Anchoring Transition of Liquid Crystals on Crown Ether Monolayers

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The monolayer films of a double-armed crown ether liquid crystal have been prepared under low and high surface pressures, which can produce homogeneous and homeotropic alignments of liquid crystals, respectively. The anchoring transition has been interpreted as the result of a conformation change of the aligning agents. This is the first clear experimental demonstration that a conformation change of aligning molecules can induce an anchoring transition of liquid crystals.

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It has been known for many years that surface properties of solid substrates play a very important role in the anchoring of liquid crystals (LCs) [1]. To promote the anchoring, the substrate surfaces are frequently coated by aligning agents, such as amphiphilic molecules or polymers, probably followed by some intentional treatments. Generally, one kind of material produces one type of anchoring. However, it has been found that the anchoring direction of LCs can be changed as a function of some parameters characterizing the solid-LC interfaces, leading to the so-called anchoring transitions [2,3]. Anchoring transitions are of fundamental and industrial interest, since they can provide more information about anchoring mechanisms and be the rationales of some information-storage media.

Anchoring transitions can be driven by many parameters. The first recognized parameter is temperature and temperature-driven transitions have been known for some time [4–6], which can be further treated according to, e.g., the interface properties [3]. Anchoring directions of LCs can also be modulated by polarized laser beams with proper wavelength, through a *trans-cis* photoisomerization if azobenzene moieties are contained in the alignment layers [7]. This kind of transition may be the basis of a new kind of information-storage media. Porte, Ichinose, Suzuki, and Goto, and Crawford *et al.* [8] reported that the variation of the surfactant chain length can change the anchoring directions of LCs continuously or discontinuously. Bechhoefer *et al.* and Jerome *et al.* [9] recently found that adsorption of small volatile molecules on the LC-crystal interface may alter the orientation of LCs, which is thus dubbed "coadsorption-induced transition." There are still other kinds of transitions, which can be found in the several recent papers [2,3] and references therein.

Some of the aforementioned transitions have been studied phenomenologically [10] and microscopically [11]. However, the possibility that a conformation change of aligning agents may produce an anchoring transition has not been addressed in terms of the above phenomenological and microscopic theories. On the other hand, in some systems [7,12], it is suggested that the transitions originate from a conformation change in the aligning agents. Unfortunately, this assumption has not been confirmed experimentally or theoretically. Therefore, it is unknown whether a conformation change in the aligning agents can really produce an anchoring transition.

In this Letter we report our experimental results on the LC alignment induced by crown ether liquid crystal (CELC) Langmuir-Blodgett (LB) monolayer films. The CELC we used here is *N*,*N*-bis[4-(4-heptoxybenzoyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetracyclooxaotadecane. Its molecular structure is shown in Fig. 1. The melting point and the clearing point of the CELC are 120.2 °C and 135.2 °C, respectively. The synthesis of the CELC has been reported in [13]. Previously, we have shown that LB films used as alignment layers for LCs are noteworthy from both scientific and industrial points of view due to their well-recognized properties [14–17]. We further demonstrate here that the LB technique can be employed to control the molecular conformations of the CELC molecules in LB films. The prepared LB films are

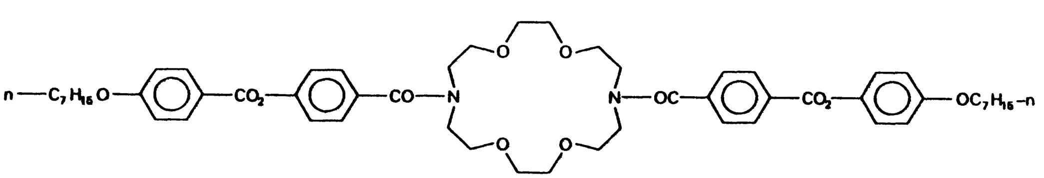

FIG. 1. Chemical structure of the double-armed crown ether liquid crystal.

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employed to align LCs and both homeotropic and homogeneous alignments can be achieved. We still argue that continuous change of the pretilted alignment is also possible in this system if a proper method for preparation of the alignment layers is employed. The alignment mechanism involved is discussed in detail. This is the first clear experimental demonstration that a conformational change of aligning agent can induce an anchoring transition of LCs.

The CELC monolayer was prepared on a Langmuir trough [18]. Doubly distilled water was used as subphase, whose temperature was controlled at 25 °C with an accuracy better than 0.5 °C throughout the whole experiment. The CELC was dissolved in chloroform (1.0 mg/ml) and the solution was delivered onto the water surface by a microsyringe. Evaporation of the organic solvent left the CELC molecules uniformly distributed on the water surface. The surface pressure was measured by a Wilhelmy balance with a precision 0.1 mN/m. The area per molecule was subsequently modified by squeezing the monolayer laterally with a movable barrier moving at a velocity of 5 Å^2/molecule min).

