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Isotropic-nematic transition at the surface of a liquid crystal embedded in an aerosil network

Satoshi Aya,[1] Yuji Sasaki,[2] Fumito Araoka,[1] Ken Ishikawa,[1] Kenji Ema,[2] and Hideo Takezoe[1,*]
[1]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S8-42 O-okayama, Meguro, Tokyo 152-8552, Japan*
[2]*Department of Physics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo 152-8551, Japan*

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We reexamined the isotropic-nematic (Iso-N) phase transitions of 4-*n*-heptyl cyanobiphenyl (7CB) embedded in aerosils of silica nanoparticle dispersions using highly sensitive differential scanning calorimetry (HS-DSC), polarizing optical microscopy (POM), and retardation measurements. We found a simple and very profound relationship between the calorimetric and optical measurements; in addition to double DSC peaks, which have been observed previously, a two-step change of the retardation was clearly observed by varying temperature. From our analysis, there is no doubt that the Iso-N liquid-crystal phase transition certainly occurs in two steps, i.e., the bulk transition takes place at first and then the surface transition takes place upon cooling. We should note that the surface transition takes place below the bulk transition temperature, the opposite of what was recently observed in a polymer-dispersed liquid-crystal system.

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I. INTRODUCTION

Extraordinary phenomena near the wall or surface of a macroscopic system attract scientists because of both theoretical [1,2] and experimental [3,4] interest. For instance, a ferromagnet shows the transition at the surface with the bulk phase remaining disordered, and this is followed by the bulk transition if the surface coupling between spins near the surface is considerably enhanced [3]. This kind of phenomenon seems to be general for systems which involve rather stronger or weaker coupling on the surface relative to bulk, such as fluid normal alkane systems which exhibit the so-called freezing transition, where a solid monolayer of molecules is found to exist well above the bulk freezing point [4–7].

In the field of liquid crystal (LC), studies on molecular interactions between LC and the surface, i.e., the surface nature of the LC, have been one of the main topics of condensed matter physics [8–12]. It offers important information to understand microscopic interactions between LC molecules and different surfaces. This in turn gives significant information from a practical viewpoint, i.e., how LC molecules align on polymer surface-alignment layer in the production of LC displays. More fundamentally, the broken symmetry and the specific interactions at the surface lead to unique orientational phenomena generally called "wetting" [e.g., surface-induced ordering even in the isotropic (Iso) phase, the discrete growth of smectic (Sm) layer structure from the surface [13–15]], which are different from that in bulk LCs. Sheng [16] studied the spatial change of the scalar order parameter $S = \langle 3\cos^2\theta - 1\rangle/2$ [a scalar component with θ being the angle made by the long axis of the molecule with director $\mathbf{n}$ in the orientational order parameter of a nematic $Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta})/2$] in temperatures for nematic LCs, and he theoretically predicted a boundary-layer transition occurring above the bulk clearing temperature based on Landau–de Gennes theory. In our earlier work [17], it was experimentally shown that nematic LCs did exhibit the surface transition above the bulk transition via the Iso-N phase transition by using polymer-dispersed LC (PDLC) systems, in which the surface-to-volume ratio is relatively high and the LC-surface anisotropic interaction is strong enough so that the bulk properties are significantly influenced by the surfaces. Moreover, this transition behavior was well explained by the generalized Maier-Saupe theory [18].

There has been an aerosil-LC system focused on studying the quenched random disorder (QRD) effect and finite-size effect [19–23] for the last quarter century. The technique employed was mainly limited to ac calorimetry. In their works, double heat-capacity peaks were observed, suggesting a crossover from a random-dilution regime (high-temperature peak) to a random-field regime (low-temperature peak), i.e., a spatial change of director field [23]. Unfortunately, however, the transition mechanism was not fully explained.

Recently, we also observed double heat-capacity peaks using a high-sensitivity heat-flux differential scanning calorimetry (HS-DSC). Based on this HS-DSC, together with retardation measurements, we report here our interpretation of the transition phenomenon, i.e., that the bulk transition occurs before the surface nematic layer is formed in an aerosil-LC system upon cooling. Namely, the higher- and lower-temperature DSC peaks are attributed to the Iso-N transitions in the bulk and the surface, respectively. This temperature variation is the opposite of that in PDLC systems reported recently [17].

