Dynamic Molecular Reorientational Behavior Induced by Polarization Inversion of Ferroelectric Liquid Crystal

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In order to clarify the rotational direction of molecular reorientation induced by a polarization inversion of ferroelectric liquid crystal (FLC), an electric current along the direction perpendicular to both an electric field and the smectic layer normal was measured for the first time for the FLC cell with a thickness of 50 μm. The electric current curve against time upon the application of an a.c. electric field with a form of triangular wave exhibited a peak attributed to a polarization inversion. The sign of the electric current peak value was inverted by the polarity inversion of an electric field, indicating that the LC molecules rotate in the same direction on the tilt cone upon polarity inversion, that is one-way rotation. The same result was given by polarizing optical microscope observation of the director change during the polarization inversion in a free-standing film. This result differs from that for a surface-stabilized FLC cell.

Ferroelectric liquid crystals (FLCs) have attracted extensive attention because of their fast electro-optical switching characteristics, unique electromechanical effects and so on.[1—5] These effects might arise from a characteristic molecular reorientation accompanied by a polarization inversion upon the application of an electric field. A simple schematic model for the molecular reorientation and the polarization inversion is shown in Fig. 1. If an external electric field is applied in the direction perpendicular to the FLC smectic layer normal, the molecules rotate around the smectic layer normal, holding the tilt angle between the molecular long axis and the layer normal constant so that the direction of the spontaneous polarization agrees with that of an electric field.[1)] The driving torque density of this reorientation is expressed by coupling the spontaneous polarization, P_s and electric field, E, $P_s \times E$. Then, the electro-optical properties of FLC devices are directly responsible for the behavior of polarization inversion. For example, the switching speed of electro-optical effect is proportional to the magnitude of the spontaneous polarization $|P_s|$ and the contrast is related with the tilt angle θ of the molecular long axis with respect to the layer normal. Then, the sign and the magnitude of these parameters, which are characteristic of the polarization inversion, have been studied by several ways.[6—12] The dynamics of polarization inversion has been also examined for a thin cell such as the surface-stabilized FLC, in which the polarization inversion progresses through nucleation and growth of reoriented domain.[13—16] There are two possibilities for rotational behavior of molecules on the tilt cone upon the application of $+E$ and $-E$: (a) one-side rotation and (b) one-way rotation as shown in Fig. 2. The one-side rotation should occur when the potential energy of the molecular rotation on the one-side differs from that of the other-side, while the one-way rotation should occur when the potential energies of both sides are almost the same. In a thin cell, since the (FLC/substrate surface) interface interaction strongly affects the alignment and mobility of FLC molecules, the one-side rotation might be likely to occur. For example, if there is some pretilt angle at the (FLC/substrate surface) interface, the potential energy for the rotation along the cone is biased, resulting in one-side rotation. Recently, the molecular motion in a thin cell with a tilted bookshelf structure was directly observed by the time-resolved FT-IR spectroscopy.[16] By monitoring an absorption band corresponding to the direction of the molecular long axis, the investigators clarified that the rotation of molecular long axis occurred along a one-side of the tilt cone during the polarization inversion.

