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High-resolution ac specific-heat and x-ray investigations of the smectic-*F*—smectic-*H* transition of HBHA

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High-resolution ac specific-heat measurements of the smectic-*F*—smectic-*H* transition of N-(4-*n*-heptyloxybenzylidene)-4-*n*-hexylaniline (HBHA) are reported. A hysteresis of 160 mK in the transition temperature is measured for the first time for transformations in thermotropic liquid crystals. The specific heat, obtained during heating, is larger and changes more rapidly at the transition than during the cooling cycle. This behavior of the specific heat may be explained by assuming that dislocations and defects play an important role at this transition. High-resolution x-ray measurements of the smectic layer thickness were made with an accuracy of better than 250 ppm. The temperature dependence of the smectic-*F* layer thickness of HBHA is qualitatively different from that of TB5A and its homologs.

INTRODUCTION

Until the beginning of 1978 only one compound¹ was known to have a smectic(Sm)-*F* phase. At present there are more than 24 compounds which exhibit this phase. In all cases this phase occurs between the Sm-*C* and Sm-*H* phases with one possible exception,² where it is reported to occur between the Sm-*B* and Sm-*H* phases. The identification of this phase is based on textural and miscibility studies. Two compounds, TB5A and 80SF, are the only ones which have been studied by x-ray diffraction. The two independent x-ray studies on TB5A differ in the nature of the Sm-*F* phase. Leadbetter *et al.*³ claim to have determined accurate cell parameters. Benattar *et al.*⁴ report only a diffuse outer ring modulated into six diffuse spots indicating the absence of long-range hexagonal ordering within the layers. Thus, due to the lack of experimental investigations of this phase by other techniques, its nature remains elusive.

In order to determine the difference between Sm-*H* and Sm-*F*, we decided to carry out ac specific-heat measurements on the Sm-*F*—Sm-*H* transition. TB5A was not suitable for such a study because of its high rate of degradation at these required temperatures. We selected HBHA (70.6) which has a much lower Sm-*F*—Sm-*H* transition temperature. Its Sm-*F* phase is continuously misci-

ble⁵ with that of TB5A. In this paper we report our results along with DSC and x-ray measurements of the (001) reflection from various smectic phases of HBHA.

EXPERIMENTAL

HBHA was synthesized by the standard method using *p*-heptyloxybenzaldehyde and *p*-*n*-hexylaniline obtained from Eastman Kodak and Frin-ton Laboratories, respectively. The product was recrystallized twice from absolute alcohol at 0°C. A gas chromatographic analysis, on a Hewlett-Packard 5750 using an OV17 column, indicated more than 99% purity. The transition temperatures and transition entropies were determined by optical microscopy and differential scanning calorimetry with a Perkin Elmers DSC-II.

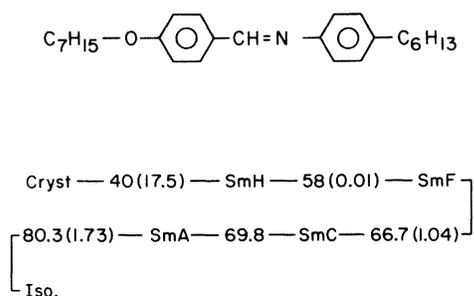
The ac specific-heat measurements were made on a high-resolution ac microcalorimeter.⁶ The calorimeter was operated at frequencies of 1.56 and 2.47 Hz. These frequencies were determined so that the sample reaches internal thermal equilibrium much faster than the period of temperature oscillations. The sample sits between evaporated films of a Chromel *A* heater and a copper-bismuth thermocouple. The thermocouple measures the temperature oscillations which depend on the

heater power. A microcomputer was used to control and measure the temperature and temperature oscillations of the sample. The temperature oscillations were converted to specific heat and plotted as a function of temperature. The amount of the sample between the heater and thermocouple was not known. The measurements, therefore, gave only the changes in specific heat and not its absolute value.

The determination of layer spacing, d was made using a three-crystal diffractometer and NaTl scintillation counter described in Ref. 7. The radiation used was copper k_α (1.541 78 Å). The accuracy of d , so determined, is 250 ppm and that of temperature 0.1 °C.

