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Heat-capacity study of one liquid-crystal compound with smectic-*A*—hexatic-*B*—crystal-*B* transition

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High-resolution heat capacity measurements have been carried out in the smectic-*A*—hexatic-*B*—crystal-*B* transitions of the compound 4-propionyl-4′-(*n*-heptanoyloxy)azobenzene. Qualitatively, the heat-capacity anomalies of this smectic-*A*—hexatic-*B*—crystal-*B* transition sequence mimic those of the smectic-*C*—smectic-*I*—smectic-*G* transition of racemic 4-(2′-methylbutyl)phenyl-4′-(*n*-nonyloxy)biphenyl-4-carboxylate. The heat-capacity data near the smectic-*A*—hexatic-*B* transition are broad and asymmetric and cannot be fitted with a power-law expression.

Detailed x-ray measurements have revealed two basic structural forms for the smectic-*B* phase, i.e., the hexatic-*B* (Refs. 1 and 2) and the crystal-*B* phases.[3,4] For example, the smectic-*B* phase of N-4-(*n*-butyloxy)benzylidene-4-(*n*-octy)aniline (4O.8) was demonstrated to have long-range positional correlations of the hexagonal in-plane packing of the molecules as well as of interlayer stacking.[3,4] This kind of smectic-*B* phase was called crystal *B*. On the other hand, the smectic-*B* of *n*-hexyl-[4-(*n*-pentyloxy)biphenyl]-4-carboxylate (65OBC) (Ref. 2) has structure similar to the model proposed by Birgeneau and Litster[5] for a three-dimensional stacked hexatic phase. This phase was called hexatic *B*, which has very little interlayer correlation and in-plane positional ordering extends only over about 70 Å, while the bond-orientational order is long range. Miscibility studies of 65OBC-4O.8 mixtures have first demonstrated that a transition can occur between these two phases in a 31 wt.%-69 wt.% mixture of 4O.8 and 65OBC.[6] Subsequent heat-capacity studies on a 4O.8-65OBC 30.5 wt.%-69.5 wt.% mixture system[7] showed only one large first-order (with thermal hysteresis) heat-capacity peak with transition temperature being consistent with the reported transition temperature for the smectic-*A*—hexatic-*B* transition. Using 65OBC and 4O.8 as the standard materials for miscibility studies, Goodby[8] has identified that two smectic phases reported by Poeti *et al.*[9] and existing below the smectic-*A* (Sm*A*) phase of 4-propionyl-4′-(*n*-heptanoyloxy)azobenzene are hexatic-*B* and crystal-*B* phases. Then x-ray diffraction measurements by Albertini *et al.*[10] confirmed this phase identification. For the convenience of our presentation, this liquid crystal will be called compound PHOAB. Its chemical formula is

$$H_5C_2\text{—CO—}(C_6H_4)\text{—N}=\text{N—}(C_6H_4)\text{—CO—O—}C_6H_{13}\,.$$

Its mesomorphic transitions are

$$\text{isotropic}\ \overset{144\,^\circ\text{C}}{\text{——}}\ \text{nematic}\ \overset{142\,^\circ\text{C}}{\text{——}}\ \text{smectic-}A$$

$$\overset{88\,^\circ\text{C}}{\text{——}}\ \text{hexatic-}B\ \overset{84\,^\circ\text{C}}{\text{——}}\ \text{crystal-}B$$

in cooling with the melting point at 92 °C. Here we will report our high-resolution heat-capacity studies on this liquid-crystal compound in the vicinity of its smectic-*A*—hexatic-*B* and hexatic-*B*—crystal-*B* transitions.

