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# Effect of alignment layer on V-shaped switching in a chiral smectic liquid crystal 

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#### Abstract

The influence of the alignment layer on V-shaped switching in thin homogeneous cells of a chiral smectic liquid crystal were studied by means of electro-optic and switching current measurements. Several polyimides with different chemical structures were used as the alignment layer in thin homogeneous cells; V-shaped switching was observed with some of them and W-shaped switching with others. It was also shown that the switching current constantly flows during the V -shaped transmittance change. In order to clarify this effect of the alignment layer on V-shaped switching, polyimide films with various polarity and thickness were examined. It is concluded that thick alignment layers assist liquid crystal materials in realizing V-shaped switching, even if the materials are not ideal for this process.


## 1. Introduction

Electro-optic switching in surface-stabilized ferroelectric liquid crystals (FLCs) is characterized by a single hysteresis (bistability) [1], while that in typical antiferroelectric liquid crystals (AFLCs) is characterized by a double hysteresis (tristability) [2, 3]. Both are associated with distinct threshold behaviour. On the other hand, thresholdless switchings are also known, e.g. deformed helix FLCs $[4,5]$ and $V$-shaped electro-optic response in AFLCs [6-12].
Thresholdless, hysteresis-free, V-shaped switching was first observed by Inui et al. in thin homogeneous cells of an apparent AFLC mixture [6]. This switching mode exhibits attractive display characteristics suggesting potential for active matrix (AM) or thin film transistor (TFT) addressing in display devices [6-10]. Inui et al. proposed a Langevin-type switching in a novel tilted smectic phase with random C-director orientation [6]. However, no clear experimental evidence of the phase has been seen. Recently, Seomun et al. have proposed that the substrate interfaces induce tilting randomization while breaking the weak intrinsic inter-layer correlation, resulting in V-shaped switching [12]. Therefore, it is

[^0]still possible for Langevin-type reorientation to occur from quasi-randomly tilted orientation to a uniform state. Here 'quasi-random' means that the size/width of domains is smaller than the wavelength of visible light, so that the texture looks uniform. Further, a sensitivity of the switching to surface conditions has been demonstrated [7]. In this paper, we systematically examine the alignment layers, taking into account, for example, the kind of polyimide and the thickness and polarity of the layers. We will show that thick alignment layers and less polar surfaces are ideal for V-shaped switching.

## 2. Experimental

In the present study, we mainly used the liquid crystalline material, 4-(1-trifluoromethyl-5-ethoxy)pentyl-oxycarbonyl-3-fluorophenyl $4^{\prime}$-( $n$-undecyloxy)biphenyl4 -carboxylate ( $\mathbf{1}$ ) shown in figure 1 . This material is one of the components of the mixture in which V-shaped switching was first discovered [6]. The phase sequences shown in figure 1 were determined by observing textural changes in thin homogeneous cells held in a Mettler hot stage while cooling from the isotropic phase with a cooling rate of $0.5^{\circ} \mathrm{C} \mathrm{min}^{-1}$. V-shaped switching was observed in the phase designated as $\mathrm{SmX}^{*}$ in thin homogeneous cells.

| 1 |
| :---: |
| DOBAMBC <br> Iso $\quad 117^{\circ} \mathrm{C}$ SmA $93^{\circ} \mathrm{C} \mathrm{SmC}{ }^{*} 61^{\circ} \mathrm{C}$ Sml* $53^{\circ} \mathrm{C}$ Cryst |
| MHPOBC <br> Iso $148^{\circ} \mathrm{C} \mathrm{SmA} 122^{\circ} \mathrm{C} \mathrm{SmC}{ }_{\alpha}^{*} 120.9^{\circ} \mathrm{C} \mathrm{SmC}{ }^{\star} 119.2^{\circ} \mathrm{C}$ $\mathrm{SmC}_{\curlyvee}^{*} 118.4^{\circ} \mathrm{CSmC}_{\mathrm{A}}{ }^{*} 65^{\circ} \mathrm{C}^{\circ} \mathrm{Sml}_{\mathrm{A}}{ }^{*} 65-30^{\circ} \mathrm{C}$ Cryst |

Figure 1. Chemical structures and phase sequences of the liquid crystals studied.

