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Phase Relation of *p-n*-Hexyloxybenzylidene-*p′*-toluidine (HBT) as Revealed by Thermal and Microscopic Studies

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Complex phase relation of a mesogen compound, HBT, was established by extensive DTA and microscopic texture observations. The two-step melting behavior reported previously was due to the coexistence of the two crystalline phases, Crystal I and Crystal II, which have different melting points to the nematic phase because the rate of transition between them is very slow. The conditions have been revealed under which each of the pure crystalline phases may be realized. Coexistence of the crystalline and the nematic phases is confirmed visually under a polarizing microscope at temperatures between the two melting points.

I INTRODUCTION

Before 1977 *p-n*-hexyloxybenzylidene-*p*′-toluidine (HBT) was known as a mesogen compound which has only a nematic mesophase between the stable crystal phase and the isotropic liquid phase.[1-4] In 1977 Bahadur[5] found a smectic B mesophase and a new crystalline phase upon cooling the nematic phase and proposed the following phase relation based on his microscopic texture observation and miscibility experiment.†

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†The following abbreviations will be used in this paper: I for isotropic liquid, N for nematic liquid crystal, SB for smectic B liquid crystal, and C for crystalline state.

$$\begin{tikzcd}
\text{Solid I} \arrow[r, "330\text{ K}"] & \text{N} \arrow[r, "347\text{ K}", "326\text{ K}"'] \arrow[d] & \text{I} \\
\text{Solid II} \arrow[u] & \text{SB} \arrow[l, "\substack{323\text{ K} \\ \sim 319\text{ K}}"']
\end{tikzcd}$$

Magnetic susceptibility,[5] Moessbauer spectra,[6] refractive indices,[7] and positron annihilation rates[8] were measured to investigate the extent of order in the N and SB mesophases of HBT.

The phase behavior of HBT, however, was soon found to be quite complex by a subsequent experimental work: Bhide *et al.*[9] found another phase transition at 336 K, above the ordinary melting point, in the heating run for a specimen cooled rapidly from the isotropic phase. The relative magnitude of the two thermal anomalies at 331 K and 336 K was dependent on the rate of cooling, whereas the sum of the excess heat was nearly constant. Annealing at room temperature had an effect of decreasing the magnitude of the 336 K peak. They interpreted these phenomena in terms of the survival of the SB nuclei in the crystalline sample cooled rapidly from its isotropic phase. According to their explanation, the 336 K transition is the SB→N transition, and the immiscible mixture of SB and N exists between 331 K and 336 K, i.e.,

$$\text{Solid I} + \text{SB nuclei} \xrightarrow{331\text{ K}} \text{N} + \text{SB} \xrightarrow{336\text{ K}} \text{N} \xrightarrow{347\text{ K}} \text{I}.$$

By his calorimetric measurements, Tsuji[10] found a new high-temperature crystalline phase, which now makes the sequence of equilibrium phases that appear

$$\text{CII} \xrightarrow{317.5\text{ K}} \text{CI} \xrightarrow{334.26\text{ K}} \text{N} \xrightarrow{346.90\text{ K}} \text{I},$$

on heating.

Thus we have three crystalline states, CII and CI named by Tsuji, and the metastable CIII (identical with Bahadur's Solid II). The nature of crystalline states seems to depend strongly on thermal history which has not been well understood. We attempted to clarify this complex phase relation by an extensive study of DTA (differential thermal analysis) and microscopic texture observations.

II EXPERIMENTAL

The sample of HBT was provided by Dr. K. Tsuji of Kwansei Gakuin University. Purity of the sample which had been determined by heat capacity measurement near the melting point was 99.84%.[10] We purified it further by molecular distillation method prior to the experiments. The specimen for the DTA experiments was sealed in a glass tube under 2.7 kPa of helium exchange gas after evacuation for ten hours with two freeze-thaw cycles.

