Appearance of a Liquid Crystalline Nematic-Isotropic Critical Point in a Mixture System of Rod- and Bent-Shaped Molecules

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Heat capacity measurements have been made on a liquid-crystal mixture system formed from bent-shaped molecule 1,3-phenylene bis[4-(4-8-alkoxyphenyliminomethyl)benzoates] (P-8-O-PIMB) and rod-shaped molecule n-pentyl-cyanobiphenyl (5CB). The obtained results can be understood assuming that the addition of P-8-O-PIMB molecules to the 5CB system affects as a field conjugate to the nematic order parameter. The B_X-B_4 transition can be viewed as the nematic-isotropic transition of 5CB, which is embedded in a framework of the B_4 structure of P-8-O-PIMB molecules. The present mixture system offers a rare example of the nematic-isotropic critical point, whose critical behavior has not been studied yet in detail.

In the study of critical phenomena, we often confront the obstacle that approaching the critical point is hindered for various reasons, which prevents us from obtaining decisive knowledge about critical behaviors. The liquid crystalline nematic-isotropic (N-I) phase transition is such an example. In spite of the presence of significant pretransitional behavior near the N-I transition, this transition is driven to first order due to a cubic invariant in the free energy [1]. Attempts to determine critical exponent values for the transition have been unsuccessful. There is still no unambiguous proof of what type of critical behavior is relevant for the N-I transition [2,3].

Efforts have been made to remove the difficulty. In principle, a first-order transition can be brought to a critical point by the application of a field conjugate to the order parameter. However, it is difficult to prepare such a field experimentally in the case of nematic order. Wojtowicz and Sheng [4] pointed out that a magnetic field causes the appearance of a critical point in a nematic fluid having a positive diamagnetic anisotropy, but the estimated critical field is of order of 10^3 T, which seems too large to realize. Surface-aligned nematic films are also expected to exhibit a critical point [5]. In fact, Yokoyama [6] studied liquid-crystal thin films with boundaries, and reported a possible appearance of a critical point. He also pointed out, however, that the experimental evidence was not sufficiently conclusive partly because his experiment measured the property averaged over a certain thickness range owing to the nonuniform configuration of the sample films. The liquid crystal placed in a confined geometry has been also studied [7]. Although the N-I transition was found to be suppressed and broadened due to confinement, the situation was complicated as a result of coexisting or dominating random effect.

In this Letter we report results of high-resolution heat capacity measurements carried out on a liquid-crystal mixture system formed from bent-shaped molecule 1,3-phenylene bis[4-(4-8-alkoxyphenyliminomethyl)benzoates] (P-8-O-PIMB) and rod-shaped molecule n-pentyl-cyanobiphenyl (n-5CB). The results demonstrate that the present mixture system offers a rare example of the N-I critical point. In particular, it has been found that by introducing specific nanoscale interactions between quite different molecules, external field effects conjugate to an order parameter can be imposed.

Liquid crystals formed by bent-shaped molecules have attracted intense attention [8–10]. The sterically induced packing of the bent-shaped molecules gives rise to novel smectic phases which have no counterpart in the field of liquid crystals formed by rod-shaped or disc-shaped molecules. At least seven such new phases, B_1 through B_7 phases, have been discovered. Further interesting phase behaviors have been found by introducing rod-shaped molecules to bent-shaped molecules.

Figure 1 shows molecular structures of P-8-O-PIMB and n-5CB. The phase transition sequences are
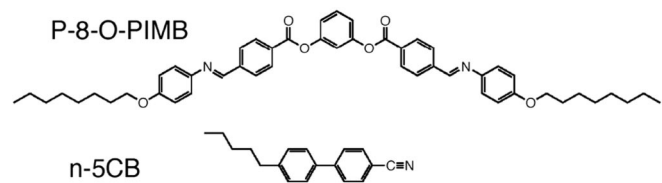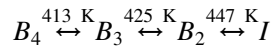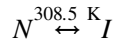

FIG. 1.　Molecular structures of the compounds studied.

$$B_4 \overset{413 \text{ K}}{\leftrightarrow} B_3 \overset{425 \text{ K}}{\leftrightarrow} B_2 \overset{447 \text{ K}}{\leftrightarrow} I$$

for P-8-O-PIMB [9], and

$$N \overset{308.5 \text{ K}}{\leftrightarrow} I$$

for n-5CB [3]. Hereafter we abbreviate P-8-O-PIMB as P8O and n-5CB as 5CB. The molecules are tilted with respect to the layer normal in the B_2 phase, and the layer chirality appears due to the tilting and bent shape of molecules. On the other hand, the structure of the B_4 phase has not been clarified yet, except that the average molecular long axis is along the layer normal, and that a twisted grain boundary (TGB)-like structure has been proposed as a plausible possibility [11]. From polarizing microscopic observations, Takanishi *et al.* [12] found that the B_2 and B_3 phases disappear while the B_4 phase persists for the 5CB mixture ratio (in weight) X [13] larger than about a few percent, and that a new phase called the B_X phase appears in the lower temperature side of the B_4 phase when X exceeds about 0.65. The information about not only the B_X phase itself but also about the B_X-B_4 transition is quite limited at present.

