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Critical behavior in an electric-field-induced anchoring transition in a liquid crystal

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We report an anchoring transition of a liquid crystal under the influence of an electric field (E field) in the vicinity of a first-order anchoring transition (ATr) temperature showing bistable homeotropic (H) and planar (P) states. By means of polarizing microscopy combined with retardation and switching and dielectric measurements, three important observations were made: (1) The anchoring transition from H to P driven by an E field is first order with a threshold E-field strength, which decreases with increasing temperature; (2) the thickness of the H layer that is to be converted to the P orientation increases toward ATr temperature T_{ATr}; and (3) the temperature dependence of both parameters is well described by a power law.

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Many examples of an orientational change of liquid crystal (LC) molecules, referred to as an anchoring transition (ATr), have been reported [1–5], showing either first or second order depending on the complex interplay of heterogeneous interactions: steric interaction, dispersion forces, short-range dipolar interaction, long-range electrostatic interaction, anisotropic elastic interaction, and so on. This temperature-driven orientational transition has attracted much attention from theoretical and experimental viewpoints for understanding the fundamental mechanism involved in as well as for realizing new thermal and electro-optic device modes [2]. From a scientific viewpoint, it is interesting to consider the anchoring transition as a wetting-dewetting transition, although the phase involved is uniform. In this Rapid Communication, we represent an anchoring transition, from a homeotropic (H) to planar (P) state, induced by an electric field (E field) on heating. Toward the ATr temperature T_{ATr}, the thickness of the H layer significantly grows to cell thickness along with a decrease of the threshold E field. The threshold E field, at which the anchoring transition from H to P is completed, decreases with increasing temperature. Both temperature dependences are well described by a power law, as in wetting-dewetting transitions.

A 3 wt% solution of poly[perfluoro(4-vinyloxy-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 ∼100 °C, typically for 1 h. The nematic (N) LC (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, SmA, and Iso stand for crystal, smectic A, and isotropic phases, respectively. The cell thickness used was 5 μm, unless otherwise stated. The cells were observed under a polarizing microscope (PM) in conjunction with a Mettler hot stage to control the sample temperature with ∼±0.1 °C accuracy. Retardation resulting from a planar or hybrid layer was measured with a Berek compensator (Nichika Inc.), which is generally utilized to ascertain the birefringence. To elucidate the detailed orientation of LC molecules over the whole sample, the capacitance measurements at 1 kHz were also carried out concomitantly with PM as a function of temperature. The anchoring transition is readily detected by a change in the capacitance; larger and smaller capacitances (dielectric constants) correspond to P and H orientations, respectively.

Let us first show the spontaneous ATr in the absence of an E field. Figure 1 shows the temperature dependence of the dielectric constant ε, together with the corresponding texture change. Upon cooling, the dielectric constant shows a small jump to a larger value at the Iso-N phase transition (dashed line), indicating P alignment because of the large negative dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} < 0$). Under PM observation, both two- (in the majority) and four-brush schlieren textures arise [Fig. 1(b), top]. It is worth noting that the two-brush schlieren texture (disclinations with half integral strength, $s = \pm 1/2$) is not topologically allowed in the director field with a large pretilt [6]. By lowering the temperature to ∼48.5 °C (dotted line), an abrupt decrease in ϵ corresponding to a $P \rightarrow H$ orientational transition takes place. It is evident from the large discontinuity in ϵ that the ATr is of first order. As reported previously [4], a giant hysteresis around 5 °C was observed in ATr; ATr occurs on heating at ∼52.3 °C (dotted line). Texture evolutions on cooling and heating are shown in Figs. 1(b) and 1(c), respectively.

Now, we describe the E-field effects on ATr; we heated an H-aligned sample to the bistable temperature region, where the H state was preserved, and applied an E field. Because $\Delta\epsilon < 0$ for CCN47, an E field stabilizes the P state. In this way, an *E-field-induced ATr* from H to P occurs. Similar measurements, ATr from P to H on cooling, have been done under the influence of an E field [7]. However, the situation is quite different from the present case. In the present study, we observed *E-field-induced ATr* under fixed temperatures, which is possible because an E field destabilizes the original H state. However, in the previous work by Kumar *et al.* [7], the original state is P in the bistable region. Since the E field further stabilizes the original P state, the same experimental condition as in the present case, i.e., varying E under a fixed