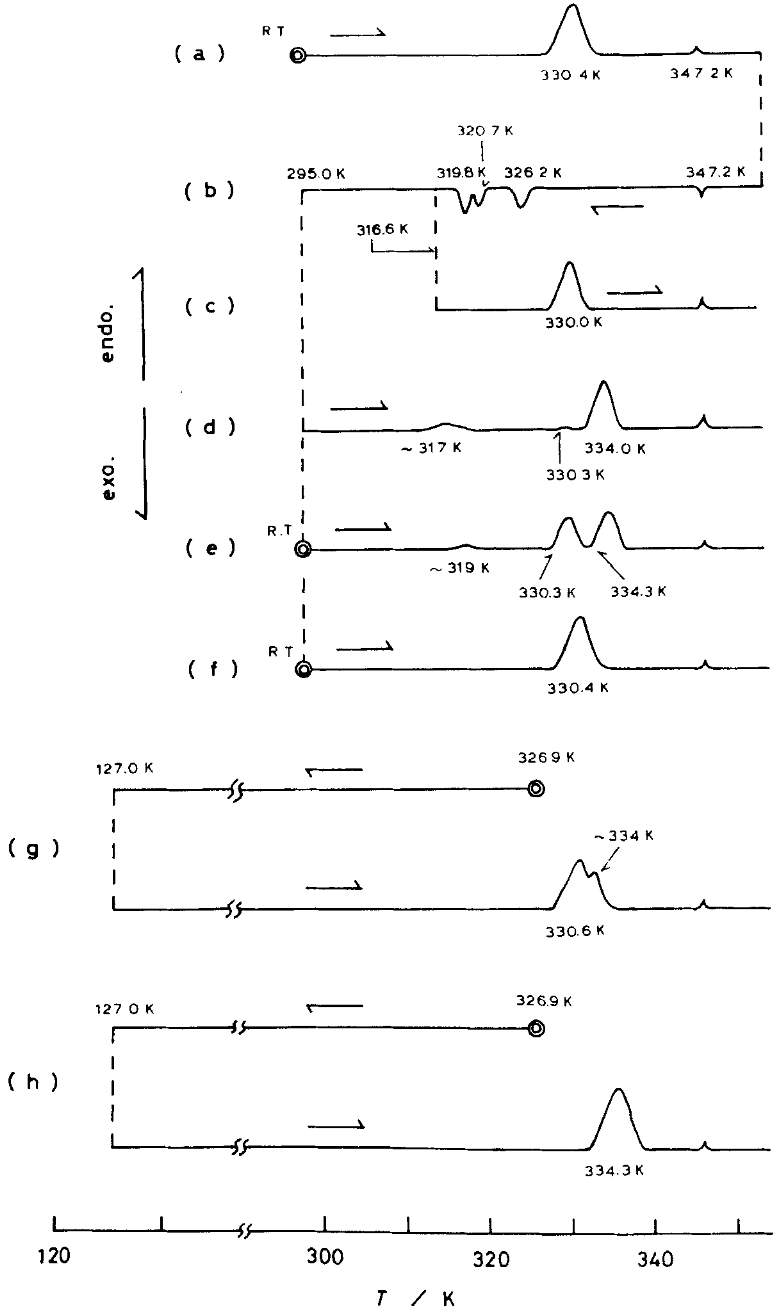
The DTA experiments were done by a homemade apparatus and the sample was annealed in situ necessary.

The textures were observed by utilizing a polarizing microscope (OLYMPUS BHA-P) equipped with a camera (OLYMPUS PM-6). The light source was a 30 watts wolfram lamp (LS 30), and the film used was daylight-type color reversals (Kodak Ektachrome Daylight 64). Observations were made in an orthoscope mode, in 100 and 400 magnifications, with crossed polarizers and without using a sensitive color plate. Temperatures were monitored by a calibrated Chromel-P-Constantan thermocouples placed immediately beneath the sample. The transition temperatures as observed visually coincided with those determined by DTA within 1 K.

III RESULTS AND DISCUSSION

III-1 DTA

The DTA experiment was first carried out by using the sample which had been stored at room temperature for thirteen months, and the results are presented in Figure 1 in chronological sequence of experiments. In the first heating run (Figure 1a), the specimen melted at 330.4 K into nematic liquid crystal and then transformed into isotropic liquid at 347.2 K. When the sample was cooled from the isotropic phase to 316.6 K and heated again, the crystal melted into the nematic phase at 330.0 K (Figure 1c). On the other hand, when the sample was cooled down to 295.0 K and heated again, three transitions (ca. 317 K, 330.3 K, and 334.0 K) appeared (Figure 1d). These three transitions were affected by annealing at room temperature. The Figures 1e and 1f represent the thermograms after the annealing at room temperature for twenty hours and three weeks, respectively. The Figure 1f exhibited the same behavior as Figure 1a. It was clarified that the annealing at room temperature restores the transition at 330 K. Annealing at 326.9 K, on the other hand, enhanced the transition at 334 K as is evident by the Figures 1g and 1h. The annealing time was longer for 1h than for 1g. Sum of the intensities of the two peaks at 330 and 334 K were almost conserved in all the experiments.


