

Observation of Two Isotropic-Nematic Phase Transitions Near a Surface

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Using specified conditions, we succeeded in observing the isotropic-nematic (Iso-N) liquid crystal phase transition at surfaces followed by that in bulk for the first time. An additional heat anomaly peak was found at a higher temperature side of a main phase transition peak using highly sensitive differential scanning calorimetry (HS-DSC). The peak is pronounced particularly in the cooling process, since the transition starts at surfaces on cooling. The temperature dependence of retardation allows us to safely conclude that the higher temperature peak that appeared in HS-DSC is attributed to the Iso-N transition at surfaces. These measurements also indicate that the surface transition is of first order. These behaviors were theoretically explained by generalized Maier-Saupe theory.

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Considerable effort has been devoted to study the behavior of liquid crystal (LC) molecules near a surface [1–4]. Until now, surface-induced ordering in the isotropic (Iso) phase and the surface memory effect have been extensively studied [5–10]. As LC molecules at the surface have fewer nearest neighbors than in bulk and have an anisotropic interaction with the surface, spontaneous symmetry breaking at the surface may be expected to be independent of that in bulk. Actually thermodynamic phase transition categorized to wetting transition was theoretically predicted [11], in which the system free energy is lowered when the surface layer is completely wetted by the different surface phase. However it is only after 1993 that several experimental systems, such as (1) normal alkane fluids [12], (2) mercury-sapphire interface, (3) superfluidity of He on thin cesium [13], and (4) a liquid-liquid transition [14], have been found to undergo the transition. Recently, Boamfa *et al.* reported a prewetting transition in a LC system by retardation measurements under a magnetic field [15]. However their result included no thermodynamic information. In this sense, experimentally well-proven surface Iso-LC phase transition in LC systems has never been reported thus far. Here we show the Iso-N phase transition on cooling occurs first at the surface followed by that in bulk for the first time. An additional heat anomaly peak was found at a higher temperature side of a main phase transition peak using highly sensitive differential scanning calorimetry (HS-DSC). The temperature dependence of retardation allows us to safely conclude that the higher temperature peak that appears in HS-DSC is attributed to the Iso-N transition at surface.

We used the same materials system as that used in our previous study [16]; mixtures of precursor NOA81 (Norland Optics) for polymer-dispersed liquid crystal

(PDLC) and LC mixtures E7 (Merck). The mixtures were heated up to about 70 °C, and injected into glass cells without any alignment treatment. The cells were next irradiated with UV light (365 nm) with a Hg lamp (35 mW · cm⁻², Electro-Lite corporation) for polymerization. The details of the sample preparation can be also found in Refs. [17,18]. Characteristics of surface interaction of E7 to NOA81 were first examined using a contact angle measurement. As shown in the inset of Fig. 1(a), NOA81 film shows a vanishingly low contact angle, signifying very high wettability with E7. Note that if the surface material like NOA81 has strong surface energy to LC molecules, the surface in contact to LCs prefers imposing ordering and may induce the surface phase transition. HS-DSC using semiconducting thermoelectric modules was carried out for hermetically sealed gold cells containing samples. The temperature scan rates used in the present study were 0.10 or 0.05 °C/min, for which the samples were close to the thermal equilibrium state. The HS-DSC data for two samples (weight percentage of E7, X , is 69.0 and 49.4) are displayed in Fig. 1(a). A very sharp peak of the excess specific heat is observed in addition to a main broad peak for the Iso-N transition on cooling particularly for $X = 69.0$. The behavior is similar to those observed in aerosil/LC and aerogel/LC systems [19–23]. The result suggests that there are two thermodynamic transition mechanisms during the phase transition. As the weight fraction of E7 decreases, the Iso-N transition temperature shifts towards lower temperatures and the higher temperature peak decreases in intensity. Two possible reasons can be considered for lowering the Iso-N transition temperature: (1) A random cross-linked polymer network weakens the strength of the mean molecular field; (2) effective suppression of heterogeneous nucleation by finite size

