisipati, *Mol. Cryst. Liq. Cryst.* **104**, 301 (1984).
9. W. L. McMillan, *Phys. Rev.* **A8**, 1921 (1973).
10. A. Wulf, *Phys. Rev.* **A11**, 365 (1975), **A17**, 2077 (1978).
11. R. G. Priest, *J.Phys. (Orsay)*, **36**, 437 (1975).
12. C. A. Schantz and D. L. Johnson, *Phys. Rev.* **A17**, 1504 (1978).
13. T. E. Lockhart, D. W. Allender, E. Gelerinter and D. L. Johnson, *Phys. Rev.* **A20**, 1655 (1979).
14. Y. Galerne, *J. Phys (Orsay)*, **39**, 1311 (1978).
15. R. F. Byran, A. J. Leadbetter, A. I. Mehta and P. A. Tuckers, *Mol. Cryst. Liq. Cryst.* **104**, 257 (1984).
16. S. Diele, H. Hartung, P. Ebeling, D. Vetters, H. Kruger and D. Demus, in Advances in Liquid Crystal Research and Applications, Vol. 1., L. Bata, ed., Pergamon Press, Oxford, p. 39 (1980).