(a)
RT
330.4 K
347.2 K
(b)
295.0 K
320.7 K
319.8 K
326.2 K
347.2 K
316.6 K
(c)
330.0 K
endo.
exo.
(d)
~317 K
330.3 K
334.0 K
(e)
R.T
~319 K
330.3 K
334.3 K
(f)
R T
330.4 K
(g)
127.0 K
326.9 K
~334 K
330.6 K
(h)
127.0 K
326.9 K
334.3 K
120
300
320
340
T / K

The results of the DTA experiments may be summarized as follows:

1. From the difference of the annealing effect at room temperature (Figure 1f) from that at 326.9 K (Figure 1h), the stable phase at each temperature is different (CII and CI, respectively), the melting points being 330 K and 334 K, respectively.

2. When a thermogram shows both of the transitions at 330 K and 334 K (Figures 1d, 1e, and 1g), it is the thermogram of a mixture of the two crystalline phases, CI and CII.

3. Therefore, between 330 K and 334 K in Figures 1d, 1e, and 1g, the phases that exist are a mixture of CI and N, contrary to Bhide *et al.*[9] who assigned them to a mixture of N and SB.

4. The intercrystalline phase transition CII→CI at ca. 316 K is very sluggish if the sample is pure CII and contains no nuclei of CI. In this case the transition cannot be detected by DTA (Figures 1a and 1f) at an ordinary heating rate (5.5 mK s^{-1}). The existence of traces of CI nuclei, however, catalyzes and accelerates the CII→CI transition, enabling us to detect the transition (Figures 1d and 1e).

5. The schematic diagram of Gibbs' free energies of the three phases, CII, CI, and N are shown in Figure 2. If cooling of the sample from the isotropic melt is halted at a temperature above 316 K and heated again without annealing, the sample stands in the state of CII which is the metastable state above 316 K (Figure 1c), and can change to CI by annealing for a sufficiently long time (Figure 1h). If cooling of the sample is halted below 316 K, a mixture of CII and CI is obtained (Figure 1d) and annealing at room temperature assists the growth of CII (Figures 1e and 1f).

6. The phases that appear when the isotropic liquid is cooled were identified by some additional DTA experiments (Figure 3) and also by observation of textures under a polarizing microscope. Thus, the N/SB transition temperature, 326 K, does not depend on the rate of cooling,

FIGURE 1 Schematic DTA thermogram of HBT. (a); initial heating run after storage for thirteen months at room temperature. The symbol (⦿) indicates annealing. (b); cooling run from 350 K at a rate of 4.6 mK s^{-1}. (c); heating run from 316.6 K after the cooling run *a* without annealing. (d); heating run from 295.0 K after the cooling run *a* without annealing. (e); heating run after annealing for twenty hours at room temperature. (f); heating run after annealing for three weeks at room temperature. The thermograms *g* and *h* were obtained by the following procedure: (g); The sample was stored at room temperature for fourteen months, then heated to 326.9 K and annealed there for four hours, (h); the sample was annealed at 326.9 K for forty-four hours after cooling from 350 K to 295 K.

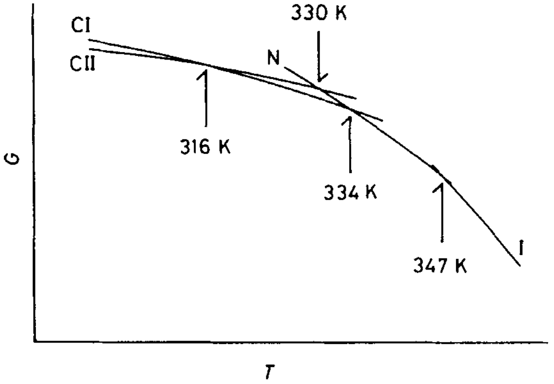


FIGURE 2 Schematic representation of Gibbs energies of the four phases, CII, CI, N, and I of HBT.

