

Stepwise heat-capacity change at an orientation transition in liquid crystalsSatoshi Aya,¹ Yuji Sasaki,² Damian Pocięcha,³ Fumito Araoka,¹ Ewa Górecka,³ Kenji Ema,⁴ Igor Muševič,⁵ Hiroshi Orihara,² Ken Ishikawa,¹ and Hideo Takezoe¹¹*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S8-42 O-okayama, Meguro-ku, Tokyo 152-8552, Japan*²*Division of Applied Physics, Graduate School of Engineering, Hokkaido University, North 13 West 8, Kita-ku, Sapporo 060-8628, Japan*³*University of Warsaw, Department of Chemistry, ul. Żwirkkii Wigury 101, 02-089 Warsaw, Poland*⁴*Department of Physics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo 152-8551, Japan*⁵*Condensed Matter Physics Department, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

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During a phase transition in a bulk material, heat is exchanged with matter to balance the changes in the internal energy and the entropy of the system. Here we report on the thermal detection of a surface-mediated anchoring transition, a spontaneous and discontinuous orientation change between planar (P) and homeotropic (H) alignments within a single nematic phase by changing temperature. In this case a stepwise change in the heat flow, similar to a glass transition, is observed by means of high-resolution differential scanning calorimetry. We found that the jump in the specific heat does not depend on the sample volume, although the contribution of molecules in the vicinity of surfaces, which trigger the transition, becomes less with increasing the sample volume. This means that different molecular orientations, H and P, with respect to surfaces have different thermodynamic free energies. We also address why the anchoring transition occurs by means of grazing-incidence x-ray diffraction measurements, which clearly reveal the formation of quasismectic layers parallel to surfaces in the nematic phase.

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I. INTRODUCTION

Phase transitions have always been a central issue in thermodynamics and statistical physics because they are associated with the onset of important physical properties, such as ferromagnetism [1], superconductivity [2], and superfluidity [3]. A phase transition occurs due to the competition between the cooperative atomic (molecular) interaction energy and the entropy of the system. Any phase transition is therefore associated with an exchange of heat to the thermal environment of the system that balances the changes in the internal free energy. Measuring the heat flow is therefore an effective method for characterizing phase-transition properties and many different calorimetric techniques have been developed and applied so far.

The orientation of nematic (N) liquid crystal (LC) molecules is greatly affected by contacting surfaces through the so-called anchoring effect. Hence, the LC molecules in a spatially confined geometry exhibit diverse alignments in response to the boundary conditions and configurations [4–6]. The confining surfaces interact with the LC molecules at the surface and the imposed molecular orientation propagates into the bulk. Thus far, it is well known that the nematic order near the surface is generally different from that in the bulk, which leads to different molecular organizations and even to distinct isotropic-nematic (Iso-N) phase-transition temperatures at the surface and in the bulk [7,8]. However, the precise role of how the microscopic surface LC structure is affecting the macroscopic LC alignment is as yet unknown, and any prediction of the molecular surface alignment resulting from complicated energetic and entropic contributions is difficult. Nevertheless, the anisotropic wettability of the substrate by LC molecules and its controllability are essential for any LC-based technology [9].

Here we report on the thermal observation of a unique transition in NLCs that is associated with a spontaneous and abrupt change in the orientation of the LC molecules at the confining surfaces. This change in the surface anchoring of the LC molecules triggers the reorientation of the LC in the bulk. In general, LC molecules prefer a given and unique orientation at the confining surface that is either parallel (planar, P) or normal (homeotropic, H) to the interface. The spontaneous reorientation of LC molecules at the interface, also called the surface-anchoring transition (ATr), occurs within a single N phase, consisting of a single-component substance. We tackled two questions related to this surface-anchoring transition and found intriguing results: (i) Is the surface-anchoring transition in a NLC thermally detectable? Yes, it is observed as an abrupt and stepwise change in the heat flow, with negligible latent heat, although it is a first-order transition, characterized by domain nucleation and a large thermal hysteresis; (ii) Why does a surface-anchoring transition occur? It is because smectic (Sm) layers of LC molecules start growing parallel to the interface in the N phase. We will discuss how both surface-orientation states are thermodynamically different. Their behavior is similar to the glass transition [10,11], and this is an example of an unconventional transition.

