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Electric Field Response of an Antiferroelectric Liquid Crystal in the Bulk and Boundary Regions

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Optical transmission and attenuated total reflection (ATR) measurements have been performed on antiferroelectric MHPOBC(R) liquid crystal films in the chiral smectic C_A phase to investigate the electric field response of the bulk and boundary layers, respectively. In the ATR measurement, a surface plasmon polariton is excited at the liquid-crystal/silver-film interface as a probe of the field response of the boundary layer. A significant difference in threshold voltage as well as in field responsivity is found between the bulk and boundary layers. These results are discussed in short in this letter.

Keywords: antiferroelectric liquid crystal, surface plasmon polariton, molecular alignment, electro-optics, attenuated total reflection.

1. INTRODUCTION

Characterization of the molecular alignment of thin liquid crystals (LCs) at the substrate surface has important relevance in applied research. Actually, while a number of methods have been used for characterizing the molecular alignment or structure of LCs in the bulk, methods of observing the very posture of LC molecules at substrate surfaces remain not fully developed. In our previous work,[1] a surface plasmon polariton (SPP)[2-3] was excited by visible light in the Kretschmann ATR geometry[4] and used as a probe of the interfacial alignment of a ferroelectric LC. This method allows us to excite SPPs on a silver electrode which is positioned almost immediately adjacent to the LC. Since the SPP excitation is accompanied by a decrease in the reflectivity of light at the ATR prism/metal interface, the reflected light intensity increases when the molecular alignment at the boundary is changed by an externally applied electric field. As a result, the magnitude of the change in the reflected light intensity depends on the extent to which LC molecules respond to the field. Indeed, this method gave evidence that while the memory effect, which is characteristic of surface-stabilized ferroelectric LCs in the chiral smectic C phase,[5] is observed in the bulk layer, but it is not observed in the boundary layer.[1]

While several reports on the alignment and structure of LCs using SPP and coupled guided modes have appeared in the literature,[6-9] none of them deals with the behavior of dynamic response to applied fields. Considerable interest has converged on the electrooptical properties of antiferroelectric LCs because of their important potential

application to display devices. However, since the study of such materials is of comparatively recent origin,[10] little information has been obtained concerning their behavior at electrode surfaces. The work presented here is the first investigation of antiferroelectric LCs by the SPP-mediated ATR method. A brief description is made on the electric field response of the boundary layer of MHPOBC(R) in the chiral smectic C_A (SmC_A*) phase. The corresponding behavior in the bulk layer observed with an optical transmission technique is also presented and discussed.

2. EXPERIMENTAL

The antiferroelectric liquid crystal (AFLC) material, MHPOBC(R), was provided by Chisso Petrochemical Co. and used without further purification. Provided data for the transition temperatures of that material are:

$$SmC_I^*\,68^\circ C \rightarrow SmC_A^*\,118.5^\circ C \rightarrow SmC^*\,122^\circ C \rightarrow SmA\,149.8^\circ C \rightarrow Iso.$$

The LC cells used for ATR and transmission experiments have been described previously.[1] In brief, the ATR cell consists of a polycrystalline ZnSe prism ($n = 2.605$ at $\lambda = 600$ nm), a vacuum-evaporated silver film of 50 nm in mass thickness, MHPOBC(R), and a NESA glass plate. The Ag film and the NESA glass used as electrodes were previously spin-coated with polyvinylalcohol (PVA, ca. 20 nm thick) and rubbed unidirectionally with a lint-free cloth (BEMCOT M-3, Asahi Chemicals Co.) in an attempt to obtain a parallel alignment of the LC molecules. The ATR cell was assembled in such a way that the rubbing direction is parallel to the plane of light incidence. In the transmission experiment, the cell windows (NESA glass) were also coated with PVA and then rubbed in the same manner as described above. This transmission cell was placed between two crossed polarizers. In both experiments, the cell spacing was maintained in 1.5-μm thickness with a polyethylene terephthalate film (Toray Co.). Radiation of 600-nm wavelength from a tungsten lamp was incident to the ATR cell or the transmission cell. An alternating electric field was applied to each cell and the reflected or transmitted radiation was detected by a photomultiplier (Hamamatsu R374). The signals generated at the detector were preamplified and demodulated with a phase-sensitive lock-in amplifier (Stanford SR510) tuned to the modulation frequencies.

