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# Relation between anchorings of liquid crystals and conformation changes in aligning agents by the Langmuir-Blodgett film technique investigation

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The anchoring direction of liquid crystals on a solid substrate surface depends upon many parameters characterizing the liquid-crystal–substrate interface, a variation of which may change this anchoring direction leading to the so-called anchoring transition. Here, based on the Langmuir-Blodgett film technique, we present two model systems to study the relation between anchoring directions and the conformation changes in aligning agents. A double-armed crown ether liquid crystal and a side chain polymer liquid crystal at an air-water interface both show phase transitions, accompanied by conformation changes. However, when the monolayers in different phases were transferred onto solid substrates to orient liquid crystals, we found that for the crown ether material the conformation change can alter the anchoring of liquid crystals between homeotropic and homogeneous alignments, while for the polymer liquid crystal, despite the conformation changes, the liquid crystals can only be aligned homeotropically. The involved mechanisms were briefly discussed in terms of the Landau-type phenomenological theory.

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## I. INTRODUCTION

Liquid crystals can be easily oriented by solid surfaces on a macroscopic scale [1]. This phenomenon of the orientation of liquid crystals is the so-called anchoring [2], which is of crucial importance for applications of these materials, in particular for liquid-crystal displays. However, the understanding of this phenomenon remains a scientific mystery. The anchoring direction of liquid crystals depends upon different parameters characterizing a liquid-crystal–solid-substrate interface. Variation of these parameters may alter the anchoring direction taken by liquid crystals, leading to the so-called anchoring transitions [3]. Recently, anchoring transitions have received much attention due to their scientific and industrial significance [4–12]. However, the origins for anchoring transitions are far from being well understood. Many suggestions exist [12]. More recently, Nazarenko and Lavrentovich have done a very nice study on the underlying mechanism behind surface alignment transition. They have clarified that ionic impurities may strongly influence the anchoring transition behavior [12].

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 liquid crystals 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]. Porte [8], Ichinose, Suzuki, and Goto [9], and Crawford *et al.* [10] reported that the variation of the surfactant chain length can change the anchoring directions of liquid crystals continuously or discontinuously. Jerome *et al.* [11] recently found that adsorption of small volatile molecules on the liquid-crystal–crystal interface may alter the orientation of liquid crystals.

Previously, we have shown that Langmuir-Blodgett (LB) films serving as orienting layers for liquid crystals are noteworthy from both scientific and industrial points of view due to their well-recognized properties [13–17]. Since the LB film technique enables one to fabricate molecularly defined and controlled films, varying the microscopic properties of the substrate surface controllably, it thus should also be very applicable to investigate the anchoring transition phenomena. In Ref. [13], by the LB film technique, we have shown that the phase transition caused by a conformational change in the LB aligning films can produce an anchoring transition of liquid crystals. Others have also reported experimental evidences implying that conformational changes of the aligning agents may produce anchoring transitions of liquid crystals on the tops of these agents [7,18]. However, presently it is unknown whether a conformational change in an aligning agent can definitely result in an anchoring transition of liquid crystals. To clarify this question, here we take a more detailed experimental investigation. Based on the LB film technique, we presented two model systems to study the relation between anchoring directions and conformation changes in LB aligning agents. We found that an air-water interface, the conformations of a crown ether liquid crystal and of a side chain polymer liquid crystal can be controlled by the LB film technique. The conformation change of the crown ether can change the anchoring direction of liquid crystals on the tops of its monolayers, while that of the polymer liquid crystal cannot.