II. EXPERIMENT

A 3 wt % solution of poly[perfluoro(4-vinyl-1-butene)] (CYTOP, Asahi Glass Co., Ltd) was prepared using the CTX-800A solvent (Asahi Glass Co., Ltd). It was deposited on an indium-tin-oxide (ITO) coated glass substrate by spin coating, then dried at $\sim 100^\circ\text{C}$, typically for 1 h. In addition to the CYTOP surface, a standard polyimide surface (AL1254, JSR Corp.) producing a stable planar alignment was also used for comparison. The NLC material used was 4'-butyl-4-heptyl-

bicyclohexyl-4-carbonitrile (CCN47, Merck), which has a negative dielectric anisotropy and the phase sequence Cry-25.6°C-SmA-28.3°C-N-58.3°C-Iso, where Cry and SmA stand for crystal and smectic A, respectively.

We used high-resolution differential scanning calorimetry (HR-DSC) [12–14] with a sensitivity of a few tens of nanowatts. In this experiment, contrary to the conventional encapsulated metal-type cell, we confine CCN47 into sandwich cells composed of thin glass substrates, whose surfaces are spin coated with CYTOP. This is done to realize the same experimental conditions as used in other experimental techniques, such as polarizing microscopy (PM). The size of the cell was fixed (i.e., the surface area was held constant, 100 mm²) and only the cell gap was adjusted by microparticles with uniform sizes dispersed on substrates. The measurements were carried out in an argon atmosphere with a very slow temperature scan rate of ± 24 mK/min over the entire monitored range, which makes it possible to reach the thermal equilibrium condition regardless of a small thermal conductivity on the glass substrates.

X-ray diffraction (XRD) measurements using traditional systems are not a surface-sensitive method, since an x-ray radiation beam has a large penetration depth into materials. In the present study, we carried out grazing-incidence XRD (GI-XRD) measurements using the Bruker x-ray general area detector diffraction system (GADDS, Cu $K\alpha$ line, $\lambda = 1.5414$ Å). The GI-XRD method allowed us to probe interfacial peculiarities on nanometer scales, thus maximizing the signal from thin layers [15]. Both microdrops and sandwich cells were used as samples.

III. RESULTS

A. Texture observation

The LC orientation results from the fact that, for ordinary interfaces, there is only one free-energy minimum, representing a balance between the internal energy and the entropy. As a consequence, there is only a single and permanent orientation of the LC molecules at the interface. The ATr, which we focus on here, is a thermally induced phenomenon, during which the constituent LC molecules (CCN47) in contact with a super-low-energy surface (CYTOP) change their orientation spontaneously and discontinuously by changing the temperature [16]. This means that the LC orientation has two free-energy minima in a certain temperature range: one corresponding to the P state, the other to the H state. In Fig. 1(a), PM images show that the two states in the N phase shuttle between P (bright, at higher temperatures; N_P) and H (black, at lower temperatures; N_H). The texture in the second left of Fig. 1(a) clearly reveals the coexistence of the H (black) and the P (bright) states. We must stress that this transition occurs in a single N phase consisting of a single-component LC. Moreover, a distinguishing property is that the system exhibits a large bistability region of around 5–10 K [16–18]. Thus, the origin of the surface bistability could be linked to the fundamental issue of unlocking how the surface atoms interact with the bulk LC molecules and force them to reorient in another direction. Previous observations, such as the changes in light transmittance, dielectric constant, and microscopic

