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Alignment instability caused by anchoring of the in-plane directors to the rubbing direction in the V-shaped switching

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In order to investigate the molecular alignment in the smectic liquid crystals showing the V-shaped switching behavior, two types of the liquid crystal cells, a sandwiched cell and an open cell, were prepared. Homogeneous alignment with the smectic layer normal formed at ~12° with respect to the rubbing direction ***r*** is obtained in the Sm-A phase in both cells. However, in the open cell, the director ***n*** is rotated towards ***r*** when the Sm-A sample is cooled into the tilted Sm-X* phase. In addition, its maximum rotation angle is ~12°. In this configuration, the molecules lie along ***r***. Meanwhile, the sandwiched cell with the one-side rubbing treatment exhibits the averaged optical axis almost parallel to the layer normal in the Sm-X* phase. In this paper, a simple small-twisted state in the thin sandwiched cell is suggested to account for the experimental results.

1. Introduction

Recently, the V-shaped switching, characterized by a novel thresholdless hysteresis-free property, is being studied intensively for its potential use in applications and for the scientific interest in the phenomenon.[1–15] This phenomenon has attracted considerable attention in the expectation of realizing attractive displays with extremely wide viewing angles, a very large contrast ratio, and a high-speed response.

Since the first reports of the V-shaped switching given in 1995, two *very different* models have been proposed to explain the switching behavior.[1,3,11,13] The initial model is based on the random process where the frustration between ferro- and antiferro-electricity is considered to diminish the interlayer tilting correlation, to randomize the molecular arrangement at the tip of the V, and to cause the two-dimensional Langevin like alignment of the C-director during the switching to the smectic-C* phase.[1,3] In the practically usable V-shaped switching, however, some interface effect of the aligning surfaces appears to be responsible for randomizing the molecular alignment and/or switching process; at the same time, the weak interlayer tilting correlation is essential for its occurrence.[5,6] Conversely, we are dealing with the V-shaped switching observed in a group of liquid crystal compounds and mixtures, in which the competition and frustration between ferro- and antiferro-electricity plays such an important role that ferri- and antiferro-electric subphases may emerge easily.[4–10,16]

On the other hand, according to the collective model recently suggested all the molecules are aligned homogeneously along the layer normal and show collective rotation on the cone under an applied field.[11,12] Support for this model came initially from the effective optical anisotropy and the polarizing FT-IR studies.[11] Meanwhile, Rudquist *et al.* suggested that strong polar surface interactions cause the twisted state in the thin surface region and that the bulk of the sample cell remains uniform through polarization space charge effects.[13,14] In this geometry, its V-shaped response to an applied field was also explained by the collective rotation of the bulk.

However, these experimental studies could not deny the random process unambiguously. We would like to emphasize that the random process can also explain all of the so far experimentally observed facts. Intuitively, we can envisage that the switching occurs layer by layer randomly. Since coherence length is not infinite in a single layer, it would be more appropriate to describe that molecules rotate collectively only in small invisible domains and that each domain switches randomly, even when the initial alignment at the tip of the V is highly ordered ferroelectric. It is plausible that some substrate interfaces may induce the ferroelectric order instead of randomization, because the interlayer tilting correlation becomes extremely weak. This may be the case especially when the liquid crystal systems are characterized by subphases with small q numbers.[15,17] However, it is another question whether such highly ordered alignment at the tip of the V is appropriate or not. We have some doubts about its appropriateness because of the instability to be discussed in this report.

In order to investigate alignment instability in the V-shaped switching, we have prepared an open cell, in which the liquid crystalline materials are deposited on a substrate plate and its upper side is left exposed to the air. The substrate interface was covered with aligning polyimide film and was rubbed in one direction and one sense. Homogeneous alignment was attained in the Sm-A phase, where the director ***n*** was deviated by ~12° from the rubbing direction ***r*** as in the ordinary sandwiched cell with only one substrate interface rubbed (hereafter abbreviated as the sandwiched cell). At the phase transition from the Sm-A to the Sm-C* like phase or state, Sm-X*, where the V-shaped switching occurs, the director almost continuously changes from the layer normal to the rubbing direction in the open cell, whereas the averaged optical axis stays unchanged nearly parallel to the layer normal in the sandwiched cell.