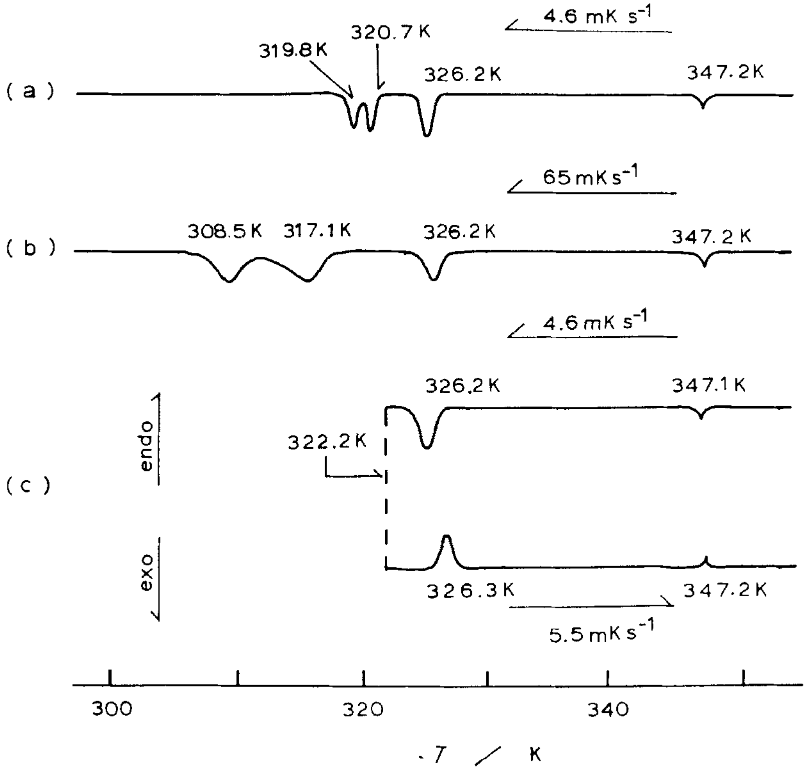


FIGURE 3 Additional thermogram of HBT. (a); cooling run from the isotropic phase at a rate of 4.6 mK s^{-1}. (b); same as *a* but at a rate of 65 mK s^{-1}. (c); test of reversibility of the N/SB transition.

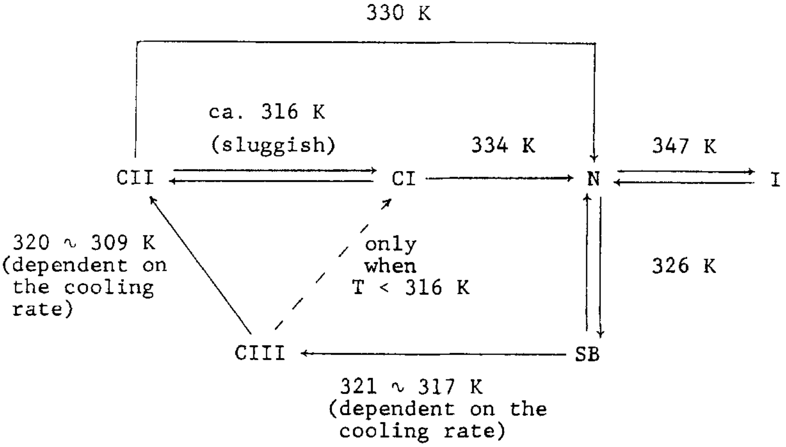


FIGURE 4 Phase relation of HBT.

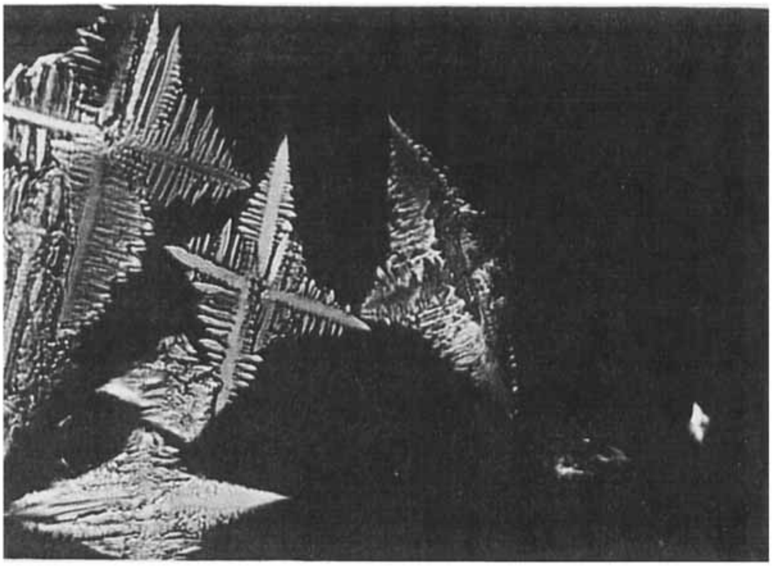
and is reversible in the cooling and the heating runs. This is another evidence against the statement by Bhide *et al.*[9] that the transition at 336 K (corresponding to 334 K in the present experiments) is the SB→N transition. The transition temperature SB→CIII was dependent on the cooling rate, which fact is characteristic of the transitions from a metastable liquid crystal to a crystalline phase.