In order to identify the phase, transmittance measurements at normal and oblique incidence were made using a free-standing film of about $100 \mu \mathrm{~m}$ thickness. Figure 2 shows the temperature dependence of the wavelength of the selective reflection peaks observed in normal and oblique incidence. The full pitch band was observed only in the low temperature region, and the pitch diverged at about $50^{\circ} \mathrm{C}$. The existence of the full pitch band clearly excludes the $\mathrm{SmC}_{\mathrm{A}}^{*}$ phase, suggesting a ferrielectric phase. However, we call this phase $\mathrm{SmX}^{*}$ in this paper, since the assignment has not been confirmed. In this material the spontaneous polarization and the apparent tilt angle at


Figure 2. Temperature dependence of the wavelength of half-pitch and full-pitch bands of selective reflection, measured at $30^{\circ}$ oblique incidence in a free standing film of compound 1 .
$25^{\circ} \mathrm{C}$ were found to be $260 \mathrm{nCcm}^{-2}$ and $41^{\circ}$, respectively For comparison, we also used the well known FLC and AFLC compounds, DOBAMBC and MHPOBC, shown in figure 1.

In order to investigate the influence of the substrate surface on V-shaped switching, various polyimides (PI-1-6) with the chemical structures shown in figure 3 were used as the alignment layer. The chemical structures of PI-4 and 6 are proprietary, though PI-4 and 6 could be supplied by Nissan Chemical Ind. Ltd as a polyimide for DHFLC and by Toray as SP-550, respectively. The thicknesses, dielectric constants at 1 kHz and contact angles (see §3.1.3) of PI-1-6 are shown in the table.
(SP550)

Figure 3. Chemical structures of the polyimides used as the alignment layer.

Table 1. List of polyimide films used. Thicknesses, dielectric constants and contact angles are also shown; those underlined are standard ones first used.

| Polyimide films | Thickness/A | Dielectric constant at 1 kHz | contact angle $/{ }^{\circ}$ |
| :---: | :---: | :---: | :---: |
| PI-1 | 2129 | 3.0 | 60 |
| I-2 | 2100 | 3.1 | 50 |
| PI-3 | 1294 | 3.3 | 54 |
| PI-4 | 1360 | 3.1 | 59 |
| PL-5 (PA 1) | 434 | 3.4 | 77 |
| PI-5 (PA 1) | 699 | 3.4 | 78 |
| PL-6 (SP 550) | 565 | 3.3 | 27 |
| PI-6 (SP 550) | 721 | 3.3 | 39 |
| ITO | - |  | 8 |
| Glass | - | - | 14 |

Glass plates with ITO electrodes were spin coated with all the above polyimides with a spinning speed of 4500 rpm for 50 s . In order to achieve polymerization, plates coated with PI-1, 2, 3 and 4 were baked at $250^{\circ} \mathrm{C}$ for 1 h , while those coated with PI-6 were baked at $270^{\circ} \mathrm{C}$ for 1 h . The plates coated with PI- 5 were prebaked at $100^{\circ} \mathrm{C}$ for 1 min and then cured at $180^{\circ} \mathrm{C}$ for 1 h . Using these polyimide-coated glass plates, one-side-rubbed thin cells were prepared, the cell gap being controlled by the use of a polyester film of $2 \mu \mathrm{~m}$ thickness. These cells were filled with LC material 1 in the isotropic phase. The alignment was confirmed under a polarizing optical microscope.

The optical transmittances of these cells were measured under crossed Nicols, using photomultiplier tube attached to the polarizing microscope, while applying a triangular wave voltage at different frequencies and temperatures. During these measurements, the layer normal was always kept along one of the polarizers. Polarization switching current peaks were observed in the same cells by applying a 1 Hz triangular wave voltage at the same temperatures. Contact angle measurements were made by directly measuring the contact angle of a water droplet on the substrates using a microscope.

## 3. Results and discussion

3.1. Electro-optic characteristics

### 3.1.1. Effect of temperature and frequency

The electro-optic responses, as a function of applied field measured at $40^{\circ} \mathrm{C}$, are summarized in figure 4 , which includes the results of the cells made using the underlined polyimides in the table at frequencies of 5, $10,50,100$ and 1000 mHz . The underlined PI films were coated onto ITO glass plates according to a standard recipe using the same conditions of spin coating ( 4500 rpm for 50 s ). Good V-shaped switching was observed in the cells of $\mathbf{1}$ when PI-1,2,3 and 4 were used as the alignment layer at all frequencies, though slight hysteresis was seen at frequencies less than 10 mHz . On the other hand, W-shaped switching was observed for PI-5 and 6 at all frequencies.