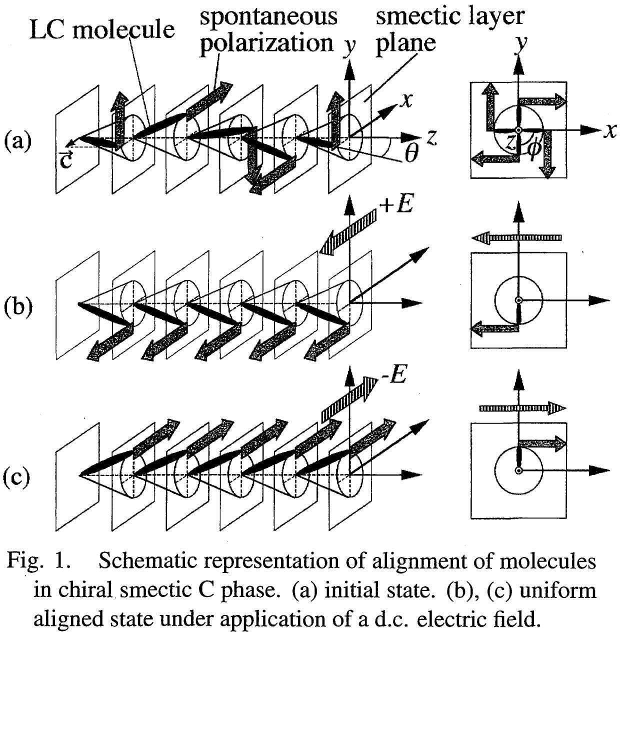

Fig. 1. Schematic representation of alignment of molecules in chiral smectic C phase. (a) initial state. (b), (c) uniform aligned state under application of a d.c. electric field.

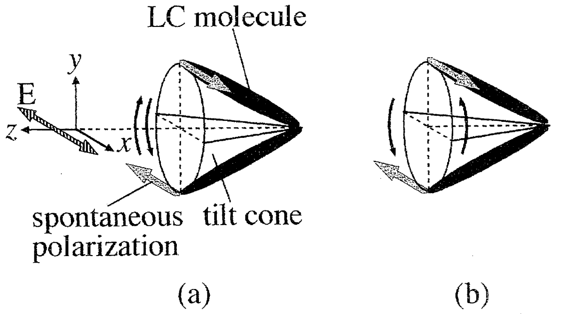

Fig. 2. Two possible rotation of molecules on the tilt cone upon the application of $+E$ and $-E$.

However, little attention has been given to the switching process for a thick cell in spite of its practical importance. Though the electro-optical effect based on transient light scattering and the electro-mechanical effects do appear in a thick cell, more detailed studies of the molecular reorientation behavior, such as the direction on the side of rotation on the cone during the polarization inversion, are required to attain high efficiencies of the electro-optical effect and the electro-mechanical effect. Since the extent of the effect the interface interaction on the behavior of the molecular reorientation becomes smaller with increasing cell thickness, the original bulk properties of FLC should govern the behavior of polarization inversion for a thick cell. Therefore, a different behavior of molecular reorientation from that for a thin cell is expected. However, there are few reported experimental results on the rotational direction of molecular reorientation at the polarization inversion in a thick cell.

In this study, an electric current in the direction perpendicular to both electric field and layer normal was measured to clarify the rotational direction of molecular reorientation which is induced by the polarization inversion in a FLC thick cell. The rotational direction was also confirmed on the basis of direct optical observation of a director change corresponding to the polarization inversion in a free-standing film.

Experimental

Material. The chiral smectic C mixture CS1024 (supplied by Chisso Co., Ltd.) was used in this study. The physical properties of CS1024 are shown in Fig. 3.

Electric Current Measurement. The cross-sectional view of a sample cell for electric measurements is shown in Fig. 4. Two pairs of electrodes, that is, the deposited Au electrodes and the ITO (indium tin oxide) electrodes were attached along the x- and the y-axes, respectively. An electric current in the direction perpendicular to an applied electric field was measured in order to decide the rotational direction of the polarization inversion. CS

CS1024 (Mixture)

$$K \xleftrightarrow{261} S_C^* \xleftrightarrow{335} S_A \xleftrightarrow{355} N^* \xleftrightarrow{363} \text{Iso.}$$

Ps : -46.9 nC·cm^{-2}
θ : 25 ° **[298 K]**
Pitch : > 20 μm

Fig. 3. Physical properties of CS 1024.

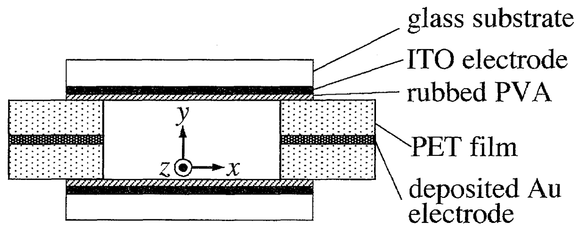

Fig. 4. Schematic representation of cell in cross-section.