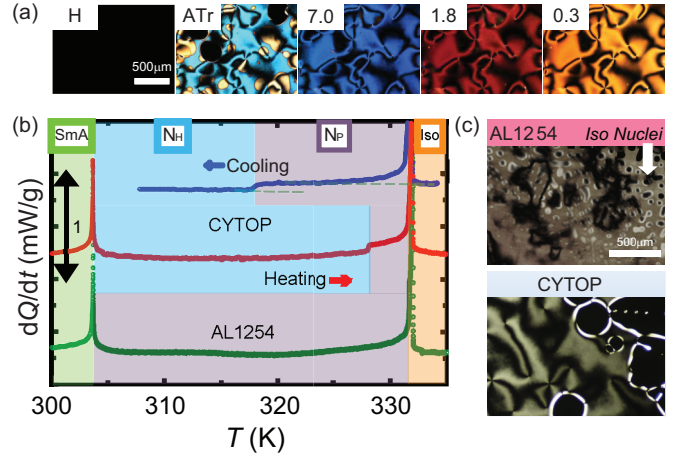


FIG. 1. (Color online) Anchoring transition observed in the N phase of CCN47 in a cell with CYTOP surfaces. (a) Texture evolution on cooling in a CYTOP cell. The labeled numbers stand for the temperature difference from the Iso-N phase-transition temperature. First, the P state emerges as typical schlieren textures with two and four brushes (three in the right). At T_{ATr} , the domains of the H state are observed as dark spots (second left). In the SmA and N_H temperature windows, a dark image persists (left), signifying that the molecules point to the surface’s normal direction (parallel to the viewing direction). (b) HR-DSC charts in a 25- μ m-thick CYTOP cell upon both cooling and heating. The result in a 25- μ m-thick AL1254 cell upon cooling is also shown. The base lines of three HR-DSC charts are properly shifted. A double-angled scale bar corresponds to 1 mW/g. Dashed lines are drawn to emphasize that the heat flow in the H state is smaller than that in both the N_P and Iso phases in the CYTOP cell. (c) The nucleation of Iso domains in the N phase for both AL1254 and CYTOP surfaces. Clearly, AL1254 has a greater ability to create nuclei, i.e., a strongly wettable surface.

texture [16–18], were used to detect the orientation change of the molecules at the ATr transition. Here, we provide a deeper insight into the physics of this phenomenon by using HR-DSC and GI-XRD.

B. Thermal measurements

In order to reveal the distinctive thermodynamic phenomena that separate the ATr from the other LC phase transitions, we utilized HR-DSC [12–14]. The measured heat flows in CCN47 cells with CYTOP surfaces and AL1254 surfaces are shown in Fig. 1(b). First, the heat anomalies of the SmA-N transition at ~ 303.8 K and the N-Iso transition at ~ 331.9 K are clearly captured for both surfaces. The liquid crystal CCN47 on the AL1254 surface shows no ATr, resulting in a smooth DSC curve in the nematic range. In contrast, a remarkable stepwise change in the heat flow appears at the ATr temperatures T_{ATr} [19]; ~ 328 K (~ 318 K) upon heating (cooling) for the CYTOP surfaces, at which the LC molecules change their orientation from the H (P) to the P (H) states. Despite the giant thermal hysteresis of ~ 10 K, reflecting the first-order nature, a quasistepwise change in the heat flow at T_{ATr} does not accompany any measurable latent heat L . This is different from the normal LC and crystalline phase transitions, which normally involve a substantial latent heat [20–22]. This

means that the heat flow rate per unit volume $\frac{dQ}{dt}$ is directly associated with a thermodynamically “sensible” parameter, i.e., the specific heat capacity C_p , $\frac{dQ}{dt} \sim C_p$. Note also the different nucleation of Iso domains in the N phase for AL1254 and CYTOP surfaces [Fig. 1(c)], as will be discussed later.

Enlarged views of the DSC curves are shown in Fig. 2(a) for cells with different thicknesses, w , upon heating. We