The temperature dependence of V-shaped switching in the SmX * phase of compound 1 measured at 1 Hz is shown in figure 5. At all the temperatures throughout the SmX * phase, ideal V-shaped switching was exhibited for PI-1, 2, 3 and 4, whereas W-shaped switching was seen for PI-5 and 6. The solid straight line in each frame shows the transmittance when the field is switched off. The data were recorded using a roll mode of an oscilloscope for several seconds, so that the abscissa is not a field but a time. The bottom line (abscissa) of all the figures given in this article corresponds to the complete dark state when no light enters the photomultiplier tube. The transmittance in the field off state is very low for


Figure 4. Optical transmittance as a function of applied electric field, measured at a temperature of $40^{\circ} \mathrm{C}$ by applying a triangular wave form at various frequencies, for cells of compound 1 treated with the underlined polyimides shown in the table.
$\mathrm{PI}-1,3$ and 4 throughout the SmX * phase, whereas it is high for PI-2 at higher temperatures such as $70^{\circ} \mathrm{C}$ and $55^{\circ} \mathrm{C}$. In the former case, the transmittance remains at the low level whenever the field is turned off. In the latter case, on the other hand, the level of the transmittance strongly depends on the moment when the field is turned off. Hence, PI-2 is not a good alignment layer for V-shaped switching. Furthermore, a rapid increase in the transmittance was observed with the field off in the cells made with PI-5 and 6, which show W-shaped switching in the SmX* phase. We observed that the level of transmittance in the field off state decreases with decrease of temperature for all the rubbing cells of compound 1 (see figure 5). It is clear from these figures that good V-shaped switching can be achieved in the SmX* phase of compound $\mathbf{1}$ when PI-1, 3 or 4 are used as the alignment layer.


Figure 5. Optical transmittance as a function of applied electric field at $25,40,55$ and $70^{\circ} \mathrm{C}$, measured by applying a triangular wave form of frequency 1 Hz , for cells of compound 1 treated with the underlined polyimides in the table.

As mentioned above, we observed V-shaped switching for all polyimides except PI-5 and 6. What is the key factor(s) of the alignment layer for the appearance of V-shaped switching? All these polyimides have approximately the same dielectric constant, as shown in the table. The most distinctly different factor between PI-1-4 and PI-5 and 6 is the film thickness; it is clear that the films of PI-5 and 6 used were thinner than the others.

### 3.1.2. Effect of alignment film thickness

In order to investigate the effect of polyimide film thickness, we made thicker films of PI-5 (699A) and PI-6 (721 A) on the ITO glass substrate and used them to prepare single-side-rubbed homogeneous cells of compound $\mathbf{1}$. The switching characteristics of these cells were studied by observing the optical transmittance under the same conditions as used in the previous measurements. The frequency dependence and temperature dependence
of the switching characteristics in the cells thus prepared are shown in figure 6. The electro-optic responses as a function of the applied field measured at $40^{\circ} \mathrm{C}$ and at $5,10,50,100,1000,20000 \mathrm{mHz}$ are summarized in figure $6(a)$; those measured at a frequency of 1 Hz and at four different temperatures, $25,40,55$ and $70^{\circ} \mathrm{C}$ are shown in figure $6(b)$ for thicker films of PI-5 and 6. Ideal V-shaped switching could be observed at all frequencies and temperatures when PI-5 and 6 films became thicker. The tip of the $V$-shape remains always in the darkest level, although the level of the transmittance in the field off state is relatively high at higher temperatures such as $70^{\circ} \mathrm{C}$ and $55^{\circ} \mathrm{C}$.

In order to confirm this dependence of V -shaped switching on the thickness of the alignment layer, PI-4 was chosen and films thicker ( 2249 A ) and thinner ( 594 A ) than that shown in the table were made. We confirmed


Figure 6. Optical transmittance as a function of applied field measured at (a) $40^{\circ} \mathrm{C}$ and various frequencies, and (b) 1 Hz and various temperatures for cells of compound $\mathbf{1}$ with thick PI-5 and PI-6.
that compound $\mathbf{1}$ shows good V-shaped switching for a thicker film and W -shaped switching for a thinner film of PI-4 at all frequencies and temperatures [13]. The thicker the polyimide film, the better the V-shape.
We should also comment on the effect of insulating layers between ITO and PI. An ideal V-shaped switching was observed in the cell fabricated using glass plates with ITO, an insulating layer and thin PI-6. Thus, the use of an insulating layer and thin alignment layer instead of thick alignment layer is effective in realizing V-shaped switching, suggesting the usefulness of layers with small capacitance and/or large resistance [13].

### 3.1.3. Effect of surface polarity

In order to understand further the influence of the alignment layer on V-shaped switching the substrate interface was changed in various ways. First we made a thin homogeneous cell of compound $\mathbf{1}$ using ITO glass substrate (without any surface treatment) by the temperature gradient method, and then another asymmetrically rubbed cell with one substrate coated with PI-4 followed by rubbing and the other with ordinary ITO glass. The optical transmittance of these cells was measured under the same experimental conditions as used throughout the present study. The frequency dependence of the optical transmittance measured at $40^{\circ} \mathrm{C}$, and the temperature dependence at 1 Hz for the cell of compound $\mathbf{1}$ made by the temperature gradient method, are shown in figures 7 (a) and $7(b)$, respectively. Surprisingly, it does not show V-shaped switching but does show typical ferroelectric switching in the absence of a polyimide layer. In this cell, when the field is off transmittance is high, as shown by the horizontal lines in figure $7(a)$.
Another interesting phenomenon was observed in the asymmetrically rubbed cell with only one substrate coated with PI-4. Figures $8(a)$ and $8(b)$ illustrate the


Figure 7. Optical transmittance as a function of applied electric field (triangular wave form) measured at (a) 1 Hz and various temperatures, and (b) $40^{\circ} \mathrm{C}$ and various frequencies for a temperature gradient cell of compound $\mathbf{1}$.