1024 was sandwiched between two ITO-coated glass substrates of which the surfaces were spin-coated with poly(vinyl alcohol) and rubbed unidirectionally along the z-axis to obtain a homogeneous alignment, that is, the layer normal of CS 1024 was parallel to the z-axis. After the cell was aged on the condition that CS 1024 showed smectic A phase, the cell was cooled slowly to the temperature which CS 1024 showed chiral smectic C phase. The ITO electrode was used to evaluate the magnitude of an electric current in the y-axis direction when an electric field was applied in the x-axis direction, as shown in Fig. 4. The cell thickness in the y-axis direction was adjusted to be about 50 μm by two poly(ethylene terephthalate) (PET) films. A gold thin film 50 nm thick was sandwiched between two PET films as another electrode, as shown in Fig. 4, in order to apply an electric field in the x-axis direction. Therefore, an electric field in the x-axis direction is perpendicular to both the glass substrate normal (the y-axis direction) and the smectic layer normal (the z-axis direction). The distance between two electrodes in the x-axis was 0.5 mm. The measurement system is shown in Fig. 5. An a.c. electric field of triangular wave was applied in the x-axis direction. In order to compensate for any leakage of an applied voltage in the direction of the y-axis, a proper magnitude of an a.c. electric field of triangular wave was applied in the y-axis direction, and any conductive current in the y-axis direction was canceled out.

Polarizing Optical Microscopic Observation. A free-standing LC film was prepared for polarizing optical microscopic (POM) observation. The sample holder of the free-standing film[17] is shown in Fig. 6. The ITO electrode was attached to CS 1024 at the edge of the hole in the glass plate, to apply a voltage in the direction perpendicular to the film normal. The LC film was drawn by a spatula over the rectangular hole, as shown in Fig. 6b. LC molecules in a free-standing film formed a homeotropic alignment state after adequate annealing treatment. This means that the smectic layer normal (z-axis) agrees with the film normal, as shown in Fig. 6c.[17] Therefore, the observed texture reflects the orientation of the projected component of the director onto the smectic layer plane, namely the c-director, c shown in Fig. 1a. POM observation was carried out in the direction normal to the film plane through a color-sensitive plate (optical retardation, $R=530$ nm). A little change of the optical retardation of the free-standing LC film can be detected by utilizing a color-sensitive plate. When the LC molecules align uniformly by applying a d.c. electric field sufficiently above threshold voltage,

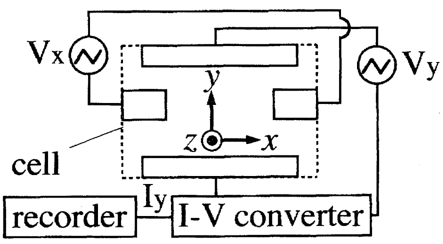

Fig. 5. Schematic diagram of measurement system.

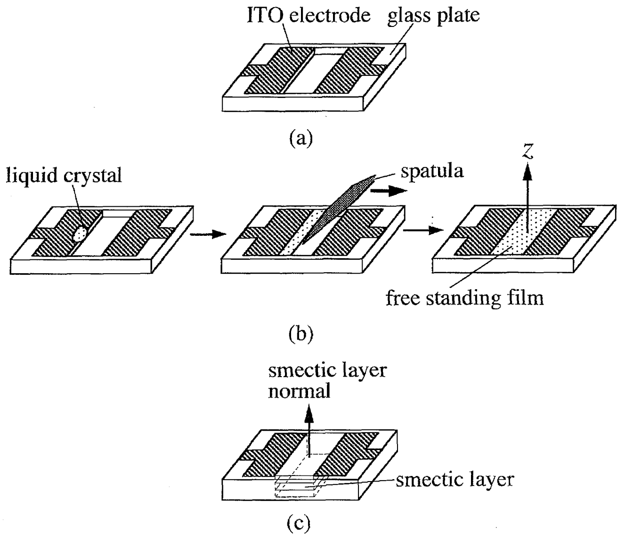

Fig. 6. Schematic representation of free-standing film. (a) sample holder. (b) preparing method. (c) alignment state.

and one of the two polarizers which are set mutually perpendicular is set parallel to the c-director so that the optical retardation of the sample may be apparently zero, the POM image through the color-sensitive plate exhibits the color of bright vermilion. Then, when the retardation increases or decreases slightly from zero, the color shifts to purple or orange, respectively. The rotational direction of the polarization inversion was decided from the color change of POM image.