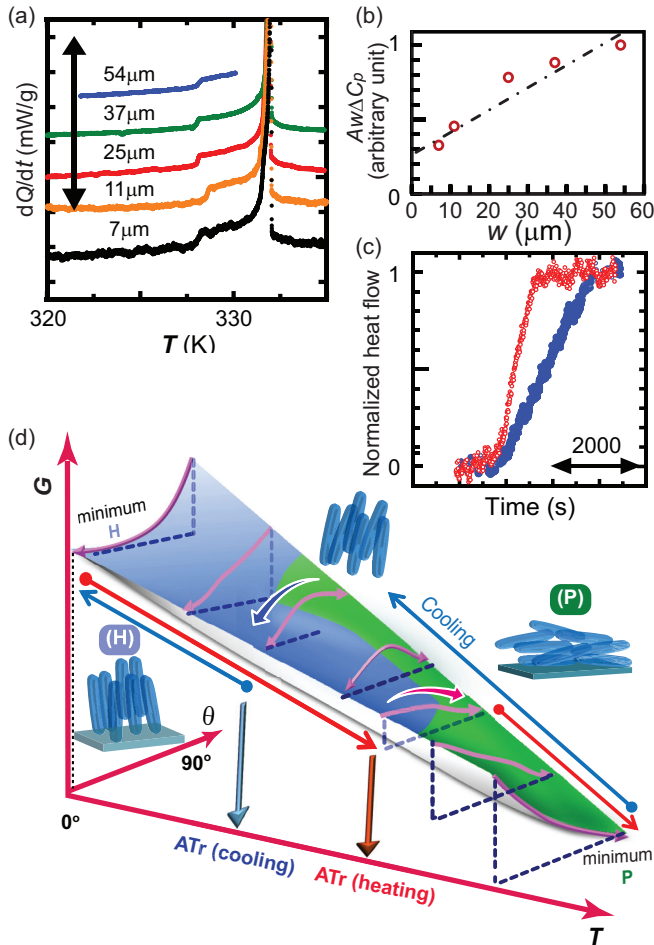


FIG. 2. (Color online) (a) Detailed DSC chart around T_{ATr} for cells with various thicknesses on heating. Despite the unchanged T_{ATr} , the magnitude of the jump in heat flow is nearly independent of the cell thickness, but increases slightly with decreasing cell thickness. Since $\frac{dQ}{dt}$ is scaled (a double-angled scale bar: 1 mW/g) by each sample volume, it is equivalent to a specific heat capacity. The baselines are properly shifted. (b) Total heat flow change upon ATr in each sample as a function of cell thickness. (c) Variation of heat flow with time upon both cooling (closed circles, slow growth) and heating (open circles, fast growth). (d) Schematic Gibbs free energy (G) vs temperature (T) and molecular tilt angle (θ), and the accompanying ATr processes in a CYTOP cell. Because the CYTOP surface reduces the distinction between two states, P and H, both free-energy curves can intersect, unlike normal surfaces that prefer only one alignment. In low- and high-temperature regions far from ATr, the stability of the H and P states is quite different, leading to a preferential alignment, whereas a metastable (superheated or supercooled) region appears due to the energy barrier between the two states, resulting in bistability.

note that w is proportional to the mass of the sample, since the surface area A is identical in all cells (100 mm²). An important observation is that the magnitude of the step at T_{ATr} , i.e., an ATr-assisted C_p change, is almost independent of the sample thickness. This observation indicates that the C_p change is mainly attributed to the bulk. In contrast, when we look closely at the total heat-flow (heat-capacity) change $Aw\Delta C_p$ versus the cell thickness w [Fig. 2(b)], a nearly linear dependence with a finite value at a cell thickness of zero is seen. Namely, the DSC signal is attributed to the surface-mediated rearrangement of the bulk orientation. As a result, the stepwise C_p change through the N_H - N_P ATr indicates an immediate increase in thermal fluctuations, showing that the P state is more disordered than the H state.

IV. DISCUSSION

A. Thermodynamic consideration

Considering the heat capacity of the bulk LC compounds is typically around 1.5–2.0 J K⁻¹ g⁻¹, the change in the magnitude of a step ~ 0.2 – 0.3 J K⁻¹ g⁻¹ corresponds to a 10%–20% increase in the net C_p value. Thus, this is not as drastic a change as seen in ordinary phase transitions. The probable reasons for this different thermal fluctuation energy between the H and P states are as follows. First, the longitudinal translational symmetry near the surfaces is broken in N_H [23], and the restricted degrees of freedom due to the different boundary conditions result in weaker long-range director fluctuations, thus causing a weaker bulk molecular fluctuation motion partly because of the fluctuations’ limited wavelength. This is consistent with the observation that the jump in the heat flow per volume at the ATr is larger in thinner cells, because the fluctuation wavelength is more restricted. Therefore, the N_H - N_P ATr can be regarded as an order-disorder transition via a surface-wetting process. A typical analogous behavior can be found in the glass transition, in which the background contribution of the specific heat capacity also shows a stepwise change in the heat flow due to the loss of internal degrees of freedom [24,25]. Moreover, the change in the internal energy is qualitatively confirmed by the dynamic process of domain growth, which is related to the diffusion of molecules. As can be seen from Fig. 2(c), the time scale for the nucleation and growth of the P domains (heating) is much shorter than that for the H domains (cooling), indicating that the P state is more diffusive because of the larger fluctuations in addition to the inherent higher diffusivity due to higher temperature.