Heat capacity C_p has been measured with an ultralow frequency ac calorimeter [14], which can also be operated in nonadiabatic scanning (NAS) mode [15]. Hermetically sealed gold cells that contained about 5–10 mg of the liquid-crystal sample were used. The temperature scan rate was about 0.03 K/h in the transition region. No noticeable drift in the transition temperature was observed, indicating the stability and high quality of the samples.

After subtracting sample cell contributions, the typical temperature dependence of C_p data is shown in Fig. 2 for the $X = 0.795$ mixture. It is seen that the heat capacity displays a distinct lambda-shape anomaly accompanying the B_X-B_4 transition located at 308.6 K. The B_4-I transition is observed at 374 K, where a steplike anomaly is seen. In agreement with the phase diagram reported in Ref. [12], no
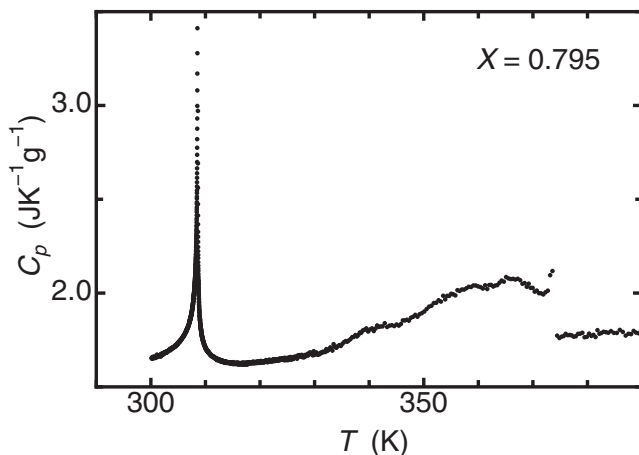
indication is observed for the existence of the B_2 and B_3 phases. Small bumps seen in the B_4 phase, around 340 and 360 K, are reproducible, but do not look like anomalies corresponding to phase transitions. Their origin is not clear at present, however.

Figure 3 shows the C_p behavior in the vicinity of the B_X-B_4 transition. The dashed line shows the background heat capacity C_p (background), determined as a linear function of temperature which joins the measured heat capacity data smoothly at temperatures away from the transition on both sides of the transition. Measurement was also carried out in the NAS mode near the B_X-B_4 transition, which revealed the existence of a latent heat L of about 0.5 J/g, showing that the transition is first order. However, the significant pretransitional heat anomaly as well as the narrow two-phase coexistence region of 80–90 mK indicate the first-order nature is rather weak.

Figure 4 shows the result from the $X = 0.500$ mixture. A distinct anomaly, although slightly smaller in magnitude than that for the $X = 0.795$ mixture, is seen at 308.7 K, which presumably corresponds to the B_X-B_4 transition. This is in contrast with the optical measurement result [12] where no indication of the B_X-B_4 transition was found, but does not seem surprising because the present high-resolution calorimetry is much more sensitive in detecting transitions. The NAS mode measurements were also done, but no indication for the existence of a latent heat was observed for this case. Thus the transition is thought to be continuous [16].

Because the B_X-B_4 transition temperature of the mixture reported in Ref. [12] is rather close to that in pure 5CB, some might have argued that a macroscopic segregation between the P8O and 5CB occurs in the mixture and that the B_X-B_4 transition merely corresponds to the N-I transition which the 5CB part exhibits. However, the present calorimetric results clearly exclude such a possibility be-