RESULTS AND DISCUSSION

The molecular structure and mesomorphology of HBHA is



The transition temperatures given are in °C and the transition entropy (inside parentheses) are in units of R (1.986 kcal/mole/°C). The Sm- F –Sm- H transition temperature is taken from ac specific-heat data while others are from microscopy. These values agree very well with those of Sakagami *et al.*⁵ except that the value of the Sm- F –Sm- H transition entropy obtained by us is much smaller. The DSC scan while heating the sample, Fig. 1, is similar to the cooling scan. The Sm- H to solid phase transition is not observed while cooling down to room temperature. Figure 2 shows a low-resolution ac specific-heat scan on HBHA. The operating frequency and temperature oscillations were 2.47 Hz and 24 mK with a heater power of 1.3 mW. The comparison of Figs. 1 and 2 illustrates the difference between DSC and ac specific-heat measurements. The ac calorimetry misses nearly all the latent heat of transitions. However, the changes in the levels in between two transitions are much bigger in Fig. 2 than in Fig.

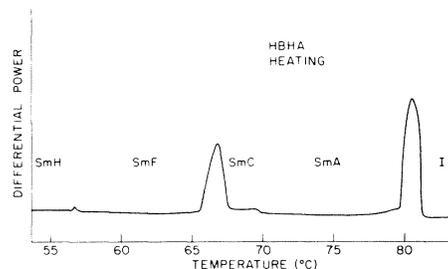


FIG. 1. Differential scanning calorimetry thermograph (heating cycle) of HBHA.

1. This shows that in ac calorimetry, specific heat is measured with much more sensitivity.

Figure 3 shows a high-resolution ac specific-heat run made in both directions across the Sm- F –Sm- H transition. This run was made at 1.56 Hz with 4.8-mk temperature oscillations. The power level was 0.13 mW. These measurements give us the following characteristics of the Sm- F –Sm- H transition. (a) The transition Sm- F –Sm- H occurs at a different temperature than the Sm- H –Sm- F transition. This type of hysteresis is a characteristic of defect mediated transitions.^{7–10} The transition temperatures are also dependent on the magnitude of the ac power input which induces a dc temperature offset. The transition temperatures were determined at different power inputs and extrapolated to zero power. The transition temperature at the zero power is the actual transition temperature. The hysteresis was about 160 mK. (b) When heating, the specific heat rises as the transition is approached and falls to a constant level in the Sm- F phase. The shape of this peak is not reproduced while cooling. The peak obtained by cooling is smaller in height and is rounded.

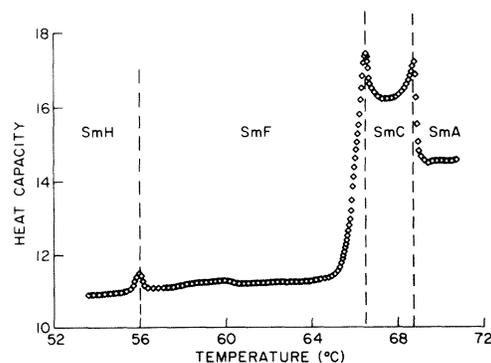


FIG. 2. Low-resolution ac specific heat of HBHA measured with temperature oscillations of about 24 mK at 1.56 Hz.

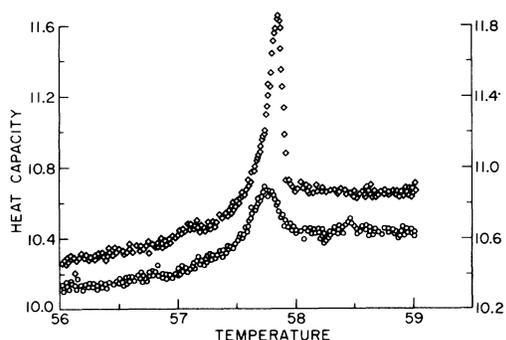


FIG. 3. High-resolution ac specific heat obtained while heating (upper curve) and cooling (lower curve) across the Sm-*F*–Sm-*H* transition. The cooling curve is shifted down (scale on the right) by 0.2. Temperature oscillations and frequency were 4.8 mK and 2.47 Hz, respectively.