Figure 8. Optical transmittance as a function of applied electric field (triangular wave form) measured at (a) $40^{\circ} \mathrm{C}$ and various frequencies, and $(b) 1 \mathrm{H}$ and various temperatures, for an asymmetric cell of compound $\mathbf{1}$ made by using PI-4 on only one substrate.
frequency dependence of the optical transmittance for this cell measured at $40^{\circ} \mathrm{C}$ and the temperature dependence of the optical transmittance measured at 1 Hz , respectively. It apparently shows V-shaped switching at all temperatures and frequencies. However, the switching region is laterally shifted toward the negative field side, and the transmittance increases up to a uniform level when the applied field is switched off, as shown in figure $8(b)$. It is still true that the interaction between the liquid crystal molecules and the alignment layer dominates and gives rise to the laterally shifted V-shaped switching, as is understood by the ferroelectric behaviour in temperature gradient cells without alignment layers.

Generally, the electro-optic properties of liquid crystals strongly depend on the surface of the substrate. The present thresholdless hysteresis-free V-shaped switching is also considered to be realized by virtue of the substrate interface that induces tilting randomization due to weak inter-layer correlation [12]. In this case the polarity of the surface could play a major role in the emergence of V-shaped switching in this particular liquid crystal which has an extremely high spontaneous polarization. In order to understand the polar interactions between the liquid crystal molecules and the polyimides, surface polarity was investigated by determining the contact angle of water on each of the polyimide surfaces. The measurements were made soon after the preparation of the polyimide films on ITO glass surfaces. The contact angles, $\theta$, measured for various surfaces are shown in the table. According to Dijon et al. [14], the smaller the $\theta$, the higher the surface polarity. Hence, the ITO
surface which has the smallest contact angle $\left(8^{\circ}\right)$ is the most highly polar surface.
Among the polyimides that we used in the present research, PI-5 is the least polar surface and PI-6 is the most polar one; PI-1, 3 and 4 have almost the same polarity, which is less than PI-2. In the case of PI-6, the polarity decreases with the increase of film thickness. As mentioned above, however, both weak (PI-5) and strong (PI-6) polar surfaces give rise to W-shaped switching if the film is thin, and to V-shaped switching if the film is thick. Hence, polarity of the surface seems to have no considerable effect on V-shaped switching. We have to consider different reasons for the fact that the most polar ITO surface favours bistability and suppresses V-shaped switching as in the temperature gradient cells without polyimide alignment layers.

### 3.1.4. Characteristics of hysteresis

In addition to these observations, another very significant characteristic was observed in the hysteresis of the optical transmittance during V-shaped switching. The directions of the hysteresis loops shown in figures 4 and 5 for PI- 5 and 6 are normally observed during typical ferroelectric switching from one uniform state to another. However, an abnormal effect was observed during V-shaped switching in most of the cells in particular ranges of temperature and frequency; i.e. the transmittance curve crosses during increase and decrease of a field and the directions of the hysteresis loops are opposite to those observed in ferroelectric switching. The appearance of various kinds of switching characteristics in all the rubbing cells of compound $\mathbf{1}$ is summarized in figure 9 . It is clear from figure 9 that this abnormal hysteresis tends to disappear with increase of frequency (see for example PI-3) and decrease of temperature (see for example PI-6, thick), and hysteresis-free V-shaped switching could be seen for some combinations of frequency and temperature. It is also true in some cases that a hysteresis similar to ferroelectric switching reappears when the frequency is further increased to say 20 Hz , though the results are not included in figure 9 . It should be emphasized that the hysteresis shown in the V-shaped switching in figures 4 and 5 is negligibly small compared with that in ferroelectric switching.