The first-order N_H - N_P transition can be described with a free-energy form using anchoring coefficients [26,27]. As mentioned above, the latent heat, which generally comes from the potential energy stored in the intermolecular interactions, is very small. The negligible latent heat indicates that the potential energy does not change very much after the ATr. Considering the present system, where both N_H and N_P are in the single N phase, this result is reasonable because macroscopic molecular orientations are the same, except for those in the vicinity of the surfaces. Then, why is a large temperature hysteresis possible? In order to discuss this, we consider a nucleus of N_P in N_H media. The energy barrier for

the ATr can be considered as an elastic distortion energy of the surface defects [28] surrounding the N_P region, whereas the energy barrier originates from the surface tension of the phase boundary separating two phases in normal phase transitions. As discussed in Ref. [27], the critical radius of the nuclei for the transitions would be the size of $\sim K/|\Delta f|$. Here, K is the elastic constant and Δf is the free-energy difference, $\Delta f = f_P - f_H$, which is small, as mentioned above. As a result, the nucleation barrier $\sim K^2/|\Delta f| \gg k_B T$ becomes large. Therefore, even when the energy minima of N_H and N_P change and ATr occurs, a large temperature hysteresis is realized because of the much higher nucleation barrier compared with the thermal fluctuation energy $k_B T$. In addition, no pretransitional heat-capacity change in the vicinity of the transition is also consistent with the small thermal fluctuation of the system.

Now, let us discuss why a low-energy CYTOP surface is crucial for the occurrence of ATr. The low surface energy of the CYTOP was already proven by the large contact angle measured for water ($\sim 114^\circ$) [29] and CCN47 ($\sim 62.1^\circ$) droplets. In addition, as shown in Fig. 1(c), the formation of Iso domains on approaching the N-Iso transition is quite different on the CYTOP and AL1254 surfaces; the slower nucleation rate and associated larger Iso domains on the CYTOP are due to the low wettability and the low surface energy. On a strongly interacting surface with LC molecules, we would have one stable alignment as obtained generally, like on AL1254. However, low-energy surfaces, such as CYTOP, can substantially decrease the energy difference between the two states. Hence, the P and H states get the CYTOP surfaces equally wet, which is responsible for the appearance of the metastability. Then, how is the particular state chosen at each temperature? It is known that LC molecules tend to be parallel to flat surfaces (P state) due to the anisotropic excluded volume interaction, which dominates the determination of the surface orientation of nematic molecules [30]. This is the reason why the P state is chosen in the metastability condition at high temperatures in the N phase. It is also known that the low-energy CYTOP surface strongly favors and stabilizes the SmA structure [29], since the layer structure parallel to the surface makes the surface interaction a minimum. Remember that the anisotropic surface coupling to molecules near the surface typically triggers spontaneous symmetry breaking at the surface, irrespective of the nature in the bulk [7]. Thus, we propose the following mechanism for the reorientation behavior observed: the two-dimensional growth of the quasi-SmA structure on the CYTOP surfaces in the N phase induces the discontinuous ATr.