We have thus established the phase relation of HBT as is summarized in Figure 4.

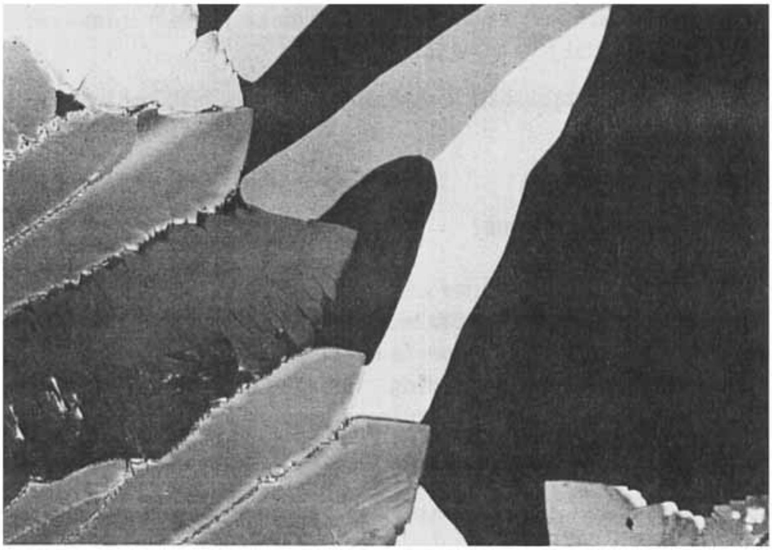
III-2 Microscopic textures

Results of texture observations are presented in Figure 5. The nematic and the smectic B phases exhibited typical schlieren and mosaic textures, respectively.[12] The Figures 5a and 5b show the textures while the transition SB→CIII is proceeding. The dendrites with orthogonal symmetry growing in the homeotropic (pseudoisotropic) area of SB mosaic can be seen clearly in Figure 5a. The characteristic shape of the growing dendrites reflects the symmetry of this metastable crystalline phase. This phase, CIII, soon transformed spontaneously into the stable crystalline state CII even if the temperature was held where the transition SB→CIII occurred (see Figure 5c).

The complex melting behavior was also studied. Following the procedure established by the DTA experiments, a mixture of CII and CI was prepared and its melting behavior was observed (Figures 5d

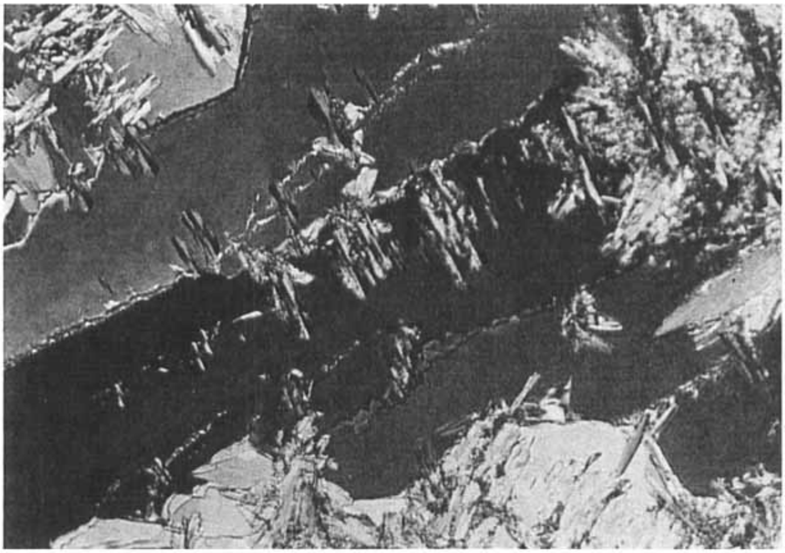


(a)