### 3.1.5. Effect of ionic accumulation

The abnormal hysteresis mentioned above can be explained with the help of the ionic process that occurs during switching. Figure 10 illustrates the charge distribution in a cell under a d.c. electric field. When an electric field, $\mathbf{E}_{\text {ext }}$, is applied to an FLC cell, dipoles align and surface charges appear at the interface of the polyimide/liquid crystal resulting in a reverse field, $\mathbf{E}_{\text {sur }}$. Since $\mathbf{E}_{\text {sur }}$ is smaller than $\mathbf{E}_{\text {ext }}$, positive and negative


Figure 9. Summary of different types of hysteresis that appear during switching at different temperatures and frequencies for cells of compound $\mathbf{1}$ with all the polyimides shown in the table.
ionic impurities or mobile charges move to opposite directions and produce an ionic field, $\mathbf{E}_{\mathbf{i o n}}$, antiparallel to $\mathbf{E}_{\text {ext }}$.

Let us first discuss the result shown in figure 8 on the basis of an ion accumulation effect. In addition to this effect, charge injection from an ITO electrode has to be


Figure 10. Illustration of electric charge distribution and internal electric fields in a SSFLC cell under the application of an external electric field, $\mathbf{E}_{\text {ext }}$.
taken into account. Figure 11 illustrates the charge distribution in an asymmetric cell, namely with and without a polyimide layer on ITO. Under an external electric field $\mathbf{E}_{\text {ext }}$, movement of ionic charge occurs, as shown in figure 10. As for carrier injection from ITO, either positive or negative carriers can be injected according to the relationship between the work function of ITO and the electron affinity and ionization potential of the LC. If we assume that negative carriers can be injected, they will only neutralize positive ionic charges accumulated on the negative electrode, thus, reducing the ionic reverse field, as shown in figure 11. Hence, the upward effective field is smaller than the downward effective field. The situation is the same when only positive carriers can be injected. This effect produces the lateral shift of the switching curve shown in figure 8. The asymmetric switching therefore indicates charge injection from ITO.
Let us next consider switching behaviour under an effective field resulting from the ion accumulation dynamics. Figure 12 illustrates a switching scheme realized under the influence of the ionic effect. Suppose that ferroelectric-like switching with normal hysteresis occurs in the absence of an ionic effect, i.e. during the field decrease switching starts at (A) and is completed at (B). Note that this is not a typical ferroelectric switching because the appearance of the completely dark state is different from figure 7. Generally FLC switching does not show complete darkness in the present polarizer positions, since molecular rotation between two ferro-


Figure 12. Illustration of the variation of the applied external field due to charge accumulation on the polyimide/ liquid crystal interface for a compound showing a typical hysteresis during switching in a SSFLC cell. The solid and dotted lines represent the applied external field and the effective field due to charge accumulation, respectively. As a result the cell shows an abnormal hysteresis shown in (c).
electric states is not coherent and domain formation is associated with the switching. The effective field caused by surface charges and ionic accumulation is supposed to be the dotted line in figure 12, i.e. the phase shifts so that a negative effective field exists at zero external field because of the finite mobility of ions. Therefore, switching actually starts at ( $\mathrm{A}^{\prime}$ ) and is completed at ( $\mathrm{B}^{\prime}$ ), which apparently correspond to ( $\mathrm{A}^{\prime \prime}$ ) and ( $\mathrm{B}^{\prime \prime}$ ), respectively. If $\left|V\left(\mathrm{~A}^{\prime \prime}\right)\right|>\left|V\left(\mathrm{~B}^{\prime \prime}\right)\right|$, an abnormal hysteresis is observed. If $\left|V\left(\mathrm{~A}^{\prime \prime}\right)\right|=\left|V\left(\mathrm{~B}^{\prime \prime}\right)\right|$, one can obtain hysteresis-free

Figure 11. Illustration of electric charge distribution and internal electric fields in an asymmetric cell under the application of (a) upward and (b) downward external electric fields. In this cell, the upper substrate is a ITO glass with a layer of polyimide and the lower one is uncoated ITO glass.


V-shaped switching. The charge accumulation and associated reverse field strongly depend on the spontaneous polarization $\mathbf{P}_{\mathrm{s}}$, the thickness of the alignment layer and the mobility of the ions. Hence, the characteristics of the hysteresis are highly dependent on the temperature and the frequency, as shown in figure 9. When the temperature is higher (mobility is larger) and/or the frequency is lower, the difference between the external field and the effective field is relatively large, since the effect of ionic accumulation is promoted. Thus, the observation shown in figure 9 , that abnormal hysteresis tends to appear at lower frequency and higher temperature, can be interpreted. In PI-6, normal hysteresis appears at very low frequencies such as 5 and 10 mHz . This phenomenon can be interpreted by considering that carrier injection screens the ionic effect, and normal hysteresis may result.
The ionic effect has been studied in relation to the bistability of surface-stabilized FLC devices [15-19]. According to these studies, surface and ionic charges accumulated on the interfaces between the FLC medium and alignment layers play a crucial role in the bistability. Namely, thinner alignment layers with high dielectric constant, high ion mobility and lower spontaneous polarization alleviate the reverse field effect and enhance the bistability. The opposite situation may prevent bistability and promote thresholdless switching. It is inferred that thicker alignment layers with low dielectric constant, low ion mobility and high spontaneous polarization may lead to quasi V -shaped switching, even if the LC materials are not ideal for V-shaped switching. This consideration is consistent with the effect of insulating layers mentioned in §3.1.2.

