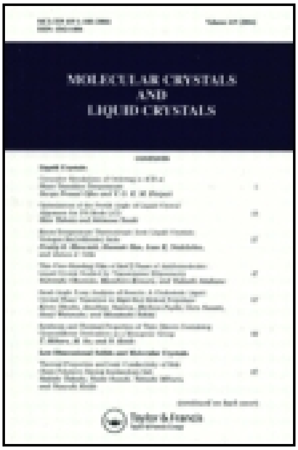

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Electric Field Response of Ferroelectric Liquid Crystal Molecules Investigated by Optical Transmission and Surface Plasmon Polariton Resonance Methods

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Electric Field Response of Ferroelectric Liquid Crystal Molecules Investigated by Optical Transmission and Surface Plasmon Polariton Resonance Methods

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Optical transmission and surface plasmon polariton (SPP)-mediated reflection measurements have been performed on the ferroelectric liquid crystal, (*s*)-4-(α-methylheptyloxy)-4′-(4″-*n*-octylphenyl-oxycarbonyl)biphenyl in both surface-stabilized and non-stabilized states of the chiral smectic C phase. A comparison of the molecular response to an externally applied electric field is made between the bulk and boundary layers on the basis of changes in transmitted and reflected light intensities caused by alterations in the strength and polarity of the field. In particular, the changes in the reflected light intensity in the Kretschmann ATR prism geometry are referenced to the light intensity at the resonance of SPPs. When surface-stabilized cells are used, the switching in alignment between the bistable states is observed in the boundary layer as well as in the bulk layer, although the maximum frequency which allows the switching is an order of magnitude less for the boundary, indicating a stronger influence from the substrate surface. Very reasonably, such a switching is not observed when non-stabilized FLC cells are used. Moreover, it is found that the bulk layer exhibits a memory effect, but it is not observed in the boundary layer.

Keywords: ferroelectric liquid crystal, electro-optical effect, surface plasmon polariton, memory effect

I. INTRODUCTION

Considerable interest has recently converged upon ferroelectric liquid crystals (FLCs) because of their potential application to fast switching electro-optical devices.[1–7] Most of the practical applications are concerned with the use of surface-stabilized thin FLC films for which constituent molecules are aligned homogeneously with their long axes parallel to the direction of rubbing of polymer films on the electrode surfaces and therefore the intrinsic helical structure in the chiral smectic C (SmC*) phase is suppressed.[8,9] Since the surface properties can exert a strong influence on the performance of FLC devices, it is of significance to understand the behavior of FLC molecules near the electrode surfaces with or without an applied electric field.

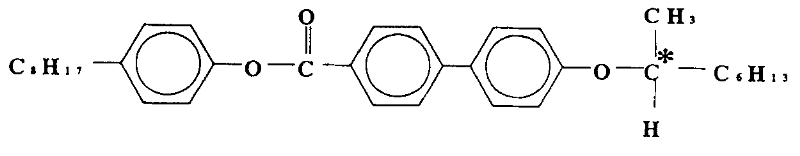
A large number of studies have been made of the electro-optical properties of bulk liquid crystals (LCs) by the measurements of dielectric anisotropy or birefringence, but studies of the interfacial properties have been quite limited. Part of the significant reason for this is the difficulty of studying a very limited area of the LC. Recently, new techniques of probing the surface alignment of LC molecules have appeared. These include infrared-visible sum-frequency generation[10] and scanning tunneling microscopy,[11-14] either of which allows observation of the structure of surface monolayers. However, information obtained by these methods is not necessarily the same as that for the boundary layers of much thicker LC films which are used in practice.

We have previously proposed the use of infrared attenuated total reflection (ATR) spectroscopy to probe the surface- and static electric field-induced alignments of nematic LC molecules in the boundary layers at electrode surfaces.[15-17] In a previous experiment using electric field modulation infrared ATR spectroscopy, we explored the dynamic response of boundary nematic molecules to alterations in the field strength.[18] While optical ATR techniques have also been used successfully for determining the surface tilt angles of LC molecules[19,20] and refractive indices of LCs,[21] no related investigations dealing with their optical switching behavior in an applied field have been reported.