3. RESULTS AND DISCUSSION

A surface plasmon plariton (SPP) was exited at the silver/PVA interface in the Kretschmann ATR geometry. The SPP field intensity is a maximum at the silver/PVA boundary and decreases exponentially with the distance from that boundary; the penetration depth of SPP is less than 300 nm. The SPP excitation is always accompanied by a decrease of the reflectivity of p-polarized radiation at the prism interface. In addition, the angle of incidence at which the SPP resonance occurs is strongly dependent on the optical properties of the medium (PVA and AFLC in our case) in

contact with the metal film. Thus, if the incident angle is adjusted to provide the minimum reflection of light, the reflected light intensity increases upon change in molecular alignment in the boundary region. Application of a static electric field to the ATR cell would then lead to shifting the SPP resonance angle due to a change of the alignment, thereby increasing the reflected light in intensity. In the transmission experiment, on the other hand, the cell is rotated so that transmitted intensity comes to a minimum in the field-off state. Figure 1 schematically illustrates three possible molecular alignments in the field-off (A) and field-on (B and C) states for the AFLC material in the SmC_A^* phase. The molecules in A are assumed to be aligned with their long axes parallel rather than perpendicularly by unidirectional rubbing of the electrode surfaces. Due to the presence of a spontaneous polarization perpendicular to the long axis of the molecule, two field-induced alignments are possible, those of which are discriminated by whether the polarization is directed up or down depending upon the direction of the applied field. Hereinafter, the molecular arrangement shown in B and C will be referred to as ferroelectric (F), whereas that shown in A as antiferroelectric (AF).

Figure 2 shows the variation of the transmitted and reflected light intensities versus applied field strength, observed by the transmission and ATR methods, respectively. In each experiment, a triangle-shaped field alternating at 0.04 Hz was applied to the cell in the SmC_A^* phase at 110°C. In this case, the lowest light intensity arises from an AF state in which each molecule is aligned, as shown in Figure 1 (A). This molecular arrangement is found to be stable as long as the field strength does not exceed the threshold value for occurring alignment change from AF to F as shown in Figure 2. It can also be seen that the thresholds for changing alignment from AF to F and F to AF are different in both the bulk and boundary layers. For the bulk layer, the threshold voltage for switching F to AF is 4.8 V, whereas it is 4.2 V for the reverse change. Upon reversal of the field direction, the change from AF to F occurs at a threshold voltage of -5.6 V and the reverse change begins at -5.3 V. For the boundary layer, on the other hand, the change from AF to F starts at 7.0 V and the onset of the reverse change is

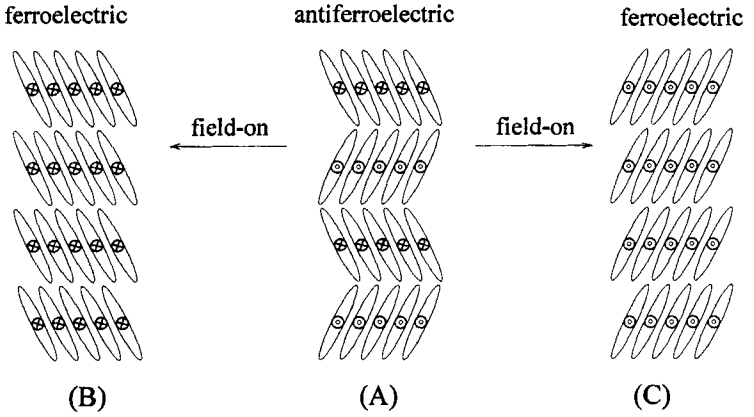

FIGURE 1 Possible molecular and spontaneous polarization alignments in the SmC_A^* phase. The applied electric field, (A): off; (B) and (C): on.

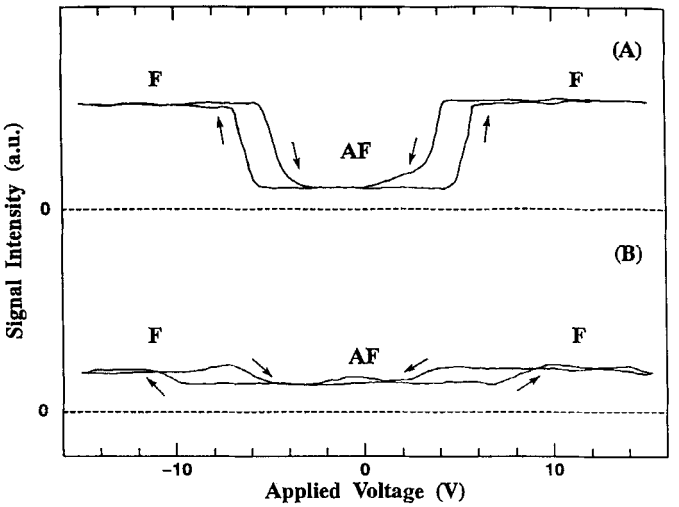

FIGURE 2 Variation of the light signal intensity as a function of applied field strength. (A) and (B) refer to the bulk and the boundary layer, respectively. Antiferroelectric and ferroelectric polarization states are designated by AF and F, respectively. The light wave length is 600 nm.

observed at 4.2 V. In another direction of the field, a threshold voltage of −9.7 V is required to cause the AF to F change, while that for the reverse change is −6.9 V. Thus, it is clear that the threshold field strength for switching the molecular alignment from one state to another depends on the field polarity in either case. Particularly, it is significant to note here that such a polarity dependence is more prominent for the boundary layer. Though this origin is not fully resolved, we may surmise that the strong polarity dependence is mainly concerned with the influence of the electrode surface. This influence can also act on the bulk layer, as observed above and also reported in the literature.[11] Another fact having relevance to the surface effect is that the threshold voltage for either AF to F or F to AF change is higher for the boundary layer than for the bulk layer. This reasonably indicates that the AF state is more stable than the F state in the boundary layer. The surface effect also influences the responsivity of the AFLC molecules to a high-frequency field modulation, as described below.