II. EXPERIMENTAL

We prepared five dispersion systems of hydrophilic silica nanoparticle aerosil300 (Evonik Industries, using 7-nm-diam particles and a 300 m^2 g^{-1} specific area) in a pure nematic LC 7CB (4-*n*-heptyl cyanobiphenyl, Aldrich) with a phase sequence of Cry 29.8 °C N 43.2 °C Iso. Each sample with densities of aerosil ρ of 0.0104, 0.0294, 0.0494, 0.0954, and 0.1135 g cm^{-3} was prepared to be dissolved in very-high-purity acetone (Cica) and sonicated for more than 1 h to produce microscopically uniform aerosil-LC mixtures. After evaporation of the solvent, each mixture was injected into glass cells with a 5.0–6.5 μm gap for polarizing optical microscopy (POM) observations and optical measurements.

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[*] Corresponding author: takezoe.h.aa@m.titech.ac.jp

To study thermal properties of the samples, we have carried out a heat-capacity investigation by using HS-DSC. Since DSC detects the heat-flow difference in a sample cell and a reference cell as a function of temperature, this technique is applicable both for first-order transitions, accompanying a substantial latent heat, and second-order transitions. In this work, semiconducting thermoelectric modules were used to detect the temperature difference between a sample and a reference cell. The sample is loaded into a gold cup and hermetically sealed with a gold lid under a helium atmosphere. The details of the cell structure can be found elsewhere [24]. Aerosil300-LC mixtures of 3–7 mg were used for the measurements. Standard measurements are performed with scan rates of ±0.05 °C/min.

Measurements of the temperature dependence of retardation and transmittance were made with the setups described below. A He-Ne laser (632.8 nm) was used to illuminate sample cells located between crossed polarizers at normal incidence. The macroscopic retardation was obtained by recording the dc signal of transmitted light, which was detected by a *p-i-n* photodiode, and then the output signal was fed to a lock-in amplifier. To measure the transmittance, the same setup except for the removal of the analyzer was used in front of the pinhole, which cut out diffracted and stray light.

III. RESULTS AND DISCUSSION

First, we show the result of calorimetric investigation. It should be noted that the observed heat-capacity $C_{\mathrm{p-obs}}$ data include both contributions from the empty gold cell and aerosil300, which are regarded as background terms to the heat-capacity data and must be removed from $C_{\mathrm{p-obs}}$ to extract the heat capacity of 7CB. However, since the primary interest in this study is the anomalous behavior in the heat capacity associated with the Iso-N phase transition, the excess heat capacity ΔC_{p} is simply calculated by subtracting a smooth background signal from $C_{\mathrm{p-obs}}$ and dividing by the mass of 7CB used in the mixture. ΔC_{p} against $T - T_{\mathrm{IN}}$ on cooling for various concentrations is presented in Fig. 1, where T_{IN} corresponds to the higher transition peak for the mixtures. The origin of abscissa is properly shifted in each sample. Actually the temperature of the main peak scarcely changed with increasing aerosil300 content. For pure 7CB (not shown), a peak associated with the Iso-N phase transition is evident at 43.2 °C, which agrees with the result using a previous adiabatic measurement [25]. On the other hand, double-peak anomalies are observed for all mixtures; the lower-temperature peak grows, whereas the transition enthalpy for the higher-temperature peak diminishes with an increase of ρ. Both lower- and higher-temperature peaks exhibit thermal hystereses, indicating first-order transitions. Hence, we can infer that the higher-temperature peak originally corresponds to the Iso-N phase transition for the bulk 7CB, and the emergence of the second peak originates from the mixing of aerosil300. It is important to note that the total transition enthalpy was found to be almost constant for all samples, which will be discussed later. These experimental facts strongly suggest that the high- and low-temperature peaks are attributed to the bulk and surface contributions in the Iso-N phase transition, respectively.

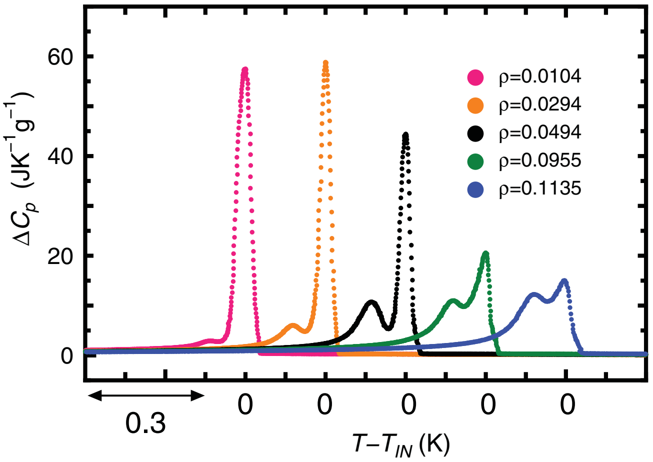

FIG. 1. (Color online) HS-DSC data of all mixtures with different densities ρ of aerosil300 show the characteristic double-peak heat anomalies via the Iso-N transition in contrast to pure 7CB. The values of ρ increase from the left-hand side to the right-hand side. The two well-split peaks are indicative of the underlying two distinct thermodynamic phase transitions.