### 3.2. Switching current

It is interesting to observe the switching current response in various cells made with different polyimide alignment layers, since molecular orientational change is also associated with dipole switching. Figure 13 shows polarization current peaks, measured by applying a triangular wave form at a frequency of 1 Hz , for cells with all the polyimides used and also for the temperature gradient cell. For PI-1, 2, 3 and 4 which give rise to V-shaped switching, we observed broad switching current peaks, whereas the current peaks are relatively sharp for thin films of PI-4 and 5 throughout the SmX* phase. In the temperature gradient cell of compound 1, which shows typical ferroelectric switching, very sharp switching current peaks were observed. Although the switching current peaks shown in figure 13 for thin films of PI-5 and PI-6 are not as broad as those that give rise to V-shaped switching, they become broad when the films become thicker, as shown in figure 14. Evidently, the switching current becomes broader with the increase


Figure 13. Observed switching current peaks and the applied triangular wave form of 1 Hz at various temperatures for cells of compound $\mathbf{1}$, with the underlined polyimides from the table, and in the temperature gradient cell.


Figure 14. Switching current peaks and the applied triangular wave form of 1 Hz at various temperatures for cells of compound 1 with thick PI-5 and PI-6.
of the polyimide film thickness. This broad switching current peak would be a characteristic feature of V-shaped switching.

Figure 15 compares the behaviour of switching current peaks of V-shaped switching with ferroelectric switching observed in compound 1. During V-shaped switching, when the applied field is decreased there is a sudden increase in the switching current at the point where molecules start to switch from one uniform state; the current remains unchanged throughout the process and then drops at the transition to the other uniform state. Thus, it is clear from figure 15 that dipole switching and the associated orientational change occur continuously in the case of V-shaped switching.

### 3.3. Texture observation

Simultaneously with the electro-optic study of the effect of the alignment layer on V-shaped switching, the textures of compound $\mathbf{1}$ in the SmA and SmX * phases were observed in all these cells under a polarizing microscope. In the SmA phase, the extinction direction under crossed Nicols was $13^{\circ} \sim 15^{\circ}$ tilt from the rubbing direction. Hence, in the SmA phase, layers are not perpendicular to the rubbing direction. In the $\mathrm{SmX}^{*}$ phase, layer normal was along the same direction as the


Figure 15. Optical transmittance and switching current peaks as a function of applied electric field observed at 1 Hz and $40^{\circ} \mathrm{C}$ for (a) V-shaped switching for a cell of compound 1 with thick PI-3, and (b) ferroelectric switching for a cell of compound 1 made by the temperature gradient method without polyimide.
extinction direction in the SmA phase, i.e. $13^{\circ} \sim 15^{\circ}$ tilt from the rubbing direction. The virgin state of the SmX * phase in all the rubbed cells (except the one made with two different substrates) showed twisted states whereas that made by the temperature gradient method showed bistable uniform states. The asymmetrically rubbed cell of compound 1 made with one substrate coated with PI-4 and the other with only ITO showed an extinction along the layer normal under crossed Nicols only in the virgin state in the SmX * phase. This condition could be easily changed by a small perturbation. In general, it is considered that during the alignment of ferroelectric liquid crystals, if only one surface is rubbed the results is less bistable alignment and more twisted states [20]. The twisted states observed in all our rubbed cells may have arisen due to the one side rubbing method that we adopted in the present study.
The switching was video-recorded with a CCD attached to the polarizing microscope. In all these rubbed cells similar textural changes were observed during $V$-shaped switching. Figure 16 displays a series of micrographs recorded during switching in a cell of compound $\mathbf{1}$ made with a thick film of PI-6 on applying a triangular wave voltage of $60 \mathrm{~V}_{\mathrm{pp}}$ at 0.01 Hz and at $40^{\circ} \mathrm{C}$ while keeping the layer normal along one of the polarizers. Figure 16 (a) displays one of the uniform states under 60 V . When the applied field was decreased, fine stripe-like domains started to appear along the layer direction [figures 16 (b) and $16(c)$ ]; these soon disappeared, changing the colour of the texture uniformly [figure $16(d)$ ], and became completely dark at zero field [figure $16(e)$ ]. When the applied field was switched off, a dark texture with some domains could be seen [figure $16(f)$ ]. These stripe domains always appeared along the layers at the transition to and from the ferroelectric state. Thus, V-shaped switching in the present cell of compound $\mathbf{1}$ is associated with domain formation. However, domain formation does not seem to play a major role in the switching, since a simple V -shaped switching was observed. In this sense, the switching characteristics observed in compound $\mathbf{1}$ are slightly different from the previous observation of ideal V-shaped switching with continuous brightness change without domain formation [12].