FIG. 2. Temperature dependence of heat capacity C_p of the $X = 0.795$ mixture. The data are acquired in a cooling run.
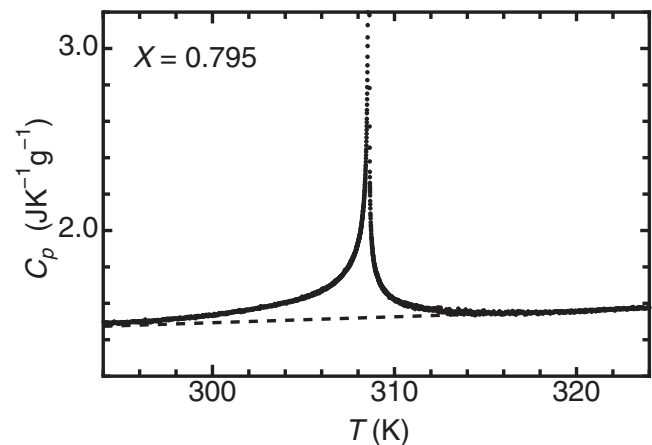
FIG. 3. Temperature dependence of heat capacity C_p of the $X = 0.795$ mixture in the vicinity of the B_X-B_4 transition. The data are acquired in a cooling run. The dashed line shows the background heat capacity contribution.
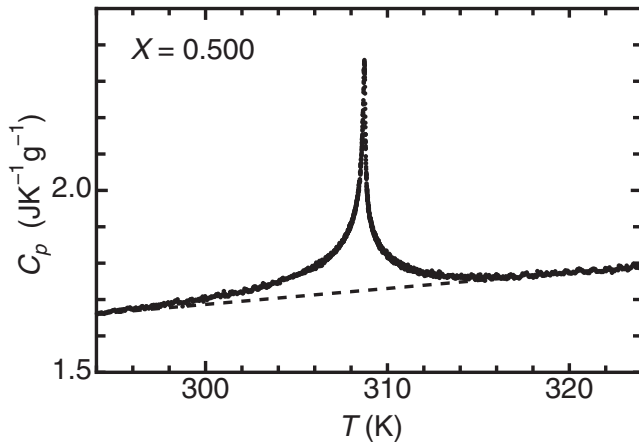
FIG. 4.   Temperature dependence of heat capacity C_p of the $X = 0.500$ mixture. The data are obtained in a cooling run. The background heat capacity contribution is shown as the dashed line.

cause both data for $X = 0.795$ and 0.500 show sharp, single-peaked anomalies, indicating the mixing is quite uniform over the sample. Therefore, the difference in the anomaly for different mixture ratios should be ascribed to the existence of the P8O molecules which are mixing with the 5CB in a microscopic sense.

For comparison, we also carried out measurement for pure 5CB ($X = 1.000$). It was found that the result is in a good agreement with the previous report by Iannacchione and Finotello [17], for instance.

The excess heat capacity accompanying the transition, denoted as ΔC_p, has been obtained by subtracting C_p (background) from the measured C_p data, and the results are plotted in Fig. 5 for the data with $X = 1.000, 0.795$, and 0.500. We see that the anomaly for pure 5CB ($X = 1.000$) shows a distinctly first-order nature. On the other hand, the
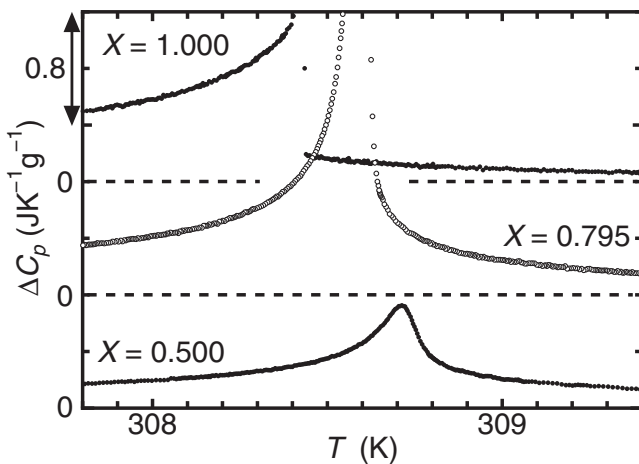

FIG. 5.   Comparison of excess heat capacity ΔC_p from the $X = 0.500, 0.795$, and 1.000 mixtures. Vertical scales have been shifted to reduce overlap of the data points.

result for $X = 0.795$ can be viewed as a quasicritical behavior, having pronounced wings on the both temperature sides. The anomaly for the $X = 0.500$ mixture is smaller than the above two, with a noticeable rounding near the peak, which reminds us of a supercritical behavior.

The overall trend described above can be summarized as follows: (i) The distinct first-order nature of the transition for pure 5CB moves closer to the critical one in the $X = 0.795$ mixture, and finally reaches beyond the critical point and shows a supercritical behavior for the $X = 0.500$ mixture. Besides, we see another feature: (ii) The transition temperature shifts monotonically to the higher side as P8O concentration increases.