An alternating triangular field of ± 15 V was then applied to the ATR cell and the modulated light signal from the boundary layer was recorded as a function of field frequency. The results are shown in Fig. 3. The signal obtained at each frequency corresponds to the change in light intensity and hence in molecular alignment caused by the field switching + 15 and − 15 V. Therefore, the observed signal intensities are directly related to the field responsivity of the AFLC molecules in the boundary layer in the present case. It is clearly seen in Figure 3 that the signal intensity is essentially constant up to a frequency of 200 Hz, but it decreases gradually with more increasing frequency in the range of 200 to 5 kHz. A similar experiment was performed on the transmission cell, the results of which are shown by Figure 4(a). In this case, the crossed polarizer was rotated so that the modurated light signal becomes the maximum. In comparison to the case of the boundary layer, the field response is quite high; the

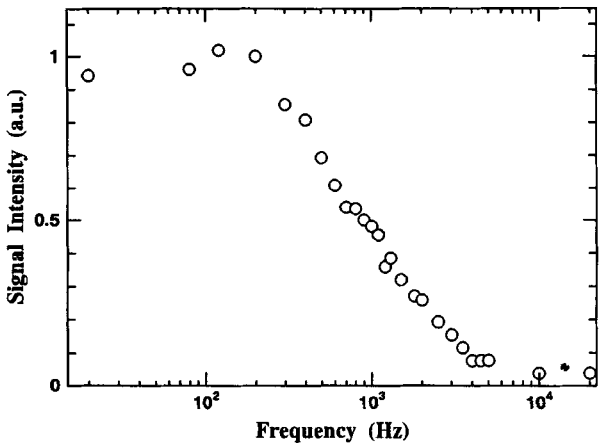

FIGURE 3 Variation of the modulated reflected light intensity in the Kretschmann ATR geometry with applied field frequency. A triangular field of ± 15 V was applied to the ATR cell.

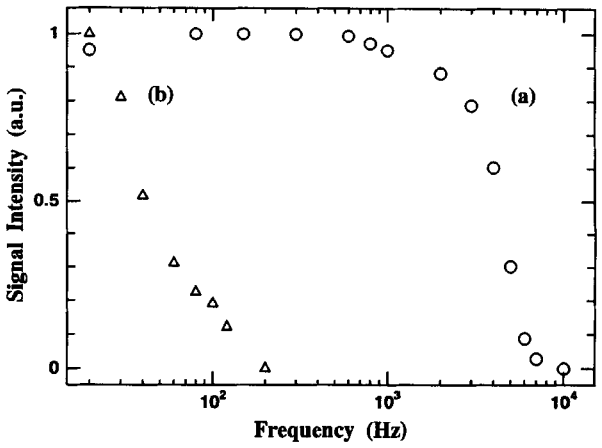

FIGURE 4 The modulated transmitted light intensity vs. applied field frequency (f). The field applied to the transmission cell was triangular ± 15 V. Locked-in frequency: (a), f; (b), 2f.

switching time is faster by a factor of 20 at least. It is also noted that the decay of the signal intensity occuring at high frequencies is significantly sharp for the bulk layer. These features, characterized for the bulk layer, can be explained by a field switching between the two different F states, shown in B and C in Figure 1. This situation is like that of ordinary bulk ferroelectric LC materials when applied an alternating electric field. To support this argument we also detected 2f-modulated light signals, f being the frequency of the applied electric field. In this case, the alignment of the crossed polarizer was the same as in the case of Figure 2(A). A plot of the resulting signal intensity against frequency (f) is shown as b in Figure 4. It should be noted that each signal intensity is

normalized with respect to the maximum intensity in Figure 4. Obviously, the switching time is roughly two orders of magnitude slower than the very fast switching time operating in the *f* mode. This slow response to the applied field should correspond to a switching between the AF and F alignments in the bulk layer.

In summary, optical transmission and SPP-mediated ATR reflection measurements were carried out on antiferroelectric MHPOBC(R) films in the SmC_A^* phase under the combined influences of surface interactions and externally applied fields. As a consequence, a significant difference between the bulk and boundary layers was elucidated in molecular switching between the two ferroelectric states. In particular, we observed a "hysteresis loop" in the process of increasing and decreasing field strength in both layers but its shape was asymmetric with respect to the field polarity. The asymmetry observed for the bulk layer quite likely arises from the fact that boundary conditions of the two electrodes facing each other were not exactly the same. This asymmetry was more amplified for the boundary layer, probably suggesting that there is an easy direction of the spontaneous polarization up or down with respect to each of the electrode surfaces when it is switched by the electric field. This effect may be attributed to some interactions between the molecule and the PVA surface and would play a part in the switching behavior of the bulk layer too. The SPP resonance method we used in the present work is powerful for the examination of molecular alignment in the boundary region of a LC cell, because the SPP field is highly localized to the interface and decays exponentially with the distance from that interface.

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