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Optical switching and alignment of antiferroelectric liquid crystals containing an azo group

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The optical properties of two kinds of photochromic antiferroelectric liquid crystal (AFLC) containing an azo group have been examined. Depending on the substituting group at the chiral centre, these AFLCs showed different photoinduced phase transitions by Ar^+ laser light irradiation. This phase transition has led to a new form of optical switching controlled by a bias voltage. In addition, it was found that these AFLCs caused an azimuthal photoalignment effect regulated by linearly polarized Ar^+ laser light irradiation. These phenomena were applied to image storage.

1. Introduction

Optically addressed spatial light modulators (OASLMs) are important in applications such as information recording and processing. With the progress of liquid crystal (LC) technology, OASLMs using LCs have been extensively studied [1–4]. In particular, two kinds of unique smectic LC, ferroelectric LCs (FLCs) and antiferroelectric LCs (AFLCs), have attracted great attention because of their fast response times.

Since commercial LCs are not photoresponsive, an ordinary LC-OASLM consists of a LC and a photoconductive layer. To construct a simple LC-OASLM without the photoconductive layer, we have studied an OASLM using an AFLC doped with a photochromic dye [5]. The photoisomerization of the dye molecules triggered optical switching in the AFLC, and hence the sensitivity of the switching increased with the concentration of dye molecules. The dopant molecules, however, disturb the ordering of smectic LCs, and so a smectic LC cell doped with a high concentration of dye molecules is not suitable for an OASLM. AFLCs containing an azo group enable us to overcome this problem. Negishi *et al.* [6] have already reported the fast optical switching of such AFLCs. The AFLCs underwent the phase transition from SmC_A^* to SmC^* by UV light irradiation. Using the third harmonics of a YAG laser, the phase transition took place with a response time of 340 μs at 90°C. Dinesu and Lemieux [7] have reported the photomodulation of the spontaneous polarization in FLC with a thioindigo dopant for visible light. In practice, it is desirable to use visible and low intensity light for the excitation.

On the other hand, an azo-dye in a polymer matrix is known to be a highly efficient material for polarization holographic recording [8]. Similar phenomena occurring in liquid crystalline side group polymers containing azobenzene mesogenic groups have been reported [9]. Linearly polarized light leads to the effective reorientation of the optic axis in the glassy state of liquid crystalline side group polymers. These effects are caused by photoinduced *trans*-*cis*-isomerizations of azobenzene. Since the direction of the transition moment of azobenzene molecules is parallel to the molecular long axis, the azobenzene director tends to be perpendicular to the polarization direction. However, the optical alignment properties of AFLC have never been examined.

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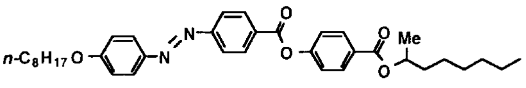
In this study, we observed the optical switching properties of an AFLC containing an azo group brought about by visible Ar$^+$ laser light. Laser light irradiation of wavelength 514.5 nm caused a photochemically induced phase transition. The type of optically induced phase transition depended on the substituting group at the chiral centre, and these phase transitions caused optical switching in different ways. Furthermore, we observed an optically induced azimuthal alignment effect in these AFLCs caused by linearly polarized Ar$^+$ laser light irradiation. We have applied this phenomenon to image storage. The spatial resolutions of these AFLCs were evaluated by a resolution chart.

2. Experimental

The samples used were two photoresponsive AFLC compounds Azo-Me and Azo-CF3. The chemical structures and phase sequences are shown in figure 1. These AFLCs were injected into 2 µm thick cells. The cells were made using two glass substrates with indium tin oxide (ITO) on which polyimide (Hitachi Chemical Co., Ltd., LX-1400) was coated and rubbed. The temperature was maintained within an accuracy of ± 0.1°C by a temperature controller (Chino, Model DB 1000).

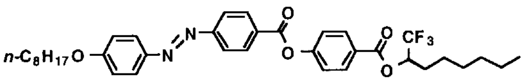
The optical set-up for measuring the transmittance has been described elsewhere [5]. We used an Ar$^+$ laser (Coherent, INNOVA90, 3 W, 514.5 nm) as a pump beam for the photoresponsive AFLC and a He-Ne laser (5 mW, 632.8 nm) as a probe beam. The intensity of the Ar$^+$ laser incident on the cell was measured by an optical power meter (Advantest, TQ8210). The transmittance of the probe beam through the cell between crossed polarizers having their axes parallel or perpendicular to the smectic layer normal was measured by a photodiode. These signals were monitored by a digital storage oscilloscope (Tektronix, TDS340). The voltage applied to the cell, 0.5 Hz triangular wave, was generated by an arbitrary waveform generator (HP, 33120) and amplified by a high speed power amplifier (NF, 4005).