Both of these observations were reproduced with two different specimens of HBHA. The Sm-*C*–Sm-*A* transition was also studied with high resolution for such effects. The scans in two directions across the Sm-*A*–Sm-*C* transition were identical. This excluded the possibility that the above results, (a) and (b), were instrumental artifacts. The Sm-*C*–Sm-*F* transition has a heat of transition two orders of magnitude larger than the *F*–*H* transition. However, as estimated from a low-resolution scan, it has only half as much hysteresis.

This peculiar behavior at the Sm-*F*–Sm-*H* transition might be caused by the presence of dislocations and defects in the Sm-*F* phase which may be less mobile in the *H* phase. Upon cooling they freeze into the Sm-*H* phase and take a long time to move out of the system, thus causing hysteresis and smearing of the specific-heat peak.

Layer thickness in the smectic phases of HBHA as a function of temperature is shown in Fig. 4. The behavior of d is similar to that of TB5A (Ref. 11) at temperatures above the Sm-*F*–Sm-*C* and below the Sm-*F*–Sm-*H* transition. The jump in the value of d at the Sm-*C*–Sm-*F* transition is also in the same direction for both. However, d behaves differently in the Sm-*F* phases of these two compounds. For TB5A (and its three higher homologs) d in the Sm-*F* phase remains almost unchanged, but for HBHA it changes even more sharply than in the Sm-*H* phase. The profiles of the (001) spot in various smectic phases, normalized to the same scale, are compared in Fig. 5 along with the direct beam profile (FWHM < 35 sec). The Sm-*C* peak is the widest, wider than even the Sm-*A*, because layer undulations⁷ arise

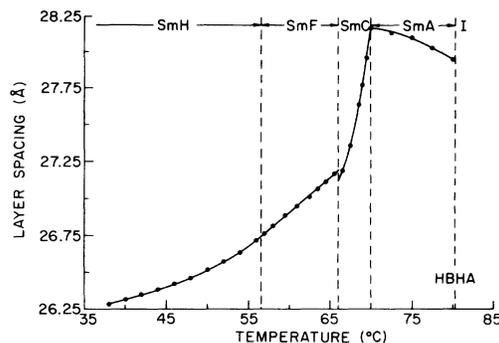


FIG. 4. Layer thickness of the smectic phases of HBHA as a function of temperature.

during the cooling of the sample. The profile of the Sm-*F* reflection is broader than that of Sm-*H*. The (110) reflection from the Sm-*H* phase of TB5A was found to disappear at the transition to the Sm-*F* phase, with our high-resolution diffractometer. This supports the conclusion of Benattar *et al.*^{4,12} that long-range hexagonal ordering, which exists in the Sm-*H* phase, is lost at this transition. An accurate determination of cell parameters in the Sm-*F* phase is, therefore, not possible.

CONCLUSION

The measurements reported in this paper show that the Sm-*F*–Sm-*H* transition of HBHA is hysteretic and that defects probably play an important role at this transition. The hysteresis in transition temperature (160 mK) and the difference in the specific-heat curves obtained while heating and cooling are intriguing. This transition should be examined with other techniques. Similar ac

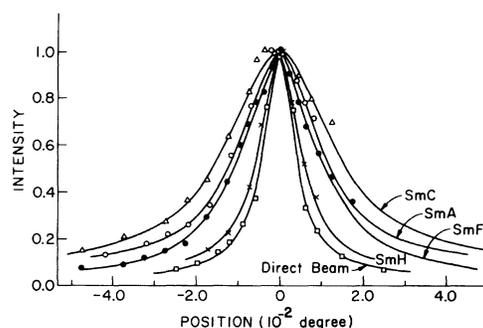


FIG. 5. Profiles of the (001) Bragg reflection from the various smectic phases, normalized to the same scale. The direct beam profile, also shown, has FWHM of less than 35 sec.

specific-heat studies on other compounds are of interest to see if this peculiar behavior is characteristic of all Sm-*F*–Sm-*H* transitions. It is also concluded that in the Sm-*F* phase of TB5A, Sm-*H*-like hexagonal ordering within the smectic layers is absent. Powder x-ray diffraction should help determine the difference in the ordering in Sm-*H* and Sm-*F* phases. Such measurements are planned for the future.

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