In this paper, we report a new optical ATR study on the switching behavior of surface-stabilized FLC alignment in the boundary layer. In this work, surface plasmon polaritons (SPPs) were excited by light using the Kretschmann ATR prism geometry[22] and used to probe the optical properties or molecular alignments of the FLC. The utility of the SPP-mediated reflection measurements are demonstrated in this paper.

2. EXPERIMENTAL

The FLC material used in the present work is (*s*)-4-(α-methylheptyloxy)-4′-(4″-*n*-octylphenyl-oxycarbonyl)biphenyl (MHOPOB), which was purchased from Chisso Petrochemical Co. Figure 1 shows the molecular structure of MHOPOB and its thermal phase-sequence. The LC cells used for ATR and transmission experiments are shown in Figure 2. The transmission measurements were performed to obtain information about the bulk LC layer. In the ATR experiment, an SPP was excited at an Ag film surface to probe the boundary LC layer. In this case the Ag film



$$\text{Cryst.} \xrightarrow{54^\circ\text{C}} \text{SmC}^* \xrightarrow{70^\circ\text{C}} \text{SmA} \xrightarrow{80^\circ\text{C}} \text{N}^* \xrightarrow{90^\circ\text{C}} \text{Iso.}$$

FIGURE 1 Molecular structure of MHOPOB and phase-transition sequence.

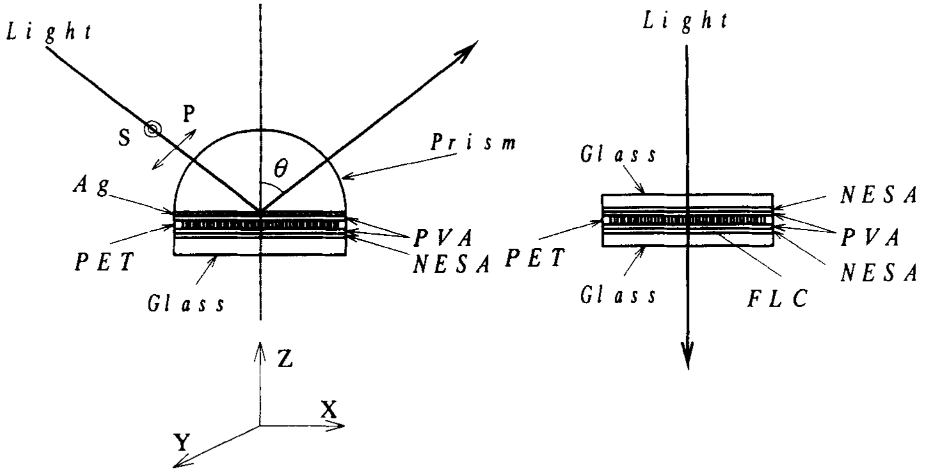


FIGURE 2 Schematic representation of ATR (left) and transmission (right) cell geometries.

served as an electrode. The ATR cell consists of a hemicylindrical ZnSe prism (n = 1.62 at 600 nm), an evaporated silver film of 50 nm in mass thickness, a spin-coated polyvinylalcohol (PVA) film (ca. 10 nm thick), MHOPOB, and a PVA-coated NESA glass plate. The PVA films were rubbed unidirectionally by a lint-free cloth (BEMCOT M-3, Asahi Chemicals Co.) to obtain a parallel alignment in the cell. The transmission cell was assembled with two PVA-coated NESA glass plates rubbed parallel to each other in the same manner as described above. The cell spacing was maintained by a 1.5 μm thick polyethyleneterephthalate (PET) film.