It is noticed that these observations are in accordance with a behavior which is seen when a field conjugate to the order parameter is applied to a system undergoing a first-order phase transition in the absence of the field. Thus we are led to an idea that the addition of the P8O molecules to the 5CB system serves as a field conjugate to the nematic order parameter. In this sense we can say that the B_X-B_4 transition is in other words the N-I transition of 5CB which is embedded in a framework of the B_4 structure of P8O molecules. If this is the case, the present mixture system offers a rare example of the N-I critical point, whose critical behavior has not been studied yet in detail. A preliminary analysis of the present ΔC_p data for the $X = 0.795$ mixture with a standard power-law expression gave a critical exponent value $\alpha = 0.49$–0.59, showing a tendency to decrease as the fitted data-range becomes wider. The largest value seems to approach $\alpha = 2/3$ expected for mean-field critical case [5,18], while the smaller value can be compared with the former result for bulk 5CB suggesting quasitricritical behavior [17]. More detailed analyses are now in progress. However, the $X = 0.795$ mixture is still some distance away from the critical point, and a weak but finite first-order nature still seems to prevent one from obtaining a decisive answer. Further attempts may be necessary to reach close enough to the critical point.

A question arises as to what acts as this field and how. Although the structure of the B_4 phase has not yet been fully clarified, the proposed TGB-like structure [11] is at present attributed to the origin of the chirality seen in the B_4 phase. The monotonous decrease in the B_4-I transition temperature reported in Ref. [12] implies that the addition of 5CB results in the reduction of the interaction between P8O molecules. Significantly, the B_4 phase persists in very high 5CB concentration ratios. Assuming that 5CB molecules are distributed among P8O molecules in a uniform manner down to length-scale of molecular size, each P8O molecule is expected to be surrounded by about 12 molecules of 5CB on the average in case of the $X = 0.795$ mixture. We can imagine that the 5CB molecules tend to align parallel to the P8O molecules, so that the interaction between the P8O molecules is not seriously broken. This picture is also in agreement with the scenario that the B_4

structure of the P8O molecules acts as a field which biases the 5CB molecules to form the nematic structure. Another possibility would be that 5CB molecules are distributed mainly in grain boundaries of the TGB-like structure, and the B_4 structure acts as an ordered surface against 5CB molecules. This latter idea, however, seems to need a regular and systematic rearrangement of molecules of both kinds in a mesoscopic scale, and hence would be rather artificial.

Comparison of the present result with earlier studies for liquid-crystal systems in confined geometries [6,7,17] deserves attention. It was observed there that the heat capacity anomaly accompanying the N-I transition is suppressed, rounded, and broadened due to the confinement. In case of systems confined in porous media [7,17], lowering of the N-I transition temperature was seen, which is understood to be introduced by surface disordering effects. The explanation of the results had to be complicated because of coexisting factors such as the distribution of radius of the pores. On the other hand, it was reported that liquid-crystal thin films with boundaries showed increase in the transition temperature for an ordering surface, resulting a possible appearance of a critical point [6]. However, the experiment had a limitation that measured property had to be averaged over a certain thickness range. In comparison with these former studies, the situation reported in this work has an advantage that it is a bulk uniform phenomenon free from the averaging or random effect, so that the critical point can be approached in a more clear, controlled way. We also mention that the phase behavior of mixtures may be more complex. Several models suggest that the phase transition is lowered for mixtures because the second component acts as an impurity to the first component in the homogeneous phase [19,20]. Thus more work is still needed.

In any case, a direct observation of the B_4 structure is greatly desired for more detailed understanding. We are now undertaking a freeze-fracture transmission electron microscopy for this purpose.

In conclusion, we have carried out heat capacity measurements on the liquid-crystal mixture system formed from bent-shaped molecule P8O and rod-shaped molecule 5CB. Significant anomalies were found not only for the $X = 0.795$ mixture but also for the $X = 0.500$ mixture. The overall trend of the results can be explained with a scenario that the addition of the P8O molecules acts as a field which biases the 5CB molecules to form the nematic order. In this sense, the B_X-B_4 transition can be viewed as the N-I transition of 5CB molecules which is embedded in a framework of the B_4 structure of P8O molecules. The $X = 0.795$ mixture is expected to be very close to the N-I critical point. A preliminary analysis of the ΔC_p data yielded critical exponent values lying between the mean-field critical ($\alpha = 2/3$) and quasitricritical ($\alpha = 1/2$)

ones. The situation reported in the present work has an advantage that it is a bulk uniform phenomenon free from averaging or additional random effect, and the critical point can be approached in a more clear, controlled manner.

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