Results and Discussion

Figure 7 shows the variation of the response current in the *y*-axis direction, I_y, with the application time upon the application of an electric voltage of triangular wave in the *x*-axis direction, V_x. It is apparent that the I_y curve shown by the closed circles might involve an electric charge current with a form of rectangular wave, a conductive current with a form of triangular wave and a polarization inversion current with a peak. Since the electric change current and the conductive one should appear in the case of the presence of an electric

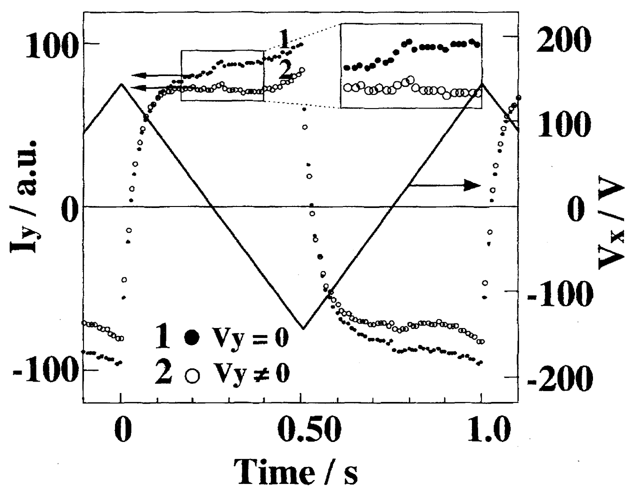

Fig. 7. Change in current under application of an a.c. electric field with a form of square wave.

field in the *y*-axis direction, the detection of these currents apparently indicates that a part of V_x leaked in the *y*-axis direction. A slope of the base line of I_y in the vicinity of the peak surrounded square corresponds to the magnitude of the conductive current. When the amplitude of the a.c. electric field applied in the *y*-axis direction, V_y, with the same phase as V_x increased from zero, the slope of the base line of I_y decreased. Therefore, the conductive current in the *y*-axis direction induced by leakage from V_x might be eliminated with an adequate amplitude of V_y. Since the peak area of I_y corresponding to the polarization inversion did not change even if the amplitude of V_y was modulated, it seems reasonable that the peak of I_y might be due to the polarization inversion induced by the application of V_x.

Next, we will discuss a relation between molecular reorientation and electric current in the *y*-axis direction. It is interesting and practically important to decide if the molecular reorientation during the polarization inversion is clockwise or anticlockwise around the *z*-axis. If most FLC molecules rotate simultaneously on the one-side of the tilt cone, a transient current arising from the polarization inversion occurs in the *y*-axis direction. For example, in the case of a reorientation process from one uniform state described in Fig. 1b (+*E* state) to another uniform state described in Fig. 1c ($-E$ state), when the reorientational direction is anticlockwise, an electric current might pass from the plus side to the minus side with respect to the *y*-axis, that is, the sign of the electric current is plus. In each case of one-side rotation or one-way rotation as shown in Fig. 2, the sign of electric current arising from polarization inversion is expected to be fixed or reversed, respectively, for the I_y curves upon inversion of an electric field, that is, $+E \rightarrow -E$ and $-\mathrm{E} \rightarrow +\mathrm{E}$. As shown in Fig. 7, the sign of the I_y was plus in the polarity inversion after switching the sign of an electric field from $+E$ to $-E$. This indicates that the reorientational direction of LC molecules is anticlockwise. Since Fig. 7 shows that the sign of a transient current was reversed from plus to minus corresponding to the polarity inversion after switching the sign of an electric field of $+E \rightarrow -E$ and $-E \rightarrow +\mathrm{E}$, it is reasonable to conclude that the anticlockwise one-way rotation of LC molecules mainly occurred for the thick cell of CS 1024.