2. Experimental

We studied the three-component Inui mixture (Tokyo mixture) used for modeling the V-shaped switching.[1,3,11,13] For the preparation of an open cell, indium-tin-oxide (ITO)-coated glass was used to maintain the same conditions as a sandwiched

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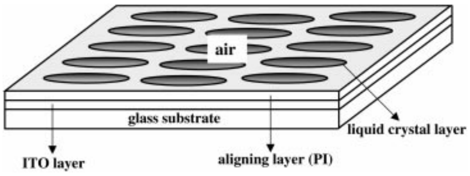

Fig. 1 Schematic diagram of an open cell.

cell. The glass substrate was first coated with polyimide (RN1266) obtained from Nissan Chemical Industries, Ltd., and then rubbed in a single direction. A very thin liquid crystalline film was obtained by spreading the mixture with a cover glass in the isotropic state just over Iso–Sm-A transition (Fig. 1). For a sandwiched cell, a rubbing glass plate was assembled with an unrubbed glass plate. The cell spacing was maintained by spacers of 2 μm thickness. In both kinds of cells, the phase transition was measured by the observation of the texture. The apparent tilt angle in the sandwiched cell was defined by a half angle between the two field-induced uniform states. Transmittance of the normally incident light through the sample was monitored under the uncrossed polarizers in order to investigate the twisted state in the sandwiched cell.

3. Results and discussion

The phase sequences of these kinds of planar cell are as follows:

In the sandwiched cell[8]

AF (20–43 °C: co-existence with Sm-X*) Sm-X* (64 °C) Sm-A (68.5 °C) Iso

In the open cell

AF (20 °C) Sm-X* (64 °C) Sm-A (68.5 °C) Iso

(The Sm-X* phase is identified as a ferrielectric phase by conoscopy in free-standing films.)[8,18]

The phase sequences in both cells are almost the same but, in the sandwiched cell a coexistence region of AF and Sm-X* exists. Furthermore, the Sm-X*–AF transition in the open cell was completed after leaving the cell alone over about 2 hours at room temperature. These results indicate that the molecule–surface interaction near the aligning surface is very strong.

Fig. 2 shows the photographs of the texture taken in the open cell. In Fig. 2 (a) and 2 (c), one of the crossed polarizers is set parallel to the director ***n*** and makes an angle of 45° in Fig. 2 (b) and 2 (d). As shown in Fig. 2(a), the smectic layers in the Sm-A phase form with the layer normal at ~12° with respect to the rubbing direction ***r***. It is consistent with the result of the sandwiched cell and is due to the surface electroclinic effect.[19–21] However, in the Sm-X* phase of Fig. 2 (c), ***n*** parallel to ***r*** was obtained: that is, the molecules lie along the rubbing direction.

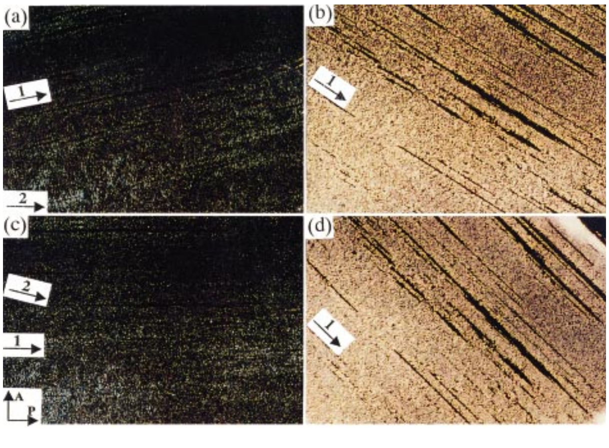

Fig. 2 A series of photographs taken in the open cell at $T = 66$ °C, Sm-A ((a) and (b)) and $T = 50$ °C, Sm-X* ((c) and (d)). Arrow 1 and 2 show the rubbing direction and the layer normal, respectively. The director ***n*** in (a) and (c) lies along one of two polarizers and at an angle of 45° with respect to polarizers in (b) and (d). There is no liquid crystalline molecule in the black regions seen as a stripe line which is parallel to the rubbing direction ***r***.