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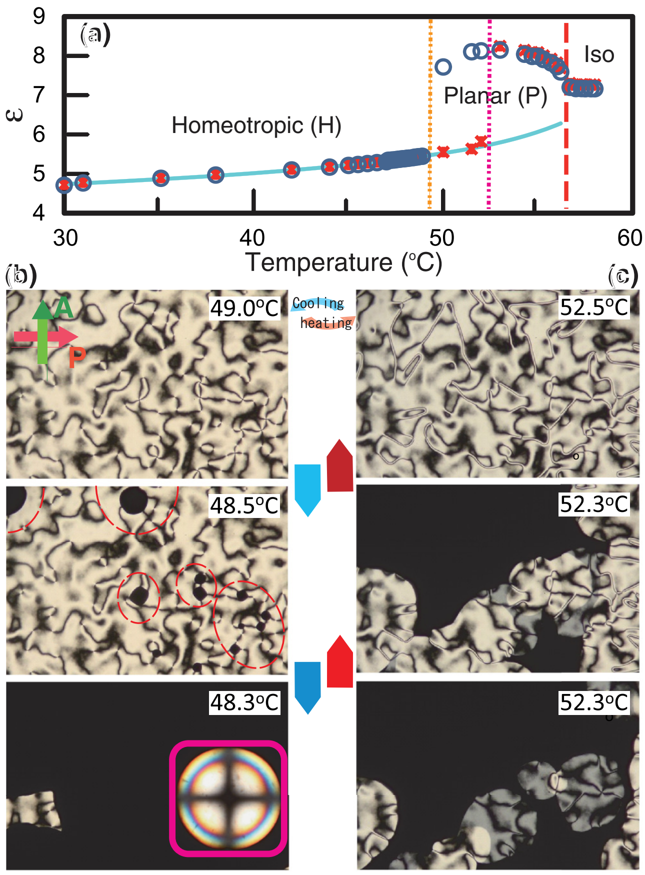

FIG. 1. (Color online) (a) The temperature dependence of the dielectric constant measured upon both cooling (open circles) and heating (cross marks). Texture variation on (b) cooling (blue downward arrows) and (c) heating (red upward arrows). (b) Top: The planar state appears just below the clearing point. (b) Middle: At T_{ATr}, the H state emerges from the point defect of a predominately four-brush schlieren texture (red dashed circles). (b) Bottom: The H state expands and covers the whole view field as supplemented by an inset of a conoscopic image. (c) Bottom: Upon heating, the dark and bright schlieren textures can be seen, suggesting the coexistence of thin and thick layers with a P orientation. (c) Middle: Dark domains are transformed to bright domains. (c) Top: The entire director field is covered by a P state with a thin four-brush schlieren texture, differing from the initial P state in the width of brush.

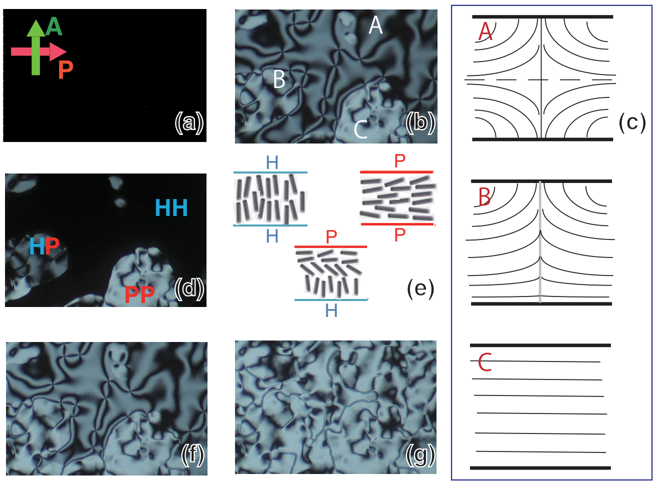

FIG. 2. (Color online) Photomicrographs at 49.7 °C. (a) Zero field. (b) Under an E field very close to $E_{H\to P} \sim 0.31$ V/μm. (c) Schematic representation of director configurations of areas A, B, and C. (d) After an abrupt termination of the E field. (e) Graphic diagrams for complete H (HH), bent-splay (HP), and complete P states (PP) for each state in (d). (f), (g) Application of a higher E field ($\sim$0.49 V/μm) to promote ATr, where the P state quickly grows and propagates to cover the whole regime (see text).

T, cannot be adopted. Hence they decreased the temperature under fixed E's. Namely, they observed *temperature-induced ATr* under fixed E's.

We need to define two thresholds in the present experiments: (1) the threshold voltage of the Freedericksz transition V_{th}, which is defined as the voltage at which the director reorientation starts to occur in bulk and is independent of cell thickness as in the conventional Freedericksz transition, and (2) the threshold field of ATr $E_{H\to P}$, which is defined as the field above which ATr from H to P is completed, i.e., no H layer remains after terminating the E field above $E_{H\to P}$, whereas an H orientation is recovered from the emergence of the P orientation if the applied field is below $E_{H\to P}$. This definition is justified by the fact that, once one surface undergoes the dewetting transition by an E field, it expands and promotes the other surface to do so by only slightly increasing the E field, and finally comes up to cover the entire area.