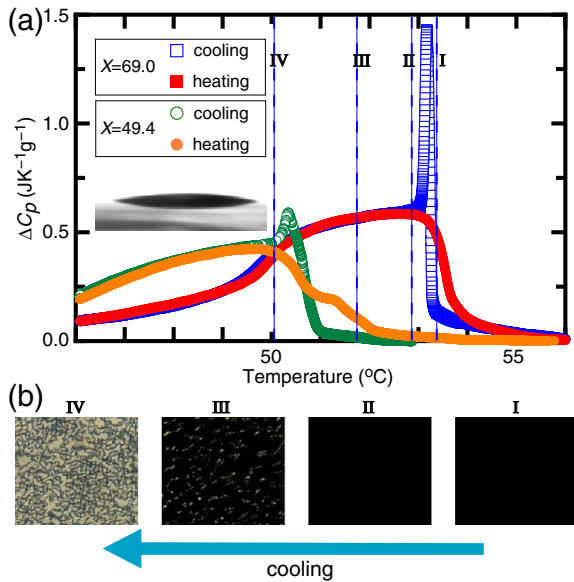


FIG. 1 (color online). Thermal analysis and texture observation in the Iso-N transition. (a) Excess specific heat capacity ΔC_p calculated from the HS-DSC data as a function of temperature. (b) Textures for the sample $X = 69.0$ at temperatures indicated by vertical dashed lines in (a). The textures are completely dark both at high and low temperature sides of the sharp peak (I and II). In the middle of the broad peak, birefringent regions emerge here and there (III), then finally typical schlieren texture covers the whole area after the I-N phase transition (IV). Contact angles of an E7 droplet on NOA81 are also shown in the inset.

effect arises; i.e., nucleation of the N domain does not occur in the bimodal region of the phase diagram, but much deeper below the spinodal line. In other words, the pretransitional fluctuation in the Iso phase is strongly suppressed. We speculate that both work at the same time but different in degree.

The following two observations and associated considerations must be made as key information deduced from the calorimetry data. (1) The higher temperature peak upon cooling is much sharper than the lower temperature one, particularly for $X = 69.0$. The transitional enthalpy change due to the heat anomaly at the lower temperature is definitely larger than that at the higher temperature. Because of the experimental and theoretical considerations mentioned below, we can infer that the higher and lower temperature peaks are attributable to the Iso-N phase transitions at the surface and in bulk. (2) The presence of the thermal hysteresis is observed for the higher temperature peak, as clearly seen for $X = 49.4$ in Fig. 1(a). The temperature width of the hysteresis strongly depends on the fraction of E7, approximately 1-2 $^{\circ}\text{C}$, being considerably larger than that of the conventional bulk transition, typically 0.05–0.20 $^{\circ}\text{C}$ in weakly first-order transitions. This implies that the change in the polymer surface-volume ratio by changing the weight fraction of E7 [24] results in a different degree of average strength of anisotropic interactions

between LCs and polymer surfaces. As a result the sharpness and height of the higher temperature peak are influenced by the interactions mentioned above.

To interpret the apparently double phase transitions, optical observation of the sample texture in the vicinity of the transition temperature offers an important clue. During the observation of the sample ($X = 69.0$), we used the same cooling rate (0.1 $^{\circ}\text{C}/\text{min}$) as in HS-DSC to avoid a nominal effect such as supercooling. Figure 1(b) shows textures under crossed polarizers at four different temperatures indicated as I, II, III, and IV in Fig. 1(a); i.e., (I) just above the sharp peak in the Iso phase, (II) just below the sharp peak, (III) at a mid temperature of the broad peak, and (IV) well below the sharp peak in the Iso phase. Upon cooling, no texture change appears even at II. This observation is consistent to the previous assignment of the sharp peak to the surface transition. Namely, macroscopic optical change must not occur if only the surface undergoes the phase transition from Iso to N. In other words, the bulk is still in the Iso phase at II. Furthermore, as temperature is lowered N domains begin to be formed in the Iso sea and coexist with Iso domains over about 2 $^{\circ}\text{C}$ around III. At IV, the quintessential N schlieren texture appears.

If the surface transition occurs, an abrupt and small change in retardation is expected near the temperature showing the sharp HS-DSC peak. To confirm this, we measured the temperature dependence of retardation with a setup described below. A He-Ne laser (632.8 nm) was used to illuminate sample cells between crossed polarizers. A photoelastic modulator (PEM) was located after the first polarizer, whose axis was oriented at $+45^{\circ}$ to the PEM's retardation axis. The transmitted light modulated at 48 kHz was detected by a PIN photodiode, then dc and ac signals were simultaneously detected by a lock-in amplifier. As observed in Fig. 2(a), nonzero retardation in the Iso phase increases gradually with decreasing temperature (pretransitional surface-induced ordering), then increases rapidly, where the jump in retardation from the nonzero retardation baseline is of the order of 0.01 radians. The retardation seems to saturate to a constant value over a narrow temperature range, the width of which well agrees with the HS-DSC data, then finally shows a divergent appearance. A rough estimate was made on the layer thickness in the surface region; about 2–3 nm for the surface-induced layer and about 9–15 nm for the surface-ordered region. It is noted that the latter is much thicker than the monolayer, although the estimate is not so accurate because of averaging over randomly oriented molecules. The observed two-step increase in retardation convinced us that the transitions at the surface and in bulk take place separately, although there is a range where N and Iso coexist in between. On cooling pretransitional retardation increase is followed by the surface transition which appears as a kink or sharp jump to an almost constant value from nonzero baseline. The retardation is kept constant, which