In the transmission experiment, radiation of 600 nm wavelength from a tungsten lamp was used. The LC cell was sandwiched between two crossed polarizers. In the ATR experiment, the cell was assembled so that the rubbing direction was parallel to the plane of light incidence (Figure 2) and mounted on a turntable on an optical bench. The p-polarized radiation of 600 nm wavelength was incident upon the basal plane of the ZnSe prism at a resonance angle for exciting SPP. An AC triangular field was applied normally to the LC film in the transmission and ATR experiments. In either case the radiation from the LC cell was detected by a photomultiplier (Hamamatsu R374) with a sufficiently high responsivity. The signals generated at the detector were preamplified and demodulated with a phase-sensitive lock-in amplifier (Stanford SR510) tuned to the frequency of the AC field. For the optical measurements in the field-off state, a mechanical light chopper was used.

3. RESULTS AND DISCUSSION

3.1. Field Responsivity of Boundary Layers

In the ATR experiment the angle of incidence was adjusted to provide the lowest reflectivity of light at the prism/Ag interface, which is an optimal condition for exciting SPPs.[22] This incident angle depends critically on the structure of the boundary LC layer at the PVA film surface or more exactly on the x-component of the dielectric constants of that layer.[23] Since the SPP excitation is accompanied by a decrease in the reflectivity of light at the prism/Ag interface, the reflected light intensity increases when the molecular alignment in the boundary layer is changed by an externally applied field. Accordingly, the magnitude of the change in the light intensity is dependent on the extent to which the molecules respond to the field.

For comparison, SPP-mediated reflection measurements in the field-off state were performed in the Kretschmann ATR prism geometry as a function of temperature and the angle of incidence. The results obtained when an Ag film and a NESA glass plate were used as the substrates are shown in Figure 3a and those obtained with the substrates coated with PVA and subjected to parallel rubbing are shown in Figure 3b. It is immediately seen that each spectrum exhibits a dip in the reflected light intensity of p-polarized radiation at its own angle of incidence (θ), due to the excitation of SPP. The maximum uncertainty in the determination of θ is $\pm 0.1°$. The position of θ describes the propagation properties of SPPs. Its detailed interpretations have been made in the literature.[24,25] It should be empha-

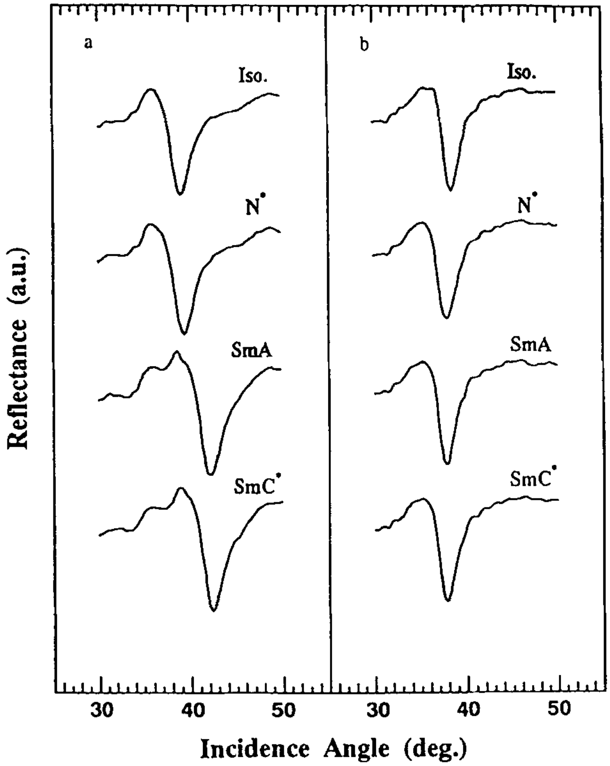


FIGURE 3 ATR spectra of MHOPOB in different phases, measured with the non-stabilized (a) and surface-stabilized (b) cell. Temperature: (Iso) 95°C, (N*) 85°C, (SmA) 75°C, (SmC*) 60°C. Each spectrum is shifted vertically to avoid overlapping.

sized here that the SPP field is concentrated in the boundary of the Ag film and its penetration depth is not more than a few 100 nm from the boundary. Therefore, it is a sensitive probe of the boundary LC layers.