Another feature in the heat-anomaly peaks is that the additional low-temperature peak originating from the addition of aerosil300 is somewhat broader compared with the main high-temperature peak. The broadness of the low-temperature peak can be attributed to (1) superposition of many transition peaks caused by the heterogeneous character of the silica soft-gel network, and (2) the finite-size effect due to nano- or microconfined space containing LC molecules. Both are consistent with the conclusion previously made, i.e., the additional broad peak originates from the transition at the surface. Both (1) and (2) could be a possible explanation, since it is well known that the structure in this system has size distribution depending on the fabrication process and that the size of the connected pore ranges from several tens to hundreds of nanometers, which is the range showing the size effect in thermal measurement [26]. Another idea connecting (1) and (2) is also proposed in Ref. [22], i.e., the external-field effect by introducing aerosil300 particles; that is, the surface of aerosil300 behaving as an external field in order to disturb the average coordination of LC molecules. Actually, the SiO surface is known to disorder LC molecules nearby [27,28]. In the present case, since the aerosil has a large surface-volume ratio which makes the disordering effect much stronger, LC molecules near the surface are strongly disordered compared to a normal cell with only a flat alignment layer. If the surface transition occurs simultaneously with the bulk transition, it is easy to imagine that there should be a great number of defect sites on aerosil surfaces. Due to the high energy cost involved in such a state, the system tends to avoid such a situation; i.e., the elastic energy due to the surface-disorder fluctuation acts as an energetic barrier for the surface component to make the phase transition at the same time, causing a temperature gap between the bulk and surface transitions.

Another important hint is shown by the transitional enthalpy change due to the heat anomalies, i.e., $\Delta H_{\mathrm{total}} = \Delta H_{\mathrm{bulk}} + \Delta H_{\mathrm{sur}}$. The value is almost the same for all samples, as shown in Fig. 2 (open blue circles). This suggests that

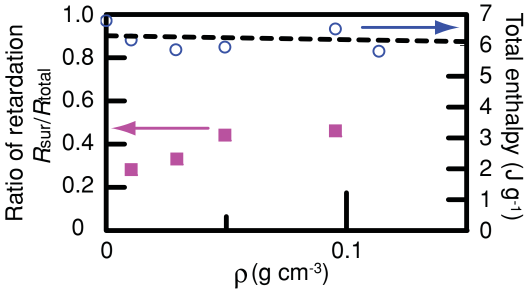

FIG. 2. (Color online) The total enthalpy exactly integrated in the whole regime of the Iso-N transition (open circles) and the ratio of retardations of surface and bulk R_{sur}/R_{total} (closed squares) are plotted as a function of aerosil300 density ρ. The dashed line is the least-square fitting for the total enthalpy.

there is no thermal loss across the Iso-N phase transition. In other words, decreasing (increasing) ρ is comparable to the increase (decrease) of the volume of the bulk LC phase, since aerosil300 has such a large surface area that the surface effect becomes important. As a result, although the ratio of the amount of bulk LC to the LC molecules localized at the surface is changed by varying ρ, the total enthalpy for the Iso-N transition remains constant. This analysis also indicates that the proposed external-field effect arising from the aerosil300 surface [22] mentioned above is not effective in the aerosil300-LC system, because there is no change in the latent heat even when we introduce aerosil300 in a large quantity. This speculation is supported by our systematic study of HS-DSC on aerosil300-*n*CB (8CB–9CB) homologous compounds. Detailed calorimetric measurements (dynamic and static behaviors) and analysis will be reported in the near future.

To see the transition behavior more clearly, we measured the retardation (the details will be shown in Fig. 4). According to the POM observation, the retardation change occurs in a two-step process, as will be discussed in Fig. 3. We measured the retardation for the entire layer ($R_{sur+bulk} = R_{total}$) and the bulk layer (R_{bulk}) by using a Berek compensator (Nichika Inc.) and deduced the surface contribution R_{sur}. The closed purple squares in Fig. 2 show the ratio of retardation R_{sur}/R_{total} as a function of ρ. R_{sur}/R_{total} increases with ρ almost linearly in a low ρ region. This behavior is consistent with our prediction, since the area of surface where LC molecules undergo the low-temperature Iso-N transition increases with ρ. The sample with $\rho \sim 0.0949$ was too viscous to be injected so that the mixture inside the cell was inhomogeneous. This is the reason why the data point with $\rho \sim 0.0949$ is deviated from the linear change. In order to support the linear dependence R_{sur}/R_{total} against ρ, the contribution of enthalpies from the bulk and surface was estimated by dissolving heat-capacity anomaly data consisting of double peaks into two components. We found that both the bulk and surface contributions linearly change with ρ, supporting our observation that the surface transition is driven by a simple surface-wetting transition.