B. Origin of anchoring transition

To ascertain the key structure (quasi-SmA structure on the surface) for ATr, we carried out GI-XRD measurements. Figures 3(a) and 3(b) present the results using a microdroplet and a sandwich cell, respectively. Figure 3(a) shows how the diffraction pattern evolves with temperature. The CYTOP surface provides distinct characteristics: below the Iso-N phase-transition temperature, well-defined directed diffractions appear. The splitting directions are perpendicular to each other in the small- and wide-angle XRD (SAX and WAX)

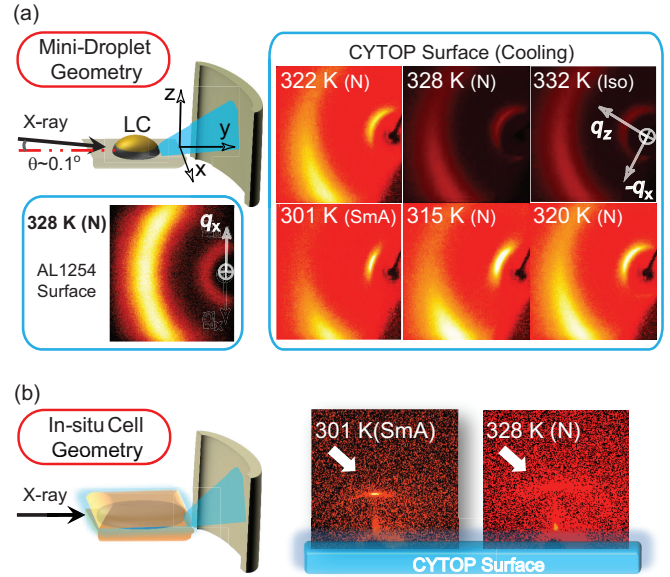


FIG. 3. (Color online) GI-XRD measurements in two sample geometries; (a) In the microdroplet geometry, the incident angle (θ) of the x ray is fixed at 0.1° to ensure the total reflection condition on the alignment surface. All the data were taken on cooling. For the CYTOP surface, a ring pattern in the Iso phase reflects the isotropic orientation of the LC molecules. Sharp SAX signals, indicating well-aligned surface-layer structures, can be confirmed immediately when cooling down to the N phase. The orthogonal splitting directions of the SAX [wave vector, q_s ($\parallel q_z$) = 0.302 \AA^{-1}] and WAX [q_w ($\parallel q_x$) = 1.202 \AA^{-1}] signals indicate a SmA-like structure. The existence of a layer structure parallel to the surfaces indicates the formation of SmA-like layers parallel to the surfaces. The intensity and sharpness increase with decreasing temperature, implying the development of the surface-induced quasi-SmA structure. In contrast, both SAX and WAX patterns exhibit rings and no observable surface Sm-like structure can be found on the AL1254, even in the lower temperature range of the N phase. (b) Similar XRD results as those in the microdroplet geometry were found for the *in situ* cell geometry. The SAX signals locate at the poles, indicating the SmA-like layer running parallel to the surface.

signals, and the SAX signal (layer diffraction) is stronger than the WAX signal. This unambiguously confirms that SmA-like surface-layer structures are formed parallel to the surface. With decreasing temperature, these signals become stronger due to the increase of both the order parameter and the surface coverage. The same behavior was confirmed in a sandwich cell [Fig. 3(b)]. On the other hand, the diffraction patterns on AL1254 used for comparison ([Fig. 3(a), left bottom]) obviously appear as ring patterns, in both small and wide angles, indicating the isotropic molecular arrangement. Moreover, the SAX signals are much smaller than the WAX signals, which is also typical for bulk NLCs. These results verify that the SmA-like surface layer is the driving force of the ATr, as expected.

V. CONCLUSION

By combining macroscopic (HR-DSC) and microscopic (GI-XRD) property observations, i.e., the stepwise change in

the heat flow and the emergence of a surface SmA-like wetting structure, respectively, we unveiled the ATr phenomenon. We demonstrate that the surface-assisted metastability, which originates from the competition between the different fluctuating conditions in the P and H states resulting from the surface wetting layer, governs the ATr. In other words, the quasi-SmA layers at the CYTOP surfaces initiate ATr, at which the heat anomaly (latent heat) is too small to be detected, even in HR-DSC. Instead, a stepwise change in the heat flow is detectable, and the excited H (or P) orientation propagates and ultimately controls the bulk. This anisotropic wetting nature

on the low-energy surface has the potential to control both the microscopic and macroscopic molecular orientations, and provides interesting perspectives to understanding how the anisotropic microscopic nature can achieve metastability and influence the macroscopic natures.

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