The remainder of this paper is organized as follows. In Sec. II, we present the experimental details. The experi-

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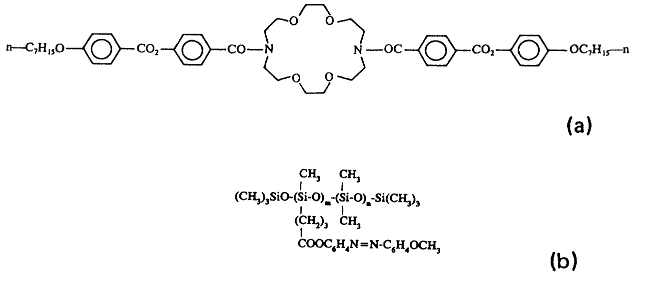
mental results are given in Sec. III. Section IV discusses the involved mechanisms, while Sec. V concludes the whole paper.

## II. EXPERIMENTS

The LB molecules used in this study are a double-armed crown ether liquid crystal (CELC) and a side chain polymer liquid crystal (PLC). Their molecular structures are shown in Fig. 1. The CELC was synthesized and provided by M. G. Xie [19]. Its melting point and the clearing point are 120.2 °C and 135.2 °C, respectively. The PLC was supplied by Z. H. Luo. Its average molecular weight $M=3680$ and $m/n=3.380$. At 66 °C, the polymer liquid crystal changes from the crystal phase to the nematic phase, and at 102 °C it changes from the nematic phase to the isotropic phase.

The CELC or PLC monolayers were prepared on a Langmuir trough (Face Langmuir trough, Japanese product). The CELC and the PLC were dissolved in chloroform at concentrations of 1.0 and 0.5 mg/ml, respectively. The solution was delivered onto a double-distilled water surface by a microsyringe. Evaporation of the organic solvent left the CELC or PLC molecules uniformly distributed on the water surface. The temperature of the subphase was controlled within $25\pm0.5$ °C. The monolayer was compressed laterally by a movable barrier at a comparatively low rate. During the compression, the surface pressure was measured by a Wilhelmy balance with a precision of 0.1 mN/m.

According to our previous reports [13,20], the monolayers of CELC and PLC both undergo transitions, accompanied by conformation changes. At this particular temperature, the transitions occur at 27 mN/m for the CELC, and 16.5 and 24.5 mN/m for the PLC, Fig. 2. Before the transition, the crown ether and carbonyl groups are anchored on the water surface. After the transition, only the crown ether is anchored on the water surface [13]. For the PLC, the phases are denoted by *a*, *b*, and *c* in the ascendant order of the surface pressures. In phase *a*, the main chain of the PLC is anchored at the air-water interface. When it is compressed, the monolayer changes to phase *b* in which the right end of the polymer backbone without side chains is lifted away from the interface. When it is further compressed, the monolayer changes to phase *c*. In phase *c*, the left end of the main chain without the azobenzene moieties is also gradually lifted from its anchored position [20].



$$(CH_3)_3SiO\text{-}(\underset{\underset{COOC_6H_4N=N\text{-}C_6H_4OCH_3}{\mid}}{\underset{(CH_2)_3}{\underset{\mid}{\overset{\overset{CH_3}{\mid}}{Si}}}}\text{-}O)_m\text{-}(\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{Si}}\text{-}O)_n\text{-}Si(CH_3)_3$$

FIG. 1. Chemical structures of (a) crown ether liquid crystal and (b) polymer liquid crystal.

The monolayers of the CELC and the PLC at the air-water interface were stable. In different phases, the CELC and the PLC monolayers were transferred to glass plates to orient the liquid crystals. When the monolayers were deposited, the surface pressure was kept constant. To prepare the LB monolayer film for liquid-crystal alignment, the glass plates with hydrophilic surfaces were placed back to back and immersed into the water subphase before spreading the monolayer. One CELC or PLC layer was deposited on each glass substrate.