It can be seen from Figure 3a that upon cooling down the LC cell from the isotropic (Iso) to the chiral smectic C (SmC*) phase temperature, the SPP peak shifts to larger θ. This change can be explained by the increase of the x-component of the wavevector k_x and the decrease of the phase velocity v_x of the SPP; the structural change of the boundary layer caused a change in the SPP dispersion relation and led to the observed shift in the k_x of the resonance. Accordingly, it is likely that the shift of θ observed in Figure 3a arises from the change from the isotropic to helical alignment of the molecules. In contrast to this observation, θ decreases on going from the Iso to the SmC* phase temperature in Figure 3b. This fact is qualitatively explained by the change from the isotropic to the uniform alignment in which the molecular long axis is parallel to the rubbing direction. A feature of interest seen in Figure 3b is that θ values for the chiral nematic (N*) and smectic A (SmA) phases are approximately the same as that for the SmC* phase, an indication of similar molecular alignments in these three phases. Thus, these results manifest that the rubbing technique employed here exerted a substantial influence on the molecular alignment over a wide range of the LC temperatures.

The response of the boundary MHOPOB molecules in the surface-stabilized SmC* phase to a triangle-shaped AC field (±15 V) was evaluated from SPP-mediated modulation measurements. It should be noted here that because of the suppression of the intrinsic helical structure in the SmC* phase resulting from the surface treatment, two stable states with opposite spontaneous polarization can exist in the molecular alignment. That is to say, there is an equal probability of the dipole moment pointing up and down with respect to the electrode surface in the field-off state. This is because in the field-off state the molecular long axis is aligned parallel to the electrode surfaces, while the dipole moment lies normal to that axis. Moreover, since the molecular dipole moment aligns in the direction of the applied field, it is expected that switching between the two states can occur by alternating changes in the polarity of the applied field. Indeed, this is what we have observed.

The results of the modulation measurements are shown as a function of the field frequency in Figure 4, with the reflected light intensity as ordinate and the angle of incidence as abscissa. For reference the reflection curve in the field-off state is also shown by a dotted line in Figure 4. Taking into account that the switching of one alignment to another in the bistable states in the surface-stabilized SmC* phase relies on the polarity of the field, the signals observed in Figure 4 were produced probably by switching between the two stable states. As described above, the angle of incidence for SPP excitation varies with the molecular alignment and hence the modulation signals appear as the difference in reflectivity associated with the shifted and unshifted SPP conditions. It is obvious from Figure 4 that the signal intensity (peak to peak intensity) decreases with increasing field frequency, indicating that a high frequency limits a rapid response of the molecules.

In Figure 5 the signal intensity is plotted versus field frequency to compare with

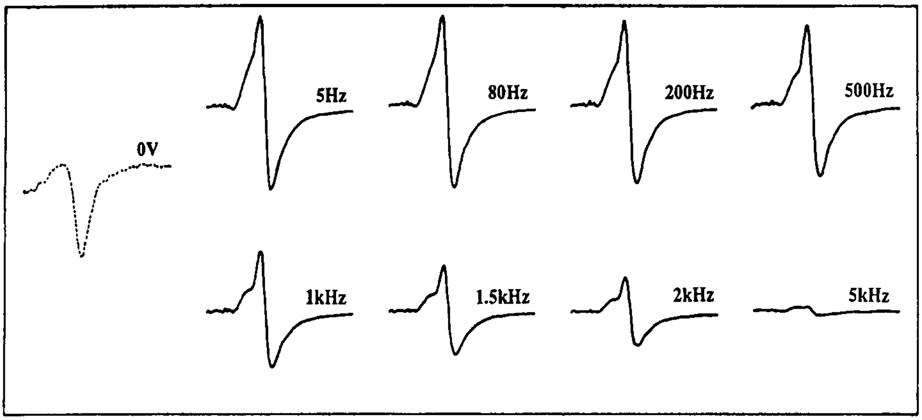


FIGURE 4 Variation of the modulated reflected light intensity in the surface-stabilized ATR prism geometry as a function of applied electric field (triangle-shaped) frequency. The field strength: AC 15 V/cm. The dotted line represents the ATR spectrum in the field-off state.