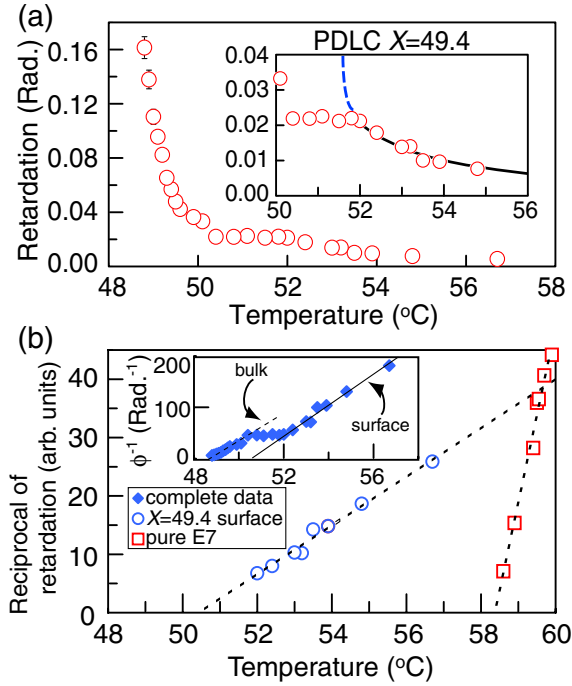


FIG. 2 (color online). Retardation as a function of temperature near the Iso-N phase transition on cooling. (a) E7/NOA81 (wt %: 49.4/50.6) PDLC sample between two untreated glass substrates. Detailed behaviors are also shown in the inset. A dashed line represents a qualitative diverging behavior at the surface transition suggested by the mean-field theory and a solid line the fitting by least squares. (b) Reciprocal of retardation ϕ^{-1} versus temperature. Open circles represent data of the transition at the surface for $X = 49.4$. The data for the bulk transition for pure E7 are also shown by open squares, for comparison. In the inset of (b), the complete data set of the temperature dependence of ϕ^{-1} is also displayed.

corresponds to the higher temperature peak in HS-DSC data. As temperature decreases, a second kink or abrupt jump can be observed and this in turn corresponds to the bulk transition. To show the pretransitional phenomenon more clearly we plot the reciprocal of retardation (ϕ^{-1}) as a function of temperature for $X = 49.4$. As shown in Fig. 2(b), ϕ^{-1} varies linearly with temperature as expected. In the inset of Fig. 2(b), a more complete data set of ϕ^{-1} for a wide temperature range above 48 °C up to 60 °C is shown to have a sigmoidal S shape. The behavior in the lower temperature side may originate from the coexistence of N and Iso phases. However, as indicated by two straight lines (solid and dotted lines), it may be possible to attribute it to the pretransitional phenomenon in bulk in addition to that at the surface. For this point, further theoretical considerations and experiments should be done in the future.

As a reference, we used pure E7 in an antiparallel rubbed cell with polyimide (PI) for planar alignment (AL1254, JSR). In contrast to NOA81, this PI surface alignment layer showed a high contact angle 93°. It is worth noting that E7 placed on the PI surface shows only one peak in the Iso-N

transition in our HS-DSC measurement, while double peaks are revealed on the NOA81 surface. Moreover, a pretransitional retardation change was observed only for the bulk transition, as observed by Miyano *et al.* [5] and Yokoyama *et al.* [25]. For the pure E7 sample, LC molecules at the surface in the Iso phase gradually form a planar uniform alignment along a preferred direction by rubbed AL1254 and develop into the bulk, which is driven by a pretransitional effect, as shown in Fig. 2(b) (open squares). The nonzero retardation in the Iso phase is about 0.01 radians which is estimated to be about one or two LC-like fluid molecular layers on both sides of the substrate in terms of thickness. To examine whether the double transition behavior is a general phenomenon or not and to exclude possible demixing of the LC constituent (nCB or nOCB), which likes or dislikes to locate at the surface, from a LC mixture E7, we also used 4-*n*-heptyl-4-cyanobiphenyl (7CB, Aldrich), which is one of components of E7. We found that pure 7CB on PI just showed well-known behavior with only small pretransitional increase of retardation, being consistent to the behavior of E7 on PI. By contrast, we clearly observed a two-step change of retardation in the PDLC sample of 7CB [26]. Hence we can conclude that the surface transition actually occurs without any demixing and is a general phenomenon.