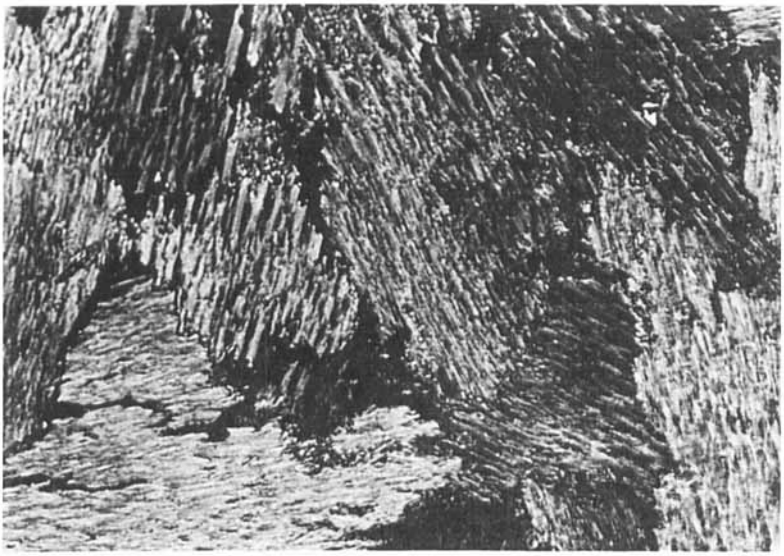


(b)

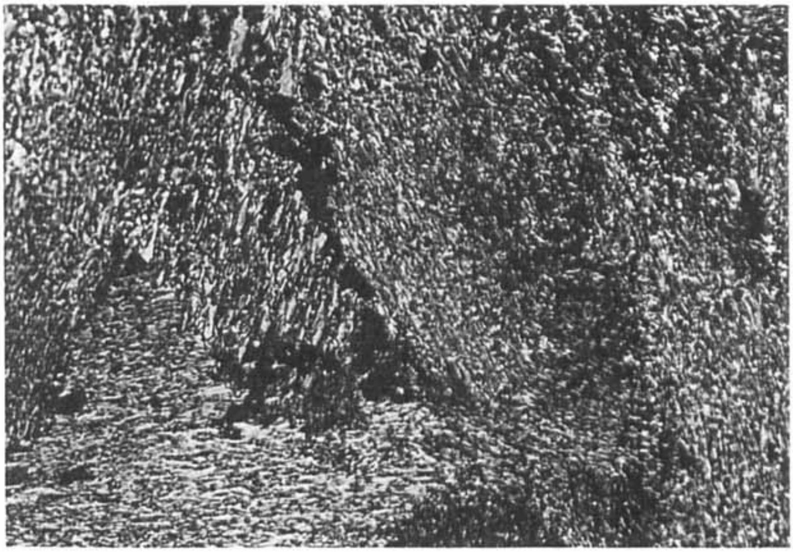
FIGURE 5 Textures of HBT. (a); Dendrites of CIII with orthogonal symmetry growing in the homeotropic (pseudoisotropic) area of SB mosaic texture, ×400. (b); Phase CIII growing (from left) in the SB mosaic texture, ×100. (c); Crystallites of CII growing in the CIII texture, ×100. (d); Crystalline state (mixture of CII and CI) at 298 K, ×400. (e); Coexistence of CI and N at 332.5 K, ×400, the same section as *d*. Some of the crystalline texture has vanished, and the large-scale dislocations (black parts in *d*) have been either smeared out or changed into holes with nearly spherical shape.



(c)



(d)



(e)

and 5e). The intercrystalline phase transition CII→CI on heating caused no pronounced change in texture. But at the temperatures between the melting points of the two crystalline phases, CII and CI, the texture exhibited a new feature which was different from either a pure crystalline state or a nematic state (Figure 5e). This presents another strong evidence in support of the coexistence of CI and N at this temperature (332.5 K).

As we have resolved the complex phase relation of HBT, we can now attempt to study physical properties of the various phases of HBT. Molecular motion in the mesophases as well as in the crystalline states was studied by nuclear magnetic resonance and relaxation,[11] and the results will be reported elsewhere.

Acknowledgments

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