the data obtained for the case in which the bare Ag film and NESA glass plate were used as the substrates and electrodes. It is evident that there are significant differences in the frequency-dependent signal variations between the two cases; using the bare substrates, the signal is virtually invariant until 150 Hz, increases a little up to 1.5 kHz, and decreases rapidly, while for the rubbed PVA substrates a lowering of the signal starts at 150 Hz, but a subsequent decrease occurs slowly compared to the case of the bare substrates. The rather restrained response observed in the rubbed case is probably a reflection of the strong interactions between the molecules and the substrates. The increase of the signal intensity observed in the bare substrate case is not fully understood, but its origin is perhaps due to a slight change in alignment of the boundary molecules under the influence of the applied field, which is expected in weak anchoring conditions.

3.2. Field Responsivity of Bulk Layers

In the transmission experiment, crossed polarizers were placed before and after the transmission LC cell so that transmitted light intensity results in the minimum in the field-off state. As described in Sec. 2, the LC cell for this experiment was assembled with the rubbing directions on the two PVA-coated NESA glass plates parallel to each other. This direction is approximately parallel to the plane of polarized light produced by one of the crossed polarizers, but of course perpendicular to that produced by another. If the LC molecules are aligned with their long axes parallel to the rubbing direction, no light signals would be observed with the above optical arrangement. However, when a sufficiently high electric field is applied to the cell, the molecular dipole is aligned parallel to the field direction and hence a molecular tilt is induced because the FLC molecule has its dipole moment perpendicular to the long axis. In this case, the intensity of light transmitted through the cell and the polarizers is given by

$$I \propto \sin^2 2\alpha \ \sin^2 \delta/2,$$

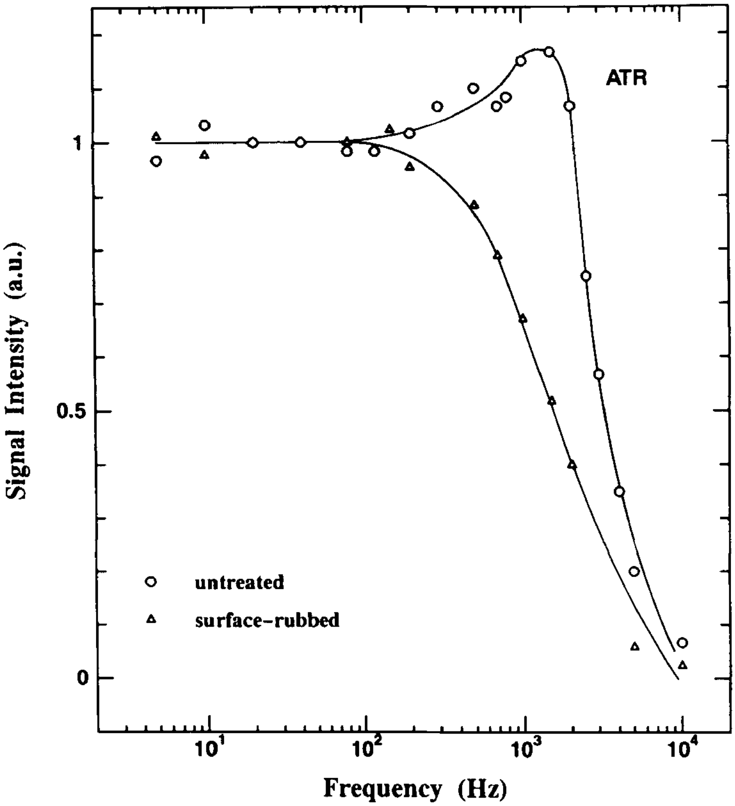


FIGURE 5 Variation of the modulated reflected light intensity in the ATR geometry with applied electric field frequency. The electrodes: untreated Ag film and NESA glass plate (○), PVA-coated Ag film and NESA glass plate subjected to unidirectional rubbing (△). The field strength: triangular AC 15 V/cm.

where α is the deviation of the long axis from the rubbing direction, measured in the substrate surfaces and δ is expressed by $2\pi\Delta n \cdot d/\lambda$, where Δn is the birefringence, d is the cell thickness, and λ is the light wavelength. Therefore, the transmitted light increases in intensity with increasing α in the range $0 \leqq \alpha \leqq \pi/4$.