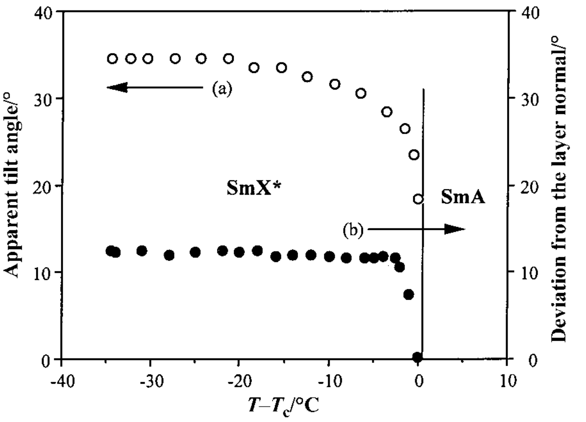

Fig. 3 (a) The temperature dependence of the apparent tilt angle. (b) The temperature dependence of the deviation of the molecular director ***n*** from the layer normal in the open cell.

Shown in Fig. 3 is the temperature dependence of the apparent tilt angle and the rotation angle of ***n*** in the open cell in the tilted smectic phase. The Sm-X* phase in the sandwiched cell has an averaged optical axis almost parallel to the smectic layer normal. So the apparent tilt angle was obtained by finding the extinction position under a high dc electric field showing a uniform state. It increases with cooling the cell and saturates at a value close to ~35° (Fig. 3 (a)). As depicted in Fig. 3 (b), ***n*** in the open cell indicates very unusual behavior with decreasing temperature below the Sm-A–Sm-X* transition. During the early stages of the transition, ***n*** continuously rotates to ***r*** with decreasing temperature but unlike the sandwiched cell, stabilizes just below ~3 °C as shown in Fig. 2 (c). As described before, the stabilized direction of ***n*** corresponds nearly to the rubbing direction ***r***. Even if some difference from the real tilt angle due to the tilted chevron structure in the sandwiched cell is considered,[22] 12° is too low to be the apparent tilt angle. Schematic diagram in Fig. 4 shows the molecular alignment at the Sm-A and Sm-X* phase in both cells described above.

It is well-known that chiral liquid crystalline molecules at the rubbed polyimide interface align along the rubbing direction, but the smectic layer normal is formed at a deviated position from the rubbing direction by the surface electroclinic effect.[19] This alignment behavior, of course, is dependent on the comparative value of the surface anisotropy and the molecule–surface polar interactions. Therefore, in the Sm-A phase of the open cell, the molecular alignment is easily explained. In fact, there exist two regions in the Sm-A cell in Fig. 4 (a). One is the interfacial region where the director ***n*** is twisted from the rubbing direction towards the layer normal. The other is the bulk region which has a uniform ***n*** along the layer normal. In this case, the former is confined in a very thin boundary region because the good extinction is obtained when one of the polarizers is parallel to the smectic layer normal between the crossed polarizers.

Meanwhile, liquid crystalline molecules in the Sm-X* phase show unusual behavior. At first, it is noted that just after the Sm-A–Sm-X* transition, the molecular director ***n*** starts to rotate to the rubbing direction ***r***. As described above, the surface electroclinic effect is induced by the polar interaction between the dipole moment of the molecules and the surface. Then, it also correlates with the sign of the spontaneous polarization $\boldsymbol{P}_\mathrm{S}$ in the tilted smectic phase, which determines the direction of the smectic layer formed.[20,23] The Inui mixture investigated has a minus (−) sign of $\boldsymbol{P}_\mathrm{S}$ in the Sm-X* phase. So the smectic layer (Fig. 4) in the Sm-A phase is deviated away from ***r*** in the same way as suggested in ref. 20. When the cone