Figure 2 shows the measured surface pressure as a function of molecular area for the CELC on the air-water interface at 25 °C. There is an evident kink around 27 mN/m in the isotherm, implying that the monolayer undergoes a phase transition. The limiting areas per molecule before and after the transition are 240 Å^2 and 76 Å^2, respectively. The change in molecular area can be reasonably ascribed to a conformational change, as shown in Fig. 2. Before the transition, the crown ether and carbonyl groups are anchored on the water surface. The molecular area projected onto the water surface given by a molecular model is close to 240 Å^2. After the transition, only the crown ether is anchored on the water surface. The corresponding area given by a molecular model is about 70 Å^2. The equilibrium surface pressure is temperature dependent. As the temperature of the subphase increases, the equilibrium surface pressure decreases. Thus the transition is first order [19,20]. The change of molecular conformation may be due to the delicate balance between inter- and intramolecular interactions in the system.

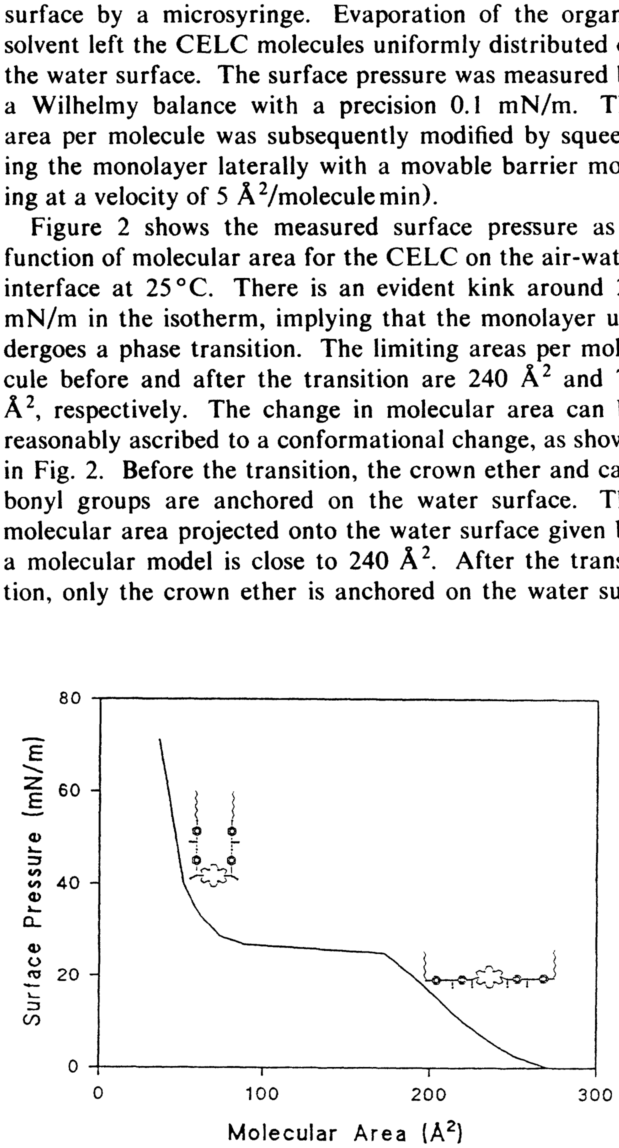

FIG. 2. The surface pressure-area curve of the crown ether liquid crystal on water surface at 25 °C. The molecular conformations in different phases are schematically illustrated in the corresponding regions.

The carbonyl parts have polar nature, and in different phases, they have different orientations. Thus if we deposit the CELC monolayers in different phases onto glass slides and use them to align LCs, it is expected that different anchoring structures of LC molecules will be produced.

To prepare the CELC LB monolayer film for LC alignment, the glass plates with hydrophilic surfaces were placed back-to-back and immersed into the water subphase before spreading the monolayer. One CELC layer was deposited on each glass substrate.

The LC cells were assembled using two CELC monolayer coated plates with their dipping directions parallel. The spacing of the two plates was controlled by glass fibers of calibrated diameter of 20 μm. LCs 4′-*n*-pentyl-4-cyanobiphenyl (5CB) were filled in the cells by capillary action. The cells that could be rotated in the plane of plates were observed under a microscope between two crossed polarizers with the incident light normal to the plates. A Bertrand lens was used to obtain a conoscopic figure.

The CELC Langmuir monolayers were transferred on glass plates at surface pressures 25 mN/m for cell 1 and 35 mN/m for cell 2, respectively, so that in the monolayers the CELC molecules may take different conformations; i.e., the polar parts of the CELC molecules have different orientations in the monolayers (see Fig. 2), which may induce LC alignment differently.