Figure 17 displays a series of micrographs recorded during W -shaped switching in a cell of compound $\mathbf{1}$ made with a thin film of PI-6 when a triangular wave voltage of $15 \mathrm{~V}_{\mathrm{pp}}$ at 0.01 Hz was applied at $40^{\circ} \mathrm{C}$. The texture in one of the uniform states is shown in figure 17 (a). When the applied field was decreased, the texture changed its colour gradually [figure $17(b)$ ], and then stripe domains appeared with the change of the colour near zero field [figure 17 (c)]; but the texture did not become dark at all during the switching. Figure $17(f)$ shows the bright texture in the field off state. Figures 16


Figure 16. A series of optical micrographs taken in a thin homogeneous cell of compound 1 made with a thick film of PI-6 during V-shaped switching with decreasing applied field. The layer normal was parallel to the polarizer and a triangular wave voltage of $60 \mathrm{~V}_{\mathrm{pp}}$ at 0.01 Hz was applied. (a) Bright texture in one of the uniform states at 30 V , (b) domains start appearing, (c) domains exist, (d) domains disappear and texture becomes grey in colour and (e) dark texture at zero field during the switching process. The texture in the field off state is shown in $(f)$.
and 17 correspond to the optical transmittance shown in figures $6(a)$ and 4 at 10 mHz for thick and thin films of PI-6, respectively. Similar textural changes were observed during V-shaped and W -shaped switchings for thick and thin films of PI-5, respectively.
In the temperature gradient cell, boat-shape-like domains appeared during the switching throughout the SmX* phase, though this is not easy to observe in figure 18 because of the small domain size. Figure 18 was recorded in the temperature gradient cell of compound 1 while keeping the layer normal along one of the polarizers and by applying a triangular wave voltage of $9 \mathrm{~V}_{\mathrm{pp}}$ at 0.01 Hz and at $40^{\circ} \mathrm{C}$. This sequence displays the switching process from one uniform state to another, from figure 18 (a) to figure 18 (e). Throughout the switching process boat-shape-like domains appeared and the texture never became dark. The texture in the field off state was bright and similar to figure 18 (e). From these micrographs, it is clear that the mechanism of V-shaped switching is different from that of W-shaped switching and normal ferroelectric switching, although the V -shaped and W-shaped switching in this particular liquid crystal


Figure 17. A series of optical micrographs showing W-shaped switching at $40^{\circ} \mathrm{C}$ under the application of a triangular wave voltage of $20 \mathrm{~V}_{\mathrm{pp}}$ in a thin homogeneous cell of compound 1 made with a thin film of PI-6. The layer normal is parallel to the polarizer and the micrographs were taken while decreasing the applied field. (a) Bright texture in one of the uniform states at 10 V , (b) uniform colour change with decreasing field, (c) the appearance of domains, ( $d$ ) texture before switching to the other uniform state and (e) bright texture in the other uniform state at -10 V . The texture in the field off state is shown in $(f)$.

1 are associated with stripe domains. A detailed study of the appearance of stripe domains during V-shaped switching is in progress and will be explained with the aid of stroboscopy in a forthcoming publication.

### 3.4. Comparison with typical FLC and AFLC materials

In order to emphasize the surface-sensitive feature in compound 1, similar measurements were also carried out on other typical FLC and AFLC materials. Among the polyimides used, PI-3 and 6 were chosen. As the first example, two thin cells, one-side-rubbed and temperature gradient cells of DOBAMBC, were prepared and measurements made at the $\mathrm{SmC}^{*}$ phase.

Figure 19 illustrates the frequency dependence of the electro-optic response of DOBAMBC cells made with PI-3 and 6 and by temperature gradient method at $T_{\mathrm{c}}-T=10^{\circ} \mathrm{C}$. The switching, particularly in the PI-3 cell, consists of two-step processes; steep at low field and slow at high field. They correspond to switching in bulk and surface regions [21]. In both rubbed cells of DOBAMBC, there appeared a hysteresis at lower