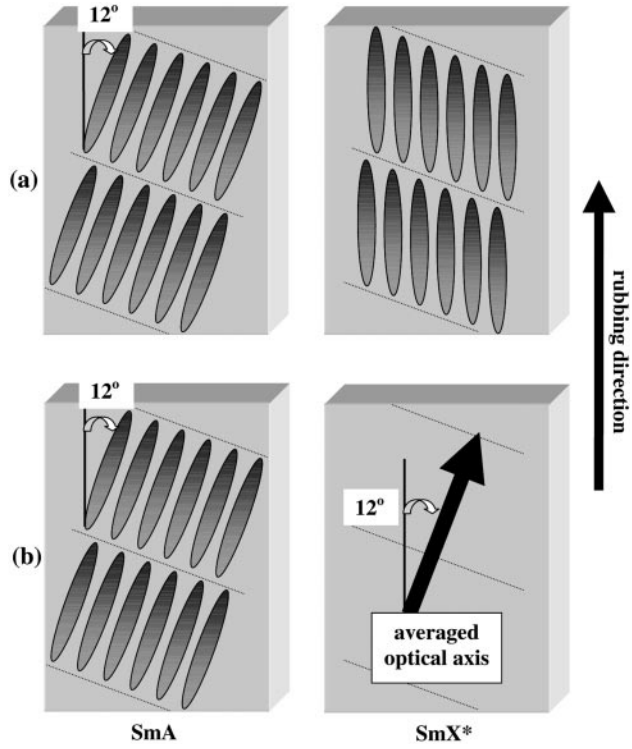

Fig. 4 Schematic representation of the molecular alignment in both cells: (a) the open cell; (b) the one-side rubbed sandwiched cell.

emerges in the Sm-X* phase, the direct combination between $\boldsymbol{P}_s$ and the polar anchoring leads to the molecular rotation to $\boldsymbol{r}$.

Taking into account the considerable large spontaneous polarization ($\boldsymbol{P}_s = 40 \sim 90\ \mathrm{nC\ cm^{-2}}$) as well as the surface electroclinic effect, the strong polar interaction is expected to affect the molecular alignment in the Sm-X* phase. Under these conditions, the corresponding configuration of $\boldsymbol{P}_s$ favors being directed into the surface; that is, $\boldsymbol{n}$ will be parallel to the aligning surface.[24] However, from the results of the apparent tilt angle ($\sim 35°$) (Fig. 3(a)) and the optical axis almost parallel to the rubbing direction near the surface (Fig. 2(c)), it is manifest that the molecular director $\boldsymbol{n}$ is not co-planar with the aligning surface. Therefore, the azimuthal angle ϕ (the angle between $\boldsymbol{P}_s$ and the aligning surface) of $\boldsymbol{n}$ on the cone is not 0 or π, and on the contrary is close to $\pi/2$. Necessarily, spontaneous polarization $\boldsymbol{P}_s$ is not oriented to the surface normal. Now, though it is not obvious how the rubbing treatment affects liquid crystal molecules in this tilted smectic phase, the fact that the Sm-X* phase shows ferrielectric behavior in the free-standing film is very important for determining this unusual alignment behavior. As mentioned before, the emergence of the ferrielectric subphase is due to the competition between the ferroelectricity and antiferroelectricity and can lead to the weak interlayer correlation from layer to layer.[17] Then, the reduced interlayer correlation also means weakening of the ferroelectricity. This can bring about a weak polar interaction between the tilted molecules and the aligning surface. As a result, the surface anchoring of the in-plane directors due to the anisotropic interaction between the molecules and the aligning surface predominates in this open cell and the molecules prefer to lie along the rubbing direction in the Sm-X* phase. If this Sm-X* phase were a common ferroelectric phase (Sm-C*), the polar anchoring should predominate due to a relatively large $\boldsymbol{P}_s$ and the azimuthal angle ϕ must be close to 0 or π.[25]