Under a polarized microscope, the 5CB textures in both cell 1 and cell 2 were uniform [see Fig. 3(a)]. When cell 1 was rotated around the normal to the surface, the transmitted light changed with a period of 90°. When the dipping direction was oriented at 0° with respect to the analyzer, the transmission of the cell was almost zero. When the dipping direction was oriented at 45° with respect to the analyzer, the transmission had a maximum value. This indicates that the 5CB molecules are uniformly aligned along the dipping direction. On a bare glass, the field of view was not uniform. Many domains were visible because the directors of 5CB are randomly oriented. When cell 2 was rotated around the direction of incident light, the transmission did not change. When a Bertrand lens was used, a dark cross could be seen [Fig. 3(b)], which did not vary when the cell was rotated around the normal to the cell, showing that the 5CB molecules are aligned homeotropically. Similar results have been obtained for other types of LC molecules, e.g., E7, which suggest that this transition does not depend upon the LC molecules aligned.

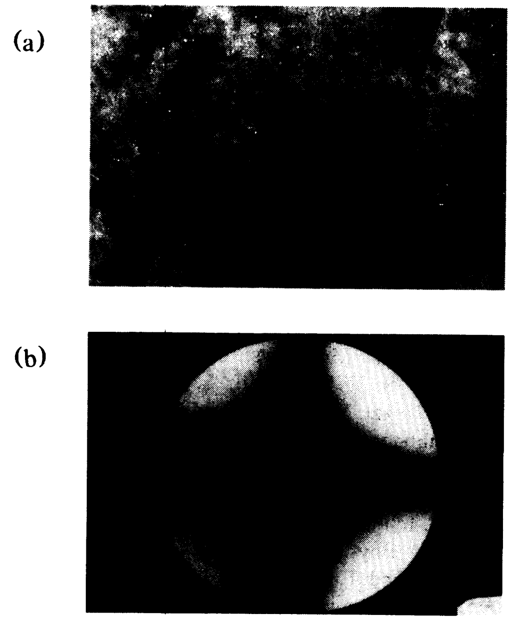

FIG. 3. (a) Optical micrograph of the homogeneous texture in cell 1 viewed by crossed polarizers when the dipping direction of the alignment layer is oriented at 0° with respect to the analyzer. The texture in cell 2 is similar to that in cell 1. (b) A conoscopic figure of the homeotropic texture in cell 2.

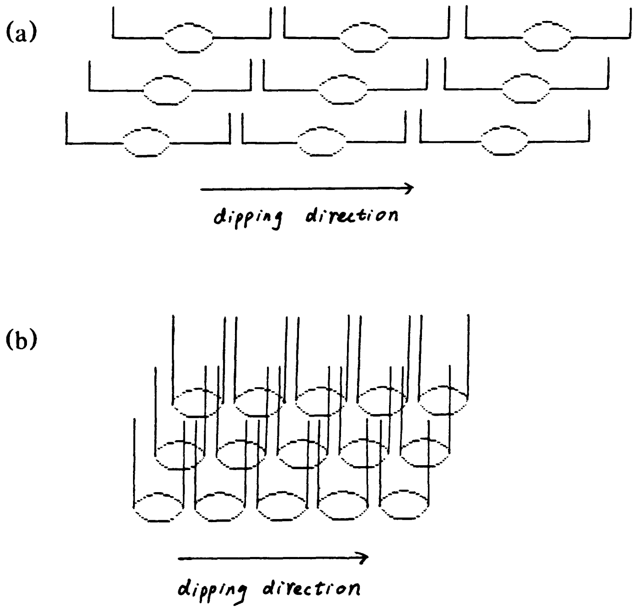

FIG. 4. Schematic diagrams of crown ether liquid crystal monolayers deposited on solid substrates (a) at a high surface pressure and (b) at a low surface pressure. The arrows indicate dipping directions.

So far we have observed that both homogeneous and homeotropic alignments of LCs can be established on LB films of the same material. We note that for the homogeneous alignment of LCs in our system, one CELC layer is sufficient, while if polyimide and other materials are exploited as the aligning agents, at least three layers are required. This indicates that the interaction between the CELC monolayer and the 5CB is stronger than that between polyimide and the 5CB. On polyimide LB films, for a uniform alignment of LCs, at least three layers are needed to screen the influence of glass surfaces [21]. In our system, it also signals that the influence of glass surfaces is less strong than the interaction between the CELC monolayer and the 5CB. The mechanism responsible for alignment should be different from that in other systems.