A fluctuation of the c-director for the free-standing film during the polarization inversion was observed by POM. The texture was uniform under the application of a d.c. electric field, because the LC molecules aligned uniformly and fluctuated simultaneously upon the polarity inversion of an electric field. The interference color of the POM image for the free-standing film was bright vermilion, that is, the optical retardation was zero when a d.c. electric field was applied. The color shifts from original vermilion into yellow and blue correspond to the clockwise and anticlockwise rotation of c-director, respectively. When the polarity of an electric field was reversed, the interference color of the POM image was changed from bright vermilion to orange through purple, that is, blue shift. When the color-sensitive plate was removed and the sample table of POM was rotated with an angle of 45°, the interference color of the texture for the free-standing film under the application of a d.c. electric field was dark gray. This indicates that retardation of the free-standing film is sufficiently smaller than 530 nm (retardation of the color-sensitive plate). Therefore, the color shift in POM observation with color-sensitive plate was caused by primary interference. Each POM image taken every 1/60 s was homogeneous in each time division. The color shifts for polarity inversion at $+E \rightarrow -E$ and $-E \rightarrow +E$ were always the same. Therefore, it again seems reasonable to conclude from the POM images that the anticlockwise one-way rotation of c-director occurred for both cases of the polarity inversion at $+E \rightarrow -E$ and $-E \rightarrow +E$.

Finally, the rotational direction of the LC molecules was decided to be anticlockwise, being independent of the polarity inversion at $+E \rightarrow -E$ or $-E \rightarrow +E$, based on both the polarity inversion dependence of electric field and the interference color change in the POM image. The dynamics of FLC molecules in a thin cell have been well discussed on the basis of some experimental results and computer simulations.[13—16] Those studies revealed that the molecular reorientation behavior is strongly affected by the (FLC/substrate surface) interface interaction such as the anchoring effect for the pretilt angle of the molecules on the (FLC/substrate surface) interface. That is, the rotational direction of each molecule is decided by the biased reorientational behavior of the FLC molecules near the (FLC/substrate surface) interface. Since each potential energy for clockwise and anticlockwise rotation along the cone is required to be different due to the (FLC/substrate surface) interface interaction, the FLC molecules near the interface preferentially reorientate with a one-side rotation, and the direction of rotation is dependent on the position in the cell. The one-way rotation might occur even in a thin cell for the particular case that some factors relating to the molecular motion are balanced suitably and the potential energy for a rotation on a one-side of the cone agrees ideally with that for the other-side by chance. However, this should be quite a rare case and there is no experimental result supporting a one-side rotation in a thin cell.

In our experiment, the thick sample cell is the one which the effect of the interface interaction against the molecular reorientation is apparently small; that is, almost all molecules might rotate without any effect of the interface interaction. Then, it can be considered that a preferential one-way molecular rotation on the tilt cone during the polarity inversion is one essential characteristic of the FLC molecules in a bulk state. It can be also expected from our result that the electromechanical effect, which is a unique phenomenon of FLC, might be induced by a large translational flow in the direction perpendicular to the smectic layer normal, due to an adding up of each reorientational motion of molecules in the smectic layer.

Conclusion

The molecular reorientation behavior of a CS 1024 thick cell was examined by measuring an electric current on the direction perpendicular to both electric field and the layer normal at molecular reorientation. We found that the FLC molecules reoriented mainly with a anticlockwise one-way rotation for cases of both the polarity inversion after switching the sign of the applied electric field of $+E \rightarrow -E$ and $-E \rightarrow +E$. The clarified molecular reorientational behavior differs from the one-side rotation which recognized for the FLC molecules in a surface-stabilized FLC cell.

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