The details of our high-resolution calorimetric measurement technique have been published elsewhere.[7] The measured heat capacity per unit area (C_A) of the sample after subtracting sample cell and addendum contribution is shown in Fig. 1 for one cooling run. The thickness of our liquid-crystal sample is 22 μm. The transition temperatures $T_{AB}=88.44\,^\circ\text{C}$ for the smectic-*A*—hexatic-*B* transi-

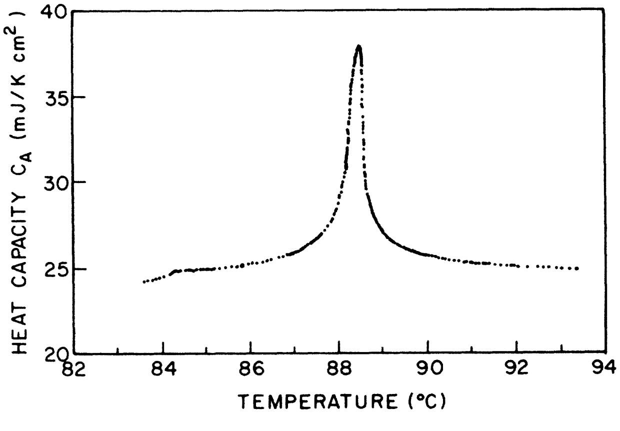

FIG. 1. Temperature dependence of sample heat capacity per unit area (sample thickness 22 μm) in the vicinity of the smectic-*A*—hexatic-*B* and hexatic-*B*—crystal-*B* transitions. This is one of the cooling run results. The cooling rate was 20 mK/min far away from the transitions and 2.7 mK/min near the transitions. For clarity only a portion of data are plotted here.

tion and $T_{BB}=84.32\,^{\circ}\mathrm{C}$ for the hexatic-*B*—crystal-*B* transition are slightly lower than the reported values obtained by differential scanning calorimetry measurements (DSC).[11] Here both hexatic-*B* and crystal-*B* phases are monotropic. Also, once the sample was cooled below T_{BB} with a slow cooling rate (11 mK/min on average; 20 mK/min far away from the transitions and 2.7 mK/min near the transitions), the heat-capacity kink associated with the hexatic-*B*—crystal-*B* transition became undetectable in the subsequent heating. The sample recrystallized after being left in the crystal-*B* phase for more than half an hour.

Qualitatively, heat-capacity peaks associated with those two transitions mimic the ones with the smectic-*C* (Sm*C*)—smectic-*I* (Sm*I*)—smectic-*G* (Sm*G*) transition in racemic 4-(2′-methylbutyl)phenyl-4′-(*n*-nonyloxy)biphenyl-4-carboxylate (2*M*4*P*9OBC).[12] A quick heating run immediately after a quick cooling run just into the crystal-*B* phase reveals that the heat-capacity anomaly for the hexatic-*B*—crystal-*B* transition in the heating run is larger than that in the cooling one. In this experiment, the heating and cooling rate is about 0.6 K/min to eliminate the effect of recrystallization. The result that the heating run has a larger heat-capacity peak than the cooling one is similar to the Sm*I*-Sm*G* transition of 2*M*4*P*9OBC. From the viewpoint of the overall molecular arrangement, Sm*C*, Sm*I*, and Sm*G* can be thought as the tilted counterparts of smectic-*A*, hexatic-*B*, and crystal-*B*, respectively. Namely, the former three phases have finite molecular tilt angle with respect to the smectic layer normal and the latter three phases have zero molecular tilt angle on average. However, the existence of the coupling between the molecular tilt angle and the bond-orientation ordering predicted by theory,[13] in principle, will make some difference in physical properties between the phase transitions among the phases with tilt angle and the ones without. To our knowledge, no one has ever seen bond-orientational order in the Sm*C* phase, which is suggested by a theoretical calculation.[13] This indicates that the coupling between the tilt angle and bond-orientational order is very weak. The similarity between heat-capacity peaks of smectic-*A*—hexatic-*B*—crystal-*B* transitions reported here and those associated with the Sm*C*-Sm*I*-Sm*G* transitions of 2*M*4*P*9OBC also hints that coupling between the tilt angle and bond orientational order is weak. In both transition sequences, the one developing bond-orientational long-range order (smectic-*A*—hexatic-*B* or Sm*C*-Sm*I*) has a much larger entropy change than the one developing further positional long-range order (hexatic-*B*—crystal-*B* or Sm*I*-Sm*G*). This is consistent with the fact that the bond orientational order is accompanied by a fairly large correlation length ($\simeq$100 Å) for the short-range positional order. The same behavior was observed in the smectic-*A*—hexatic-*B* and the hexatic-*B*—crystal-*E* transition of 65OBC.[7]