Azo-Me



Cr 76° C SmC$_A$* 102°C SmC* 118°C SmA 158°C I

Azo-CF3



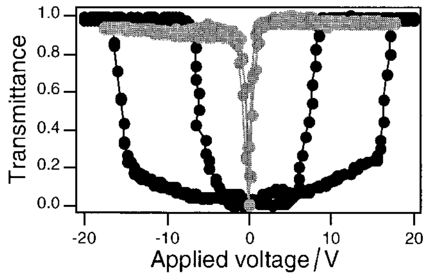
Cr 93°C SmC$_A$* 120°C SmC* 122°C SmA 133°C I

Figure 1. Chemical structures and phase sequences of the antiferroelectric liquid crystals used in the experiments.

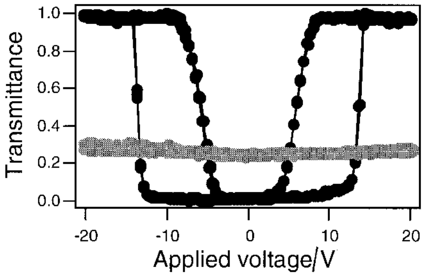
3. Results and discussion

3.1. *The phase transition*

Negishi *et al.* [6] have reported that these AFLCs underwent the phase transition from SmC$_A^*$ to SmC* with UV light irradiation, and we observed the same phase transition using visible light. Figure 2 shows the hysteresis curves in optical transmittance on applying a 0.5 Hz triangular wave electric field. Since Azo-Me exhibits the SmC$_A^*$ phase at 90°C, the transmittance–voltage hysteresis curve showed a double hysteresis loop. When the cell was irradiated by the Ar$^+$ laser at 80 mW cm^{-2}, the optical transmittance curve changed to the grey line in figure 2 (*a*). When the polarizer and the analyser were simultaneously rotated to half of the cone angle, the curve became single hysteresis. This indicated that the phase transition from SmC$_A^*$ to SmC* was induced by the Ar$^+$ laser irradiation. The SmC* phase showed a stripe texture. In the case of Azo-CF3, the profile showed a stable double hysteresis curve at 110°C without Ar$^+$ laser irradiation; black line in figure 2 (*b*). On the other hand, the transmittance was almost unchanged against the applied voltage under the Ar$^+$ laser light irradiation at 80 mW cm^{-2}; grey line in figure 2 (*b*). This result proved that the phase induced by the Ar$^+$ laser light irradiation was not the SmC* phase. We measured the reversal current by the triangular



(a) Azo-Me (90 °C)



(b) Azo-CF3 (110°C)

Figure 2. Optical transmittance change under a 0.5 Hz triangular wave field by Ar$^+$ laser light irradiation in (*a*) Azo-Me (90°C) (*b*) Azo-CF3 (110°C). Grey and black lines correspond to with and without irradiation, respectively.

method [10]. The two current peaks corresponding to SmC$^*_A$ were observed before Ar$^+$ laser irradiation. Under Ar$^+$ laser light irradiation, however, the reversal current peaks disappeared, and when the Ar$^+$ laser intensity was reduced, the transmittance became proportional to the square of the applied voltage. This phenomenon has been explained by the electroclinic effect in the SmA phase [11]. Thus, we concluded that this photoinduced phase was the SmA phase. Actually, a SmA phase has been photochemically induced in FLCs doped with azo dye by UV light irradiation [12, 13]. The molecules disturbed by a pump laser light scatter the probe light, so Azo-CF3 may have some transmittance in the SmA phase.

3.2. *Optical switching*

Having understood the optical transmittance change of the hysteresis curve, we now apply these properties to optical switching. The optical switching of an AFLC was first demonstrated by reducing the threshold voltage of the electric field-induced antiferroelectric to ferroelectric phase transition brought about by *trans-cis*-isomerization of dye molecules [14]. After new AFLC materials were developed, optical switching using a photoinduced phase transition was reported [5, 6]. A bias voltage is required to cause optical switching in an AFLC. The voltage must be adjusted to lie between the initial and reduced threshold voltages of the electric field-induced antiferroelectric to ferroelectric phase transition. This narrow permitted range of bias voltage is a problem in ordinary circumstances, but AFLCs containing an azo group overcome the problem. In the case of Azo-Me, optical switching can be realized by the photoinduced phase transition from SmC$^*_A$ to SmC* as reported for UV light irradiation [6]. The switching of Azo-Me was performed at 90°C under a bias voltage of 8.5 V, and a 100 ms Ar$^+$ laser pulse was applied to the cell at 81 mW cm^{-2}. The optical response is shown in figure 3 (*a*). As a laser pulse caused the phase transition from SmC$^*_A$ to SmC*, the transmittance increased. The rise time, which is defined as the time required for the transmittance to increase from 0.1 to 0.9, was 55 ms. There are two reasons for this slow response compared with reported data (340 μs) using UV light. The former data were measured by intense light, namely, the third harmonic of a YAG laser (355 nm). Since Azo-Me contains an azo group, it has a large absorption coefficient at 355 nm, but the molecules scarcely absorbed the 514.5 nm light.

The Azo-CF3 realizes a new form of optical switching, and the optical response of Azo-CF3 is shown in figure 3 (*b*). We performed the optical switching using a 500 ms Ar$^+$ laser pulse (81 mW cm^{-2}) at 110°C. When the cell was biased at 20 V, Azo-CF3 changed to the SmC* phase. When the cell was irradiated by an Ar$^+$ laser pulse, the phase transition from SmC* to SmA occurred, and hence the transmittance decreased. The decay time was 110 ms. While the cell was biased at 5 V, Azo-CF3 was in the SmC$^*_A$ phase. The Ar$^+$ laser light irradiation induced the phase transition from SmC$^*_A$ to SmA. The transmittance change was completed within about 328 ms. Using the Azo-CF3, the transmittance change can be controlled by the bias voltage.

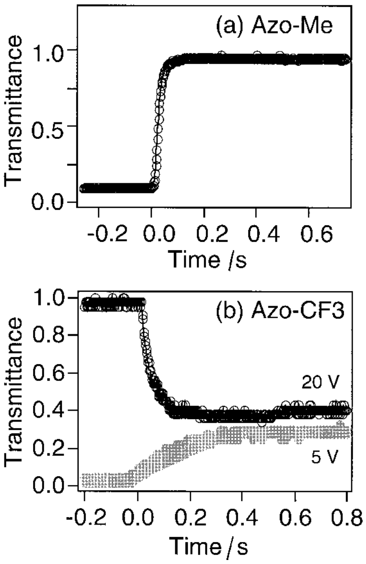


Figure 3. Optical response of Azo-AFLCs under Ar$^+$ laser pulse irradiation at 81 mW cm^{-2}. (*a*) Azo-Me; d.c. bias voltage applied to the cell is 8.5 V. (*b*) Azo-CF3; d.c. bias voltage applied to the cell is 20 V (upper) and 5 V (lower).

3.3. *Optical alignment*

Finally we report the reversible optical alignment of Azo-AFLC by linearly polarized Ar$^+$ laser light irradiation. The cell of Azo-CF3 was irradiated with linearly polarized Ar$^+$ laser light (101 mW cm^{-2}) for 120 s. The polarization direction of the irradiating light was set parallel to the smectic layer normal. After irradiation, the normal to the smectic layers was changed to be perpendicular to the polarizing direction. The experiments on optical alignment were performed with a 50 V$_{pp}$ triangular wave of 0.5 Hz at 110°C. When we irradiated the cell with a linearly polarized Ar$^+$ laser with various azimuths, the smectic layer normal was perpendicular to the polarizing direction. Azo-Me was also aligned by linearly polarized light. These effects have been reported for polymer liquid crystals [9], but the optical alignment properties of low molecular mass LCs, in particular AFLCs, have never been examined. This effect was not that of smectic layer rotation caused by application of an asymmetric voltage pulse [15], for

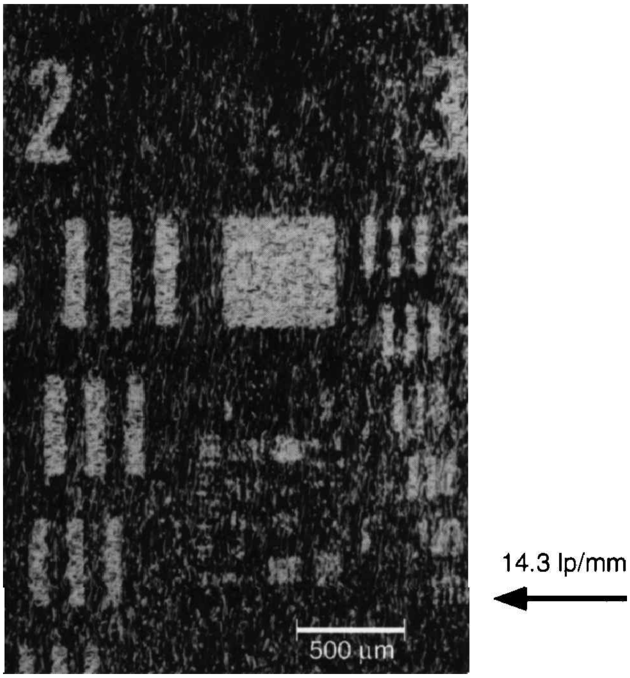


Figure 4. Polarizing micrograph of a stored image in Azo-CF3. The initial direction of the smectic layer normal is vertical in this figure. The direction of the smectic layer normal in the patterned area is horizontal.

we could photoalign the Azo-AFLC without an applied voltage. The triangular wave improved the cell alignment by smectic layer switching [16]. Using these optical alignment properties of