In order to interpret the apparent double-phase transitions, optical observation of the sample texture in the vicinity of the phase-transition temperature offers an important clue. Figure 3 shows the texture change across the Iso-N phase transition of the sample with $\rho \sim 0.0494$ in an untreated glass cell. Upon heating at a rate of ~0.1 °C/min, a schlieren texture, mainly with two brushes, is stable in the nematic phase. As the temperature approaches the N-Iso phase transition, a thin nematic layer with smaller retardation appears, coming from the higher-temperature side, which spreads to change the initial texture to a distinct schlieren texture with only four brushes. According to the HS-DSC measurements and the discussion

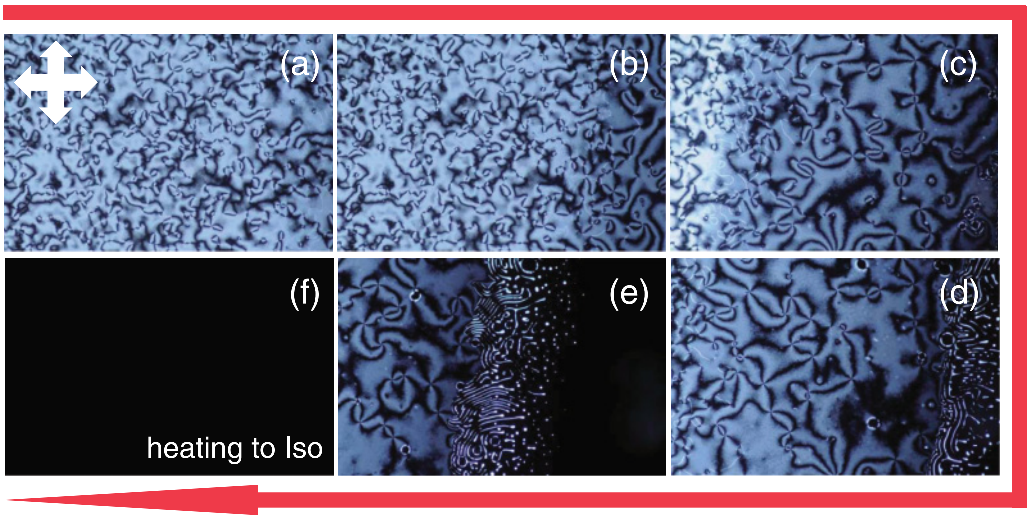

FIG. 3. (Color online) Photomicrographs under crossed polarizers of the sample with $\rho \sim 0.0494$ during a heating process in an untreated glass cell with a rate of ~0.1 °C/min. Below the N-Iso phase transition, only two-brush defects are seen (a). The darker (lower birefringent) region appears in the right-hand side (b) and then develops to the left-hand side (c). In this region, two-brush defects change to four-brush defects. This originates from the N-Iso transition at surfaces, which gives lower birefringence only from the bulk. The point defects (four-brush defects) emerge at the N-Iso boundaries. The darker region covers the whole surface (d), the N-Iso transition occurs in bulk from the right-hand side (e), and the transition is completed (f). With a progressive reduction in the size and thickness of nematic domains, an unusual fine texture emerges, as seen in the middle of (e). The director orientation giving such fine textures is not known.

above, the smaller retardation originates from bulk LC after the N-Iso transition at the surface. At the end, Iso droplets come into existence and the bulk N-Iso transition occurs. In this way, the observation of the thin nematic layer with a different schlieren texture shows a detailed transition behavior in the aerosil300-7CB system and provides topological information. We should note that the observation of this kind of two-step retardation change in aerosil300-LC systems is very rare, since the normal Iso-N transition occurs only in one step; retardation decreases without changing the texture and then melts into the Iso phase.