Let us briefly explain the occurrence of transition at the surface and in bulk using a generalized Maier-Saupe theory [27–29] for inhomogeneous distribution of the nematic order along the z coordinate. The free energy of LC per unit area can be written as a sum of the orientational entropy and the internal energy,

$$\begin{aligned}
 F = & \rho k_B T \int d^2 \mathbf{a}_1 \int dz_1 f((\mathbf{a}_1 \cdot \mathbf{n}), z_1) \ln[f((\mathbf{a}_1 \cdot \mathbf{n}), z_1)] \\
 & + \rho^2 / 2 \int d^2 \mathbf{a}_1 \int d^2 \mathbf{a}_2 \int dz_1 \int d^3 \mathbf{r}_{12} f((\mathbf{a}_1 \cdot \mathbf{n}), z_1) \\
 & \times f((\mathbf{a}_2 \cdot \mathbf{n}), z_2) V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}), \quad (1)
 \end{aligned}$$

where ρ is the concentration of molecules, and z_i is the distance of molecule i from the surface. In Eq. (1) the orientational distribution function for each molecule $f((\mathbf{a} \cdot \mathbf{n}), z)$ is assumed to depend on the distance from the surface, $V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})$ is the interaction potential between molecules 1 and 2. Minimizing F with respect to $f((\mathbf{a} \cdot \mathbf{n}), z)$, one obtains $f((\mathbf{a} \cdot \mathbf{n}), z)$. After some calculation using the distribution function, we obtain the local nematic order parameter $S(z)$. Figure 3 shows the temperature dependence of the nematic order parameter at the surface S_0 (solid squares) and far from the surface S_∞ (open circles). Two important observations should be made: (1) S_0 never becomes zero, whereas S_∞ is zero in the Iso phase; (2) the phase transition at the surface always occurs at higher temperatures than that in bulk. The main reason for this fact is the presence of the first power of S in the free energy at the surface. Such a linear term in the order parameter is very similar to the $-HM$ term for a

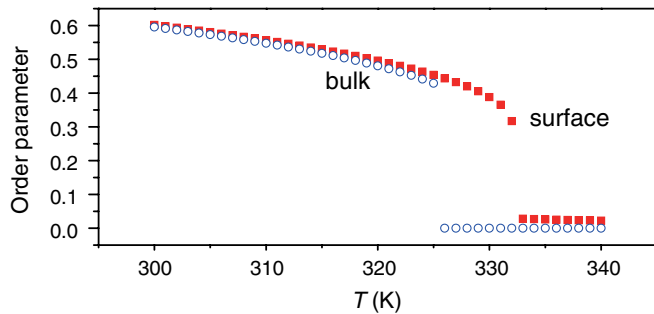


FIG. 3 (color online). Nematic order parameter in the vicinity of the surface S_0 (solid squares) and far from the surface S_∞ (open circles) under appropriate anisotropic interaction energies.

magnetic solid with magnetization M in an external field H . In the present case, the surface acts as an ordering field and gives rise to an effective $-H_{\text{surf}}S$ term. On the other hand, the ordering terms in the bulk free energy start from quadratic in S , so that the surface nematic order should exist up to smaller S (higher temperature). In this way, this simple theory well explains the present experimental results. It is noted that Sheng [30] also theoretically predicted the boundary layer transition, supporting our results and discussions. Detailed analysis will be reported in a separate paper in the near future [26].

Finally, we want to note that distinct thermodynamic phase transitions at the surface and in bulk exist for LC but occur at different levels. That is, whether or not the surface transition can be observed in LC systems is mainly governed by the following parameters, (1) sensitive balance of affinity or interfacial energy between LCs and surface materials, and (2) the degree of interaction between LCs and surface, which depends on the interfacial area of surface material in contact with LCs.

In conclusion we conducted highly sensitive DSC (HS-DSC) and retardation measurements in the vicinity of the Iso-N phase transition using mainly polymer-dispersed liquid crystal systems. We found distinct double phase transition peaks in HS-DSC and assigned them to the transitions at the surface and in bulk. Precise retardation measurements showed a pretransitional increase followed by a small jump before a pretransitional increase toward the N phase when samples were slowly cooled. The surface pretransitional behavior is coincident with the HS-DSC and polarizing microscope observation. Such double phase transitions at the surface and in bulk are a general phenomenon in the Iso-N phase transition at least in a system with a high interfacial energy, as we briefly showed theoretically.

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