Figure 18. A series of optical micrographs showing ferroelectric switching in a thin homogeneous cell of compound $\mathbf{1}$ made by the temperature gradient method at $40^{\circ} \mathrm{C}$ under the application of a triangular wave voltage of $9 \mathrm{~V}_{\mathrm{pp}}$ at 0.01 Hz . The layer normal is parallel to the polarizer and the micrographs were taken while decreasing the applied field. (a) Bright texture in one of the uniform states at 4.5 V ; $(b)-(d)$ the existence of boat-shaped domains throughout the switching process. The texture in the other uniform state at -4.5 V is shown in $(e)$.
frequencies with its direction opposite to that in ferroelectric switching; the width of the hysteresis decreases with increase of frequency apparently showing a hysteresis-free curve at 1 Hz . When the frequency is
further increased, the normal hysteresis of ferroelectric switching is seen. This abnormal hysteresis observed at lower frequencies (figure 19) may be caused by reverse switching due to the presence of ionic impurities in DOBAMBC. The cell made by the temperature gradient method shows the normal hysteresis of ferroelectric switching over the frequency range studied.

Figure 20 shows the temperature dependence of optical transmittance measured at 1 Hz for the three types of cells mentioned in figure 19. As is clear from this figure, although the optical transmittance of DOBAMBC measured at 1 Hz in the two rubbed cells shows a hysteresis-free curve and resembles the V-shaped switching in compound $\mathbf{1}$, the transmittance at the tip of the


Figure 20. Optical transmittance as a function of applied field (triangular wave) measured in thin homogeneous cells of DOBAMBC made using PI-3 and PI-6 and by the temperature gradient method at a frequency of 1 Hz and various temperatures in the $\mathrm{SmC}^{*}$ phase.

Figure 19. Optical transmittance as a function of applied electric field (triangular wave) measured in thin homogeneous cells of DOBAMBC made using PI-3 and PI-6 and by the temperature gradient method in the SmC* phase at $T_{\mathrm{c}}-T=10^{\circ} \mathrm{C}$ and different frequencies.

curve and the level of transmittance in the field off state are quite high throughout the $\mathrm{SmC}^{*}$ phase. From these results it is clear that switching in the $\mathrm{SmC}^{*}$ phase, unlike V-shaped switching in the SmX * phase of compound $\mathbf{1}$, is essentially independent of the thickness of the alignment layer or the polarity of the surface, because of the dynamic switching process. It is noted, however, that static molecular alignment in the absence of an electric field should be influenced by surface properties such as polarity. The situation is similar in LC materials showing V-shaped switching. The emergence of V-shaped switching is affected by the thickness of alignment layers because of the dynamic switching process, as well as by surface polarity as a result of static molecular alignment at the surface.

Switching current measurements were also made using the three types of DOBAMBC cells under a triangular wave form of frequency 1 Hz . All the current peaks were sharp and suggest typical ferroelectric switching in all three cells.
As for a typical AFLC material, MHPOBC was chosen for a study of the switching characteristics of thin homogeneous cells. PI-3 was chosen for the alignment layer and a thin homogeneous cell $(2 \mu \mathrm{~m})$ of MHPOBC was prepared with one side rubbed. The electro-optic response of this cell in the $\mathrm{SmC}_{\mathrm{A}}^{*}$ phase was measured under the same experimental conditions as used in the previous measurements. The frequency and temperature dependences of the optical transmittance measured at $T_{\mathrm{c}}-T=10^{\circ} \mathrm{C}$ for MHPOBC are shown in figures $21(a)$ and $21(b)$, respectively. MHPOBC clearly shows typical tristable switching due to the fieldinduced antiferroelectric-ferroelectric transition characteristic to the $\mathrm{SmC}_{\mathrm{A}}^{*}$ phase. These results in DOBAMBC and MHPOBC clearly indicate that the LC material as well as the alignment layer must be carefully chosen for the appearance of V-shaped switching.

## 4. Concluding remarks

The influence of alignment layer on V-shaped switching was studied using cells made with various kinds of polyimide alignment layers with different thicknesses. Using these cells, electro-optic response, switching current and texture observations were made. In addition to the typical compound for display of V-shaped switching, other typical FLC and AFLC materials were used for comparison. Based on these observations, it is concluded that the alignment layer plays a major role in the occurrence of V-shaped switching; namely, thick alignment layers with low conductivity are ideal for V-shaped switching. This condition is particularly crucial if the LC materials are not ideal for V-shaped switching. It is also noted that Casio Computer Co., Ltd reported the


Figure 21. Optical transmittance as a function of applied field (triangular wave) measured in a thin homogeneous cell of MHPOBC made with PI-3 at (a) $T_{\mathrm{c}}-T=10^{\circ} \mathrm{C}$ and various frequencies, and $(b) 1 \mathrm{~Hz}$ and various temperatures.
occurrence of V-shaped switching using $\pm 2.5 \mathrm{~V}$ [9]. This report suggests that a thick alignment layer is not essential if ideal LC materials for V-shaped switching are used.

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