The experimental results in the open cell also are very useful for understanding the molecular orientation in the sandwiched cell. Different optical axes between the open cell and the sandwiched cell in the Sm-X* phase suggest that the spatial in-layer structure along the cell thickness is a small twisted state in the sandwiched cell. Assuming the same polarity of both polyimide surfaces, the director $\boldsymbol{n}$ under torque is directed to opposite directions in the upper and lower surface region. As shown above, however, molecules near the rubbed surface are pinned in the rubbing direction $\boldsymbol{r}$. Accordingly, molecules near the unrubbed surface are influenced by the polar anchoring above. Furthermore, in order that the averaged optical axis in the sandwiched cell is parallel to the layer normal, their orientation must be nearly similar to that near the rubbed surface except for the opposite twist sense. It is suggested that the surface anchoring in the rubbed surface is transmitted to near the opposite surface, to some degree, through the bulk by the strong intralayer correlation. Conclusively, director $\boldsymbol{n}$ rotates along the cell thickness between two surface orientations. This small twisted state in the sandwiched cell was checked experimentally.

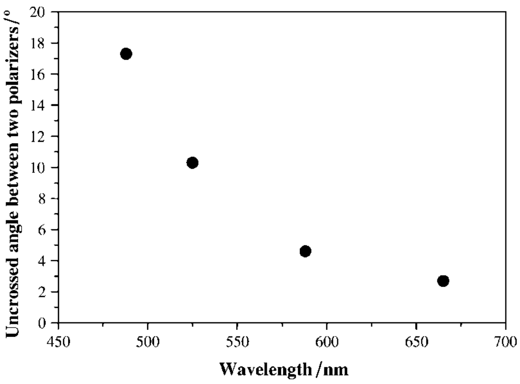

Fig. 5 The uncrossed angle between two polarizers showing the minimum transmittance at 50 °C. It depends on the wavelength of incident light.

Fig. 5 shows the wavelength dependence of the uncrossed angle between two polarizers showing the minimum transmittance in the Sm-X* sandwiched cell. The minimum transmittance is obtained under the uncrossed polarizers, not the crossed polarizers. In addition, with an increase in the wavelength, the uncrossed angle showing the minimum transmittance decreases. However, in the case that the change of the twist angle is linear along the cell thickness, the experimental low transmittance cannot be obtained even in this very small twisted geometry. Accordingly, the non-linear twisted structure along the cell thickness must be considered to explain the low transmittance obtained between the crossed polarizers.[26] Finally, the V-shaped switching as depicted in ref. 8, 11 and 13 was confirmed in the same sandwiched cell.

4. Summary

Using the open cell, we have clarified the molecular surface orientation of the chiral liquid crystals showing the V-shaped switching. The molecular director $\boldsymbol{n}$ on the rubbed surface has a polar angle $\sim 12°$ with respect to the layer normal and therefore the azimuthal angle is not 0 or π. It is believed that this strong anchoring of the in-plane directors to the rubbing direction is due to the reason that the reduced ferroelectricity in the ferrielectric phase weakens the polar interactions between the molecules and the surfaces. Meanwhile, the thin sandwiched cell has a small twisted structure along the cell thickness. It is caused by a competition between the in-plane anchoring in the rubbed surface and the polar anchoring in the unrubbed surface.

To describe the V-shaped switching behavior, some models have been proposed. However, initial states of the molecular orientation in the sandwiched cell were obtained with some assumptions. Furthermore, the switching process has been analyzed according to each assumption. Therefore, the switching process including the interaction with an electric field should be reanalyzed in the light of the observations in this work. Finally the domains in which the director ***n*** is parallel to ***r*** emerge in the sandwiched cell with increased usage time.[27] It seems to be due to the strong anchoring of the in-plane directors and thus deteriorates the stability of the molecular orientation. Therefore the Inui mixture cannot be readily put to practical use due to the problems outlined here.

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