Figure 2 shows in detail the heat-capacity peak associated with the smectic-*A*—hexatic-*B* transition from the same experimental run as Fig. 1. Because the heat-capacity peak is rather broad, the result from thermal hysteresis measurements between heating and cooling runs was not conclusive. Similar to the Sm*C*-Sm*I* transition of 2*M*4*P*9OBC, here we also obtain a steeper variation of heat capacity on the high-temperature side of the transition. An attempt to fit the data to a power-law expression with a linear background contribution failed. Integrating the area under both heat-capacity peaks after subtracting the background contribution, we obtained heat of transition $\Delta H_{AB}=4.27$ J/g and $\Delta H_{BB}=0.2$ J/g, which agree with the results from a DSC measurement.[11] In calculating ΔH, the density (1.06 g/cm^3) measured by Albetini *et al.*[14] was used.

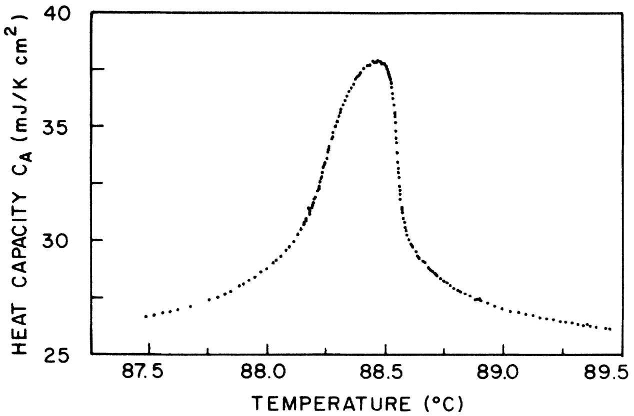

FIG. 2. Details of heat capacity per unit area in the neighborhood of the smectic-*A*—hexatic-*B* transition obtained from the same experimental run as that in Fig. 1.

After the smectic-*A*—hexatic-*B* transition in 65OBC was found to be continuous,[15] we have carried out extensive heat-capacity studies on the smectic-*A*—hexatic-*B* transition of various compounds in the homologous series of *n*-alkyl-4′-(*n*-alkoxy)biphenyl-4-carboxylate (*nm*OBC).[16] All those smectic-*A*—hexatic-*B* transitions were found to be continuous with a large critical exponent α ($\simeq$0.6) characterizing the heat-capacity anomaly. One important difference is that unlike the compound PHOAB, all those *nm*OBC compounds do not have a crystal-*B* phase below their hexatic-*B* phase.

Here we report first the heat-capacity measurements on a single-component compound with the smectic-*A*—hexatic-*B*—crystal-*B* transition sequence. One heat-capacity peak of the compound resembles the Sm*C*-Sm*I* heat-capacity peak of 2*M*4*P*9OBC but not the smectic-*A*—hexatic-*B* heat-capacity peak of *nm*OBC compounds. *X*-ray diffraction studies demonstrated that temperature variations of in-plane positional correlation length near the smectic-*A*—hexatic-*B* transition for compound HPOAB and 65OBC are similar. Another important feature characterizing the hexatic-*B* phase of 65OBC is the herringbone-type molecular arrangement, which has not been reported for the compound HPOAB. Detailed x-ray work on compound HPOAB to check the existence of herringbone structure may be a crucial hint to address the different behavior in these two smectic-*A*—hexatic-*B* transitions. In order to investigate the evolution from an almost symmetric smectic-*A*—hexatic-*B* heat-capacity peak of 65OBC to an asymmetric one in the compound HPOAB, calorimetric studies on binary mixtures of those two compounds will be performed. It would be interesting to understand what the relevant factors for the smectic-A—hexatic-B transition to be continuous or otherwise are. So far the experimental studies on the smectic-A—hexatic-B transition have been concentrated on nmOBC compounds and the homologues of the compound HPOAB. Synthesizing and investigating other kinds of liquid-crystal compounds with the smectic-A—hexatic-B transition are very important for a better understanding of this intriguing and interesting phase transition.

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