Considering the change of molecular conformations, we conjecture that the anchoring structure is mainly regulated by the agent conformation. When the monolayer is deposited at a low surface pressure, we postulate that the monolayer on a solid substrate has the schematic structure shown in Fig. 4(a). The long axis of the CELC molecule is aligned in the dipping direction, caused by the dipping process [22]. When the monolayer is transferred at a high surface pressure, the monolayer may have the structure shown in Fig. 4(b). In Fig. 4(a), the polar parts of the molecules are uniformly oriented in the dipping direction, while in Fig. 4(b), the polar parts are all upward. In the LC cells, the aligned LCs take the orientations of the polar parts of the aligning agents, so we argue that the anchoring is dominated by the interaction between the polar parts of the CELC and the aligned LCs; i.e., the dipolar interaction is the physical origin of the anchoring and the anchoring transition originates from the conformation change.

If we transfer the Langmuir monolayers when two phases coexist and use the deposited monolayers as aligning agents, then we expect a pretilted alignment will be established. The pretilted angle can be adjusted according to the proportion of molecules with different conformations. Because of the phase separation process, different phases may form different domains at the air-water interface; therefore the pretilted alignment could not be uniform and many domains (defects) in the cells could be visible under a microscope.

The above observation can be phenomenologically understood in terms of a Landau-type theory. Suppose the interfacial energy density $w_s(T,\gamma,\theta,\varphi)$ can be expanded in a series of spherical harmonics:

$$w_s(T,\gamma,\theta,\varphi)=\sum Q_{lm}(T,\gamma)Y_l^m(\theta,\varphi)\,,$$

where the amplitudes Q are functions of temperature T and the property of the CELC monolayer γ, and (θ,φ) are polar and azimuthal angles of the nematics, i.e., the angles between the normal to the surface and the nematic director and between the nematic director and the dipping direction, respectively. Considering the inversion symmetry of the nematic phase and the symmetry of the substrate (180° rotation; see Fig. 4), only terms with even l and even m can be different from zero. Assuming that only the second-order contribution is dominant, and keeping φ constant, we finally obtain $w_s(\theta)=w_0(\gamma)+a(\gamma)\cos(2\theta)$. If in the low surface pressure region $a>0$, and $a(\gamma)$ changes its sign at the transition, then the above transition diagram is realizable by minimizing the energy density w_s with respect to θ. The phenomenological coefficients can be related to the microscopic properties of LCs and substrates, which depends upon the proper assumptions of intermolecular interactions and upon a proper method to decouple the order parameter from the surface potential [11]. We are now investigating such relations and expect that this study should shed more light on the microscopic origins for anchoring and anchoring transition.

Compared with the previously reported work, our work has the following characteristics: We employ the LB technique to control the conformations of aligning agents and hence control the anchoring directions of LCs on the surfaces of these agents. In some systems [7,12], anchoring transitions are suggested to be caused by a change of molecular structure. However, such an assumption has a lack of experimental support. In our system, the origin of the anchoring transition is clear. This is the first experimental demonstration that conformation changes in the aligning agents can induce anchoring transitions of LCs. However, we should note here that not all conformation changes of aligning agents can produce transitions; for example, see [17,23]. This suggests that in order to induce an anchoring transition, the direction of the force responsible for anchoring should be remarkably changed before and after the conformation change. In terms of the above Landau-type theory, a coefficient should change its sign when the conformation of aligning agents changes.

In summary, we have controlled liquid crystal orientations in liquid crystal cells by controlling the conditions for preparing the crown ether liquid crystal monolayers as the aligning layers. Both homeotropic and homogeneous alignments of liquid crystals have been induced by the same aligning agent. We also argue that a continuous change of pretilted alignment is possible in the reported system. The alignment mechanism is the dipolar interaction between the aligning material and the aligned liquid crystals, and the physical origin of the anchoring transition is the change of molecular conformations in the aligning agent.

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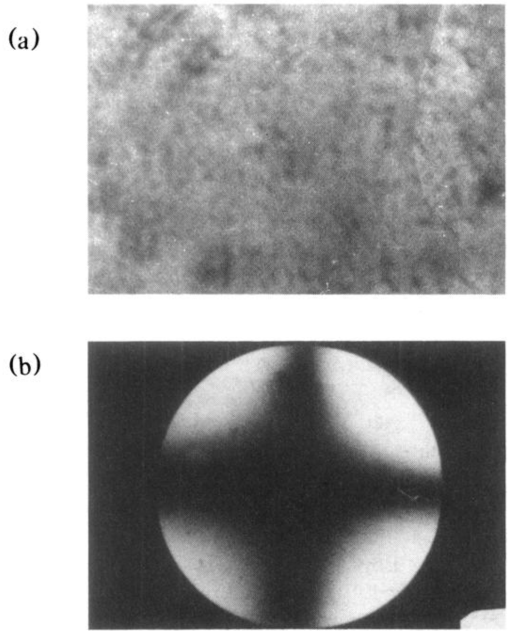

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