In order to understand the *E-field-induced ATr*, a texture observation was made at 49.7 °C. Figure 2 illustrates the texture evolution by applying an E field to the original H state [Fig. 2(a)]. Bulk birefringence appears above the threshold voltage V_{th}. Subsequently, ATr occurs with the formation of a surface P orientation [B and C in Fig. 2(b)]. Three distinct areas A, B, and C in Fig. 2(b) correspond to the structures shown in Fig. 2(c). Note that Figs. 2(b) and 2(d) are reversibly interchanged by an E field very close to $E_{H\to P}$, ($\sim$0.31 V/μm) on and off. In the absence of an E field [Fig. 2(d)], the areas A, B, and C relax to HH, HP, and PP states [Figs. 2(d) and 2(e)]. Actually the effective birefringences in the HP and PP domains that are estimated by using a Berek compensator agreed with those for both splay-bent ($\Delta n \sim 0.016$) and planar ($\Delta n \sim 0.034$) states that were determined by using hybrid and rubbed planar cells, respectively. A complete planar state over the whole area can be also achieved in the absence of an E field, after an E field that is higher than $E_{H\to P}$ is applied and the planar parts cover the viewing field [Fig. 2(g)], as shown in Fig. 2(f). It is worth noting that the planar texture exhibits thin four-brush disclinations [Fig. 2(g)] which are very similar to those obtained just after ATr upon heating with zero field [Fig. 1(c), top].

Such orientational changes starting at the surfaces can be regarded as a dewetting transition. Actually, H-aligned layers at the surfaces are differentiated from bulk orientation, where P and tilted orientations are realized by an external E field. Hence the ATr can be regarded as dewetting of the H layer. Over the past decades, a wide variety of experiments and theoretical studies have concentrated on surface wetting and dewetting by the fluid [8–17]. Generally, the wetting (or dewetting) transition is a first-order surface phase transition. In the field of soft matter such as LC systems, the anisotropic part of surface free energy should be taken into account because of the intrinsic diverse anisotropic forces between LC molecules such as long- and/or short-range orientational or positional orders, etc. [18]. Peculiar properties observed in LC systems make the wetting characteristic features more complicated and attractive. Recently, several works focusing on an anisotropic wetting transition have appeared. The most famous one is the Sm LC layer growth from Iso bulk, where a discrete change occurs in the number of emerging layers with a change in temperature [19,20]. Another intriguing (pre)wetting transition is the surface transition that was recently observed in a NLC by our group [21–23]. From both experimental and theoretical approaches [24], we have clarified that a surface can act as an external field (anchoring) for LC molecules to enhance or weaken the molecular orientational order parameter. As a result, the surface Iso-*N* transition, i.e., the nematic surface wetting transition, occurs well separated from the bulk phase transition.

The present dewetting differs from conventional wetting and dewetting phenomena, in the sense that only an orientational change of molecules at surfaces occurs instead of changing the phase, i.e., symmetry [Fig. 2(c)]. It is known that surface wettability with a new phase is seriously influenced by the surface order parameter S_{surf} [21–23,25,26]. For instance, for a liquid-liquid phase transition the relevant order parameter Q is the number density near a surface [25]. Murata and Tanaka have proposed that such a difference in the order parameter, i.e., the number density, between the bulk and the portion near a surface triggers the emergence of a new liquid state at the surface. Namely, the fluctuation in the number density near a surface changes the wetting property, and promotes the new liquid state to emerge in order to lower the total free energy in the global system. In the present case, the key factor dominating dewettability of the H state may be a specific interaction of a microscopic nature between surface and LC molecules. Smecticlike order adsorbed on the CYTOP surface is a leading candidate, as confirmed by x-ray diffraction, which will be reported in the near future. The fact that CYTOP gives a stable H alignment of smectic LCs [27] is consistent with this consideration. Let us briefly explain why the orientational structure transition can be closely related to the liquid-liquid phase transition mentioned above. First, we emphasize that the existence of smectic order in the nematic phase influences local microscopic order parameters, because the elastic constants and wettability at surfaces are different from those in the pure N phase. Hence the orientational transition occurs depending on the development of smectic order at the surfaces, which can be regarded as a counterpart to that in the liquid-liquid phase transition, i.e., the number density gradient.