Figure 6 shows a comparison of the field-modulated light intensities for the bulk layers in contact with the bare NESA glass plates and those coated with PVA films followed by rubbing. The maximum contrast ratio measured at 0.1 Hz, ie., the field-on state brightness/off-state brightness was roughly 5 times larger in the latter than in the former. As can be seen in Figure 6, the signal from the non-treated cell decreases gradually with increasing frequency. This is one of the most remarkable features in the non-treated LC cell which is most likely responsible for structural inhomogenity in the field-off state. Such a behavior is observed for nematic LCs.[26] For the rubbed cell, on the other hand, the signal is constant in intensity up to ca. 1 kHz, then diminishes relatively quickly as the frequency increases. Qualitatively, this behavior corresponds well to what one would expect from the surface-stabilized SmC* layer in the bulk.

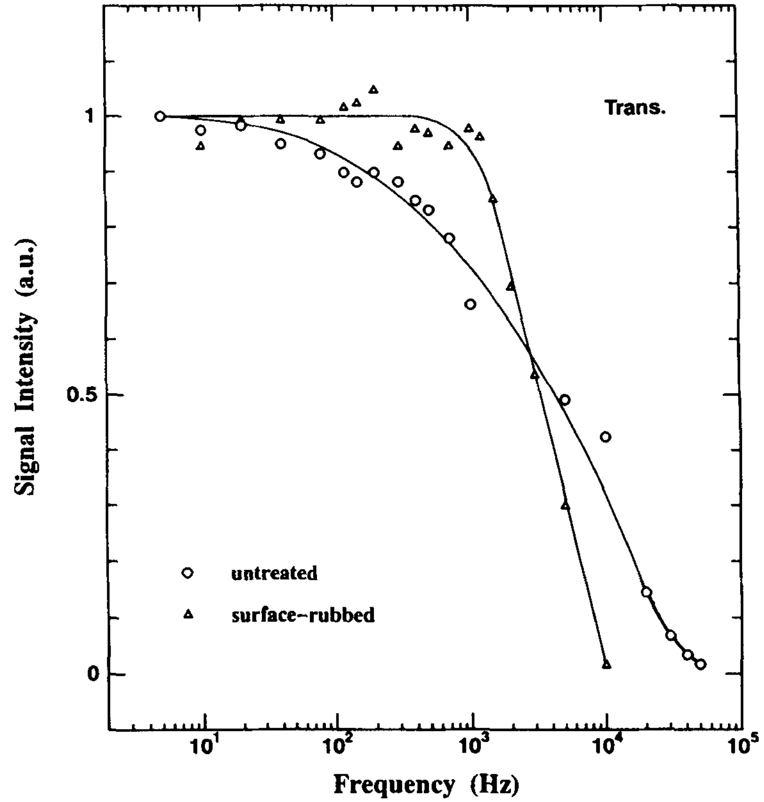


FIGURE 6 Variation of the modulated light intensity in the transmission cell as a function of the applied field frequency. The electrodes: untreated NESA glass plate (○), PVA-coated NESA glass plate subjected to unidirectional rubbing (Δ). The field strength: triangular AC 15 V/cm.