We now discuss the origin of the texture change. Half-integer defects with two brushes are line defects and stably exist in confined geometries with planar surfaces as in the present case. However, integer defects with four brushes normally exist as point defects by escaping from line defects. Hence the transformation of disclination from $|1/2|$ to $|1|$ should be a consequence of the surface change, which is brought about from surface melt. This consideration is consistent with the phenomenon mentioned above; i.e., the two-step Iso-N phase transition occurs first as surface layer melting, then the bulk melts upon heating, and vice versa upon cooling. Actually upon cooling, the birefringence gradually changes without such a clear two-step variation.

Another piece of evidence for the two-step Iso-N transition is provided by the temperature dependence of retardation, as shown in Fig. 4. For the sample with $\rho \sim 0.0104$, the retardation remains zero above the Iso-N transition, and increases monotonically in the range $\sim$0.2 °C [as indicated by a double-headed arrow in Fig. 4(a)] below the clearing temperature. This behavior is the same as that in pure 7CB [14] and in other pure LC materials. However, the situation dramatically changes in the sample with large $\rho(\sim 0.0954)$. The retardation change is not smooth but shows a plateau at $\sim$0.1 °C, as indicated by an arrow in Fig. 4(b). The first and second increases are attributed to the development of the Iso-N transition in the bulk and at the surface, respectively, upon cooling. This behavior is consistent with the HS-DSC data. It should be noted that the other samples show the same tendency as that in the sample with $\rho \sim 0.0954$. One may wonder why the sample with $\rho \sim 0.0104$ does not show the stepwise behavior, even though it also has a large surface portion. However, it agrees with the HS-DSC result; i.e., the sample with $\rho \sim 0.0104$ shows only a small low-temperature peak in HS-DSC (Fig. 1), suggesting a negligible surface effect. This is the reason why a nonmonotonic increase of retardation cannot be recognized.

This stepwise change in the retardation was also observed in our previous study [17] using PDLC systems. However, the behavior of the retardation increase is qualitatively different between the two systems, aerosil-LC and PDLC. This is due to whether the transition occurs in the bulk or at the surface upon cooling. We should note here that this difference originates from the different surface energy, i.e., the wetting behavior of LCs on surfaces. It is known that the Iso-N transition occurs in the bulk in a SiO surface, whereas it occurs at the surface in a polymer surface [27,28]. Further theoretical work is required to understand these experimental results.

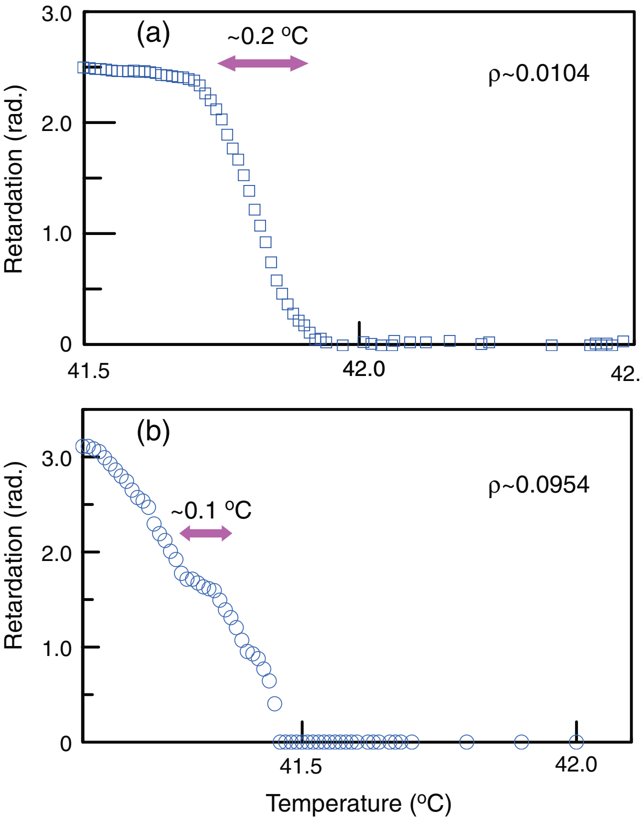

FIG. 4. (Color online) Phase retardation as a function of temperature in two samples with (a) $\rho \sim 0.0104$, (b) $\rho \sim 0.0954$.

IV. CONCLUSIONS

In conclusion, the HS-DSC and optical retardation have been precisely measured in binary mixtures consisting of rodlike LC 7CB and silica nanoparticle aerosil300. The two heat-anomaly peaks are pronounced and a two-step retardation change is observed in both the cooling and heating processes. Combined with the macroscopic POM observation, these results allow us to safely conclude that the high- and low-temperature peaks appearing in HS-DSC are attributed to the Iso-N transition in the bulk and at the surface, respectively.

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