The liquid-crystal cells were assembled using two CELC or PLC monolayer coated plates with their dipping directions antiparallel. The spacing of the two plates was controlled by glass fibers of a calibrated diameter of 20 μm. Liquid crystals 4′-*n*-pentyl-4-cyanobiphenyl (5CB) filled 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

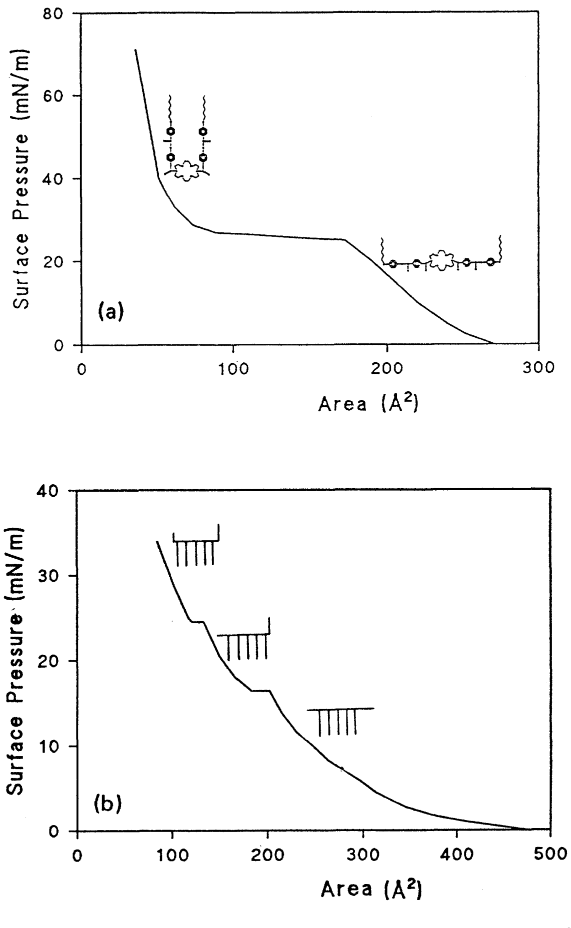


FIG. 2. Surface-pressure-molecular-area isotherms of (a) crown ether liquid crystal and (b) polymer liquid-crystal monolayers on the air-water interface at 25 °C. The molecular conformations in the corresponding phases are also schematically illustrated.

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, Fig. 2(a). When the PLC monolayers were transferred, the surface pressures were kept at 10, 20, and 30 mN/m for cells 3, 4, and 5, respectively. From Fig. 2(b), one can see that in these cases, the PLC molecules in LB films also take different conformations.

## III. RESULTS

Under a polarizing microscope, the 5CB textures in all five cells were uniform. 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. When cells 2, 3, 4, and 5 were rotated around the direction of incident light, the transmission did not change. When a Bertrand lens was used, a dark cross could be seen, which did not vary when the cell was rotated around the normal to the cell, showing that the 5CB molecules are aligned homeotropically. The accuracy of our conoscopic method is estimated to be better than 0.8°. This indicates that the anchoring structure of the liquid crystals on the CELC monolayers can be regulated by the conformation of CELC, and that on the PLC monolayers is independent of the conformation changes. To avoid the conformation degeneration during the dipping process, a horizontal lifting method was exploited for transfer, and the deposited monolayers were employed to align liquid crystals. We obtained identical results, further confirming that the conformational change in the aligning CELC agents can produce anchoring transition of liquid crystals and that in the PLC agents cannot.

The alignment stabilities of CELC and PLC are different. After some extended time, the alignment in CELC cells is unstable, particularly for cell 2. This can be ascribed to the stability of the CELC monolayers. However, the alignment in PLC cells was not degraded after the cells had been sealed one year later. Even after the cells were heated up to the clearing point of the PLC, the alignment was not disturbed when the cells were cooled down. This suggests that the PLC LB films as the alignment layers are stable. The stability comes from two factors: The alignment layer is made of a polymer, and it is known that the stability of a polymer LB film is good; The main chain of the PLC is consisted of the siloxane units, which are markedly stable.

## IV. DISCUSSION

So far we have observed that the conformation change in CELC monolayers can produce an anchoring transition of liquid crystals, and that the conformation change in PLC monolayers cannot. In this section, we discuss the origins for anchoring and its transition.