To investigate the ATr as a dewetting transition more quantitatively, we measured the effective thickness of the H dewetting layer (W_H) and $E_{H\to P}$. To estimate W_H, accurate birefringence was measured by utilizing a cell with weakly rubbed surfaces imposing a uniform molecular alignment. We measured the retardation in the condition of A and C [see Fig. 2(c)] under an E field just below and above $E_{H\to P}$ by a Berek compensator. We regarded structure A as consisting of a uniform P layer in the bulk and two H layers at both surfaces. The retardation difference between A and C is twice the surface contribution. Using $\Delta n \sim 0.034$ for a P state, we can estimate W_H. The temperature dependences of the dewetting layer thickness and $E_{H\to P}$ are shown in Fig. 3. Two important observations have to be made: (1) $E_{H\to P}$ approaches asymptotically to a certain value, ~0.20 V/μm, at higher temperature near T_{ATr}. (2) At a temperature closer to T_{ATr}, a thicker H dewetting layer is formed. It is clear that these values are mutually correlated. Upon approaching T_{ATr}, a weaker E field is necessary to induce the dewetting transition, so that thicker surface H layers can suddenly dewet, being replaced by P orientation.

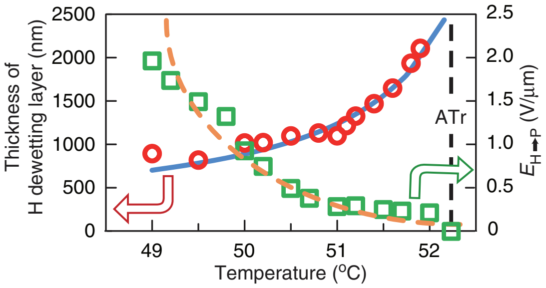

FIG. 3. (Color online) The variation of threshold E-field strength in order to convert H to the P state (open squares), and the effective thickness (nm) of the H dewetting layer (open circles) with temperature. The dashed and solid curves are the best fittings by a power law.

It is worth noting that, with elastic effects in LCs, orientational (de)wetting at surfaces strongly imposes the LC molecules toward a preferred orientation. As the key factor dominating this phenomenon should be a specific interaction of microscopic surface properties, we take elastic effects into theoretical consideration qualitatively and propose the following physical picture for the dewetting process of the H layer. Assuming a system containing only an H state and a CYTOP surface, hereafter the surface is referred to as S. Under the present circumstance, with P in the bulk due to the Freedericksz transition, elastic deformation exhibiting a bend-spay molecular structure exists near the surface, *S-H-P-H-S*. Up to the crossover thickness of H, this conformation will give the lowest energy. Since the elastic energy around the surface increases with increasing E-field strength, the H state near a surface transforms to P (complete H dewetting) in order to minimize the free energy. It is known that the growth of a nematic wetting layer near the Iso-N transition temperature is governed by competition between interface interaction energies among the substrate surface, nematic, and isotropic liquids [18]. This is analogous to the growth of isotropic liquid wetting layers in vapor, n-alkane [13], and superfluid He [17] systems. In the present case, however, some complications due to the tensor nature of the nematic order parameter play a great role in E-field-induced ATr. The key is a free-energy cost due to elastic deformation near a surface under an E field; there is a critical elastic free-energy density to destabilize the surface H state and dewet, which governs the values of W_H and $E_{H\to P}$ at each temperature. In turn, the surface layer with P orientation stabilizes the bulk P state.

Lastly, we discuss the temperature dependences of the two important parameters, $E_{H\to P}$ and W_H, which are mutually correlated, since W_H's are defined at respective $E_{H\to P}$'s. The former and the latter show diminishing (green squares in Fig. 3) and quasidivergent (red circles in Fig. 3) critical-like behaviors with increasing temperature, respectively. The temperature dependence of $E_{H\to P}$ is well fitted by $[(T - T_{d1})/T_{d1}]^{-b1}$ with exponent $b1 \sim 1.1$. On the other hand, W_H increases until it reaches half the cell thickness (∼2.4 μm) because of the present confined geometry. This behavior is also well fitted to $[(T_{d2} - T)/T_{d2}]^{-b2}$ with $T_{d2} = 53.2\,^\circ$C, which is very close to higher T_{ATr} (∼52.3 °C), and exponent $b2 \sim 1$. The measurements were also carried out using a 50-μm-thick cell. The temperature behaviors of $E_{H\to P}$ and W_H are essentially consistent with those in a 5-μm-thick cell, including the value of the exponent. The critical-like behavior described above could provide further information for a general understanding of the dewetting transition and also provoke a detailed theoretical approach.

In summary, we investigated a significant E-field effect on ATr, which is induced by specific interactions between the surface and LC molecules. It was shown that for the emergence of a new P state from the initial H state within the bistable temperature range, there is an absolute requirement to overcome the free-energy barrier between the two ordered states. The distinction between this phenomenon and conventional wetting and dewetting phenomena was discussed on the basis of a dewetting transition, where an H-aligned layer was dewetted and replaced by P orientation. We can control the occurrence of H dewetting either by T or E-field variables. The temperature dependences of the thickness of the H dewetting layer and the threshold E field for dewetting were found to be described by a power law. This study opens a new physics for the anisotropic (de)wetting phenomenon and offers a possibility to control anisotropic patterns of soft matters using (de)wetting features.

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