3.3. Memory Effect in the Surface-Stabilized SmC* Phase

Surface-stabilized FLCs in the SmC* phase are usually characterized by a memory effect, a phenomenon that a molecular alignment in the field-on state is maintained after turning the field off. In fact, this was verified in our transmission experiments using PVA-coated NESA glass plates subjected to a rubbing treatment. However, such a memory effect was not observed in the ATR measurements in spite of the use of rubbing-treated substrates, as will be described below. In the transmission and ATR experiments, triangle-shaped voltages (±15 V) alternating at 0.01 Hz for convenience were applied to the individual LC cell. The results are illustrated in Figure 7, where the middle (b) and bottom (c) refer to the bulk and the boundary layer, respectively. In Figure 7b the signal intensity in the initial state remains unchanged upon applying an increasing and decreasing positive field, whereas it increases upon applying a negative field. This bright state at the negative field continues after switching off the field, which presents unambiguous evidence for the memory effect. Another fact of importance seen in Figure 7b is that the magnitude of applied voltage is not essential in switching alignment as long as it is

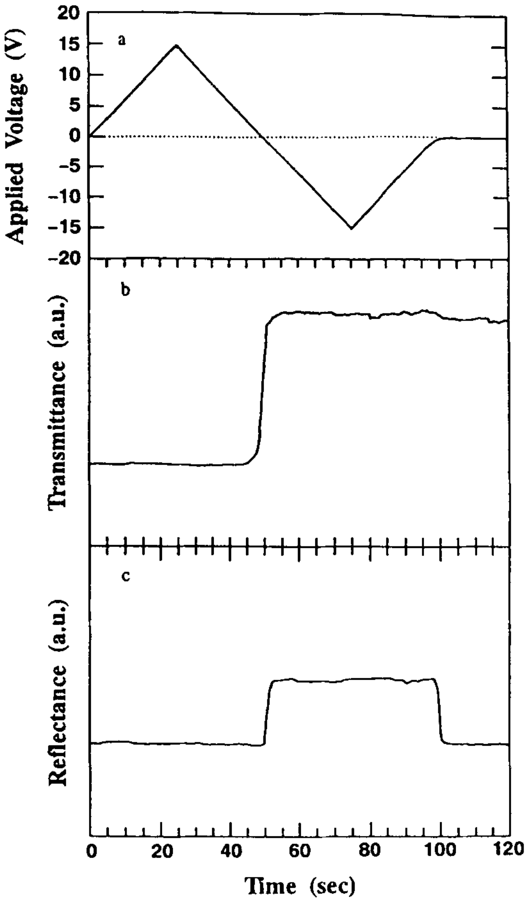


FIGURE 7 Switching behavior of MHOPOB alignment in the surface-stabilized transmission (b) and ATR (c) cell with change in the polarity and strength of the triangular electric field (a).

beyond the threshold value. This also is a characteristic of FLCs in the surface-stabilized SmC* phase.

In contrast to the bulk layer, the boundary layer exhibits no memory effect, as is evident from Figure 7c. When the electrodes were not subjected to a surface treatment, the above-mentioned memory effect was not observed in the bulk and boundary layers. In this case the anchoring force of the substrates is very weak and most probably the LC molecules tend to assume a helical alignment, though not uniform, for which no memory effect is expected.

4. CONCLUSIONS

The electric-field switching behaviors of MHOPOB FLC molecular alignment in the surface-stabilized SmC* phase in the bulk and boundary layers have been investigated through use of optical transmission and SPP-resonance methods. Basically, little difference was seen between the bulk and boundary layers in the manner of switching. For the boundary layer, however, the maximum frequency at which the molecule can respond to the applied field is approximately an order of magnitude less than that for the bulk layer. This may be an indication of stronger anchoring of the boundary molecules. The threshold voltage for the alignment switching was found to be ca. 1 V/cm or less, but this switching itself was of course independent of applied field strength in agreement with general observation with surface-stabilized FLCs in the SmC* phase. Furthermore, while a memory effect was observed in the bulk layer, it was not observed in the boundary layer, probably due to the effect of the substrate surface. In this work, unidirectionally rubbed PVA films were used for the substrates and electrodes for alignment in the field-off state. An SPP field is maximum in intensity at the boundary between the metal surface and its medium and also its generation is conditioned by the dielectric function of the medium. Therefore, the SPP field is very sensitive for probing small changes in the structure or alignment of liquid crystals. An extension of this technique to the study of antiferroelectric liquid crystals is in progress.

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