In Ref. [13] we have discussed that for liquid crystals on the CELC monolayers, the dipolar interaction between the polar parts in the CELC and the aligned liquid crystals is the physical origin of the anchoring and the anchoring transition originates from the conformation change. Consider the change of CELC conformations, we postulate that the anchoring structure is mainly regulated by the agent conformation. When the CELC monolayer is deposited at a low surface pressure, the long axis of the CELC molecule may be aligned in the dipping direction, caused by the dipping process [21]. In this case, the polar parts of the CELC molecules are uniformly oriented in the dipping direction. When the monolayer transferred at a high surface pressure, the polar parts are all upward. In cells 1 and 2, the aligned liquid crystals take the orientations of the polar parts of the aligning agents, so we believe that the anchoring is dominated by the interaction between the polar parts of the CELC and the aligned liquid crystals.

In cells, 3, 4, and 5, the orientation of PLC side chains are vertical to the cells surface and do not change. The aligned liquid crystals take the direction of these side chains. Thus, the alignment comes from the interaction between the side chains and the aligned nematics. The influence of the main chains, which though take conformation changes, on the alignment can be neglected.

The above observed transition and nontransition can be understood in terms of the Landau-type phenomenological theory. For a single-component uniform nematic phase at an anisotropic solid substrate, neglecting biaxiality, the surface term in the expression of the surface tension is [22]

$$f_s = w_0 + w_2 P_2(\cos\theta) ,$$

where $\theta$ is the polar angle, i.e., the angle between the normal to the surface and the nematic director, and $P_2$ is the second-order Legendre polynomial. The surface tension truncated after the $P_2$ term is known in the literature as the Rapini-Papoular form of the surface anchoring energy, which has been extensively used in both theoretical and experimental work. If one assumes that the phenomenological coefficient $w_2$ changes its sign at the CELC monolayer transition, for example, in the low-surface-pressure region, $w_2 > 0$, and in the high-surface-pressure region, $w_2 < 0$, then by minimizing the surface tension, one can obtain that the director of the nematics prefers to align parallel to the surfaces of the CELC monolayers in the low-surface-pressure region, and perpendicular to the monolayer surfaces in the high-surface-pressure region. For the PLC monolayers, regardless of the conformational changes, $w_2$ may not change its sign (negative) when the conformation changes, thus, liquid crystals are favored to be aligned vertically.

Although at present we cannot definitely show that $w_2$ changes its sign at the CELC monolayer transition, for the PLC, $w_2$ indeed does not change sign, as we note below.

The phenomenological coefficients appearing in the formula for surface tension can be related to the microscopic properties of the aligning agents and the aligned liquid crystals, as Teixeira and Sluckin have shown in Ref. [22]. In the framework of this microscopic theory, the coefficient $w_2$ is given by

$$w_2=\tfrac{5}{32}\rho^2\eta[\sqrt{10/7}\,\eta\bar{V}_3(222)-2\bar{V}_3(202)]+\rho\eta\bar{V}_{\text{ext,ani}} ,$$

where $\rho$ is the density and $\eta$ is the bulk order parameter (for its definition, see Ref. [22]). For the meaning of $\bar{V}_3$, please refer to Ref. [22]. In the above equation

$$\bar{V}_{\text{ext,ani}}=\int_0^{+\infty}V_{\text{ext,ani}}(z) ,$$

where $V_{\text{ext,ani}}(z)$ is the $z$-dependent anisotropic part of the liquid-crystal–solid surface interaction (the external potential), $V_{\text{ext}}(z,\theta)$, given by

$$V_{\text{ext}}(z,\theta)=V_{\text{ext,iso}}(z)+V_{\text{ext,ani}}(z)P_2(\cos\theta) ,$$

where $V_{\text{ext,iso}}(z)$ is the $z$-dependent isotropic part of the external potential and $z$ is the distance measured perpendicular to the surface.

As we have argued that the alignment comes from the interaction between the side chains and the aligned liquid crystals, the influence of the main chains, regardless of their conformations, can be neglected. Suppose the surface potentials of the PLC monolayers prepared in phases $a$, $b$, and $c$ are $V_{a,\text{ ext}}$, $V_{b,\text{ ext}}$, and $V_{c,\text{ ext}}$, respectively. For approximation, we think that these surface potentials are linear functions of the surface density of side chains. Thus, they are linearly related by two positive scalars, i.e., $1.5V_{a,\text{ ext}}=1.1V_{b,\text{ ext}}=V_{c,\text{ ext}}$. Since the anisotropic part of the surface potential is linearly dependent on the surface potential, the anisotropic surface potentials are also linearly related: $1.5V_{a,\text{ ext,ani}}=1.1V_{b,\text{ext,ani}}=V_{c,\text{ext,ani}}$. If one takes an inverse power-law surface potential such as

$$V_{\text{ext,ani}}=\begin{cases}-B(R/z)^3 , & z>R/2\\ 0 , & z\le R/2 ,\end{cases}$$

then one has the relation $1.5B_a=1.1B_b=B_c$, where $R$ is the distance of closest approach to the wall for an aligned liquid crystal and $R_a=R_b=R_c$ is assumed.

Employing the simple Telo da Gama model of liquid crystals, Teixeire and Sluckin have shown that $w_2$ can be further written as

$$w_2=\pi/8\rho^2\sigma^4\eta C-2\rho\sigma\eta vB .$$

This formula is given by taking the single-component limit in Eq. (18b) of Ref. [22]. Here $\sigma$ is the molecular diameter, $v$ is the ratio between the range of the surface potential and the molecular diameter. For a prolate molecule such as 5CB, $C>0$ (for the meaning of $C$, see Eq. (14) in Ref. [22]). Because the PLC monolayer prepared in phase $a$ can induce a homeotropic alignment of liquid crystals, $w_{2a}<0$, which gives

$$B_a>\pi\rho\sigma^3C/16v>0 .$$

On the other hand, we have $B_a<B_b<B_c$. Thus, $w_{2c}<w_{2b}<w_{2a}<0$. That is, the PLC monolayers prepared on phases $b$ and $c$ also favor the homeotropic alignment. That is why the polymer liquid-crystal conformational changes cannot result in an anchoring transition of liquid crystals.

The conformational change of CELC can produce an anchoring transition of liquid crystals. We suggested that the anchoring originates from the dipolar interaction between the polar parts of the CELC and the aligned liquid crystals. When the CELC conformation changes, the orientation of the polar parts changes noticeably, thus the direction of the force responsible for anchoring alters, leading to the anchoring transition. For PLC, although its conformation also changes, the orientation of the side chains is not varied. Since the anchoring comes from the interaction between the side chains and the aligned liquid crystals, the direction of the force is not changed, which could not give rise to an anchoring transition of liquid crystals. Thus, in order to induce an anchoring transition of liquid crystals, the direction of the force responsible for anchoring should be varied before and after the conformational change.

## V. CONCLUSION

Due to the controllability of LB films, the LB film technique is very applicable to the study of anchoring transitions of liquid crystals. We have shown that the LB film technique can be employed to control the conformation of a double-armed crown ether liquid crystal and a side chain polymer liquid crystal. When the crown ether conformation changes, the anchoring direction of liquid crystal on the crown ether monolayers is also correspondingly altered. To the contrary, the conformation changes of the polymer liquid crystal cannot mediate the anchoring direction of liquid crystals on its monolayers. That is, not all conformation changes of aligning agents can induce anchoring transitions of liquid crystals. The transition or nontransition can be understood in terms of the Landau-type phenomenological model. We suggest that in order to induce an anchoring transition of liquid crystals, from a microscopic point of view, the direction of the force responsible for anchoring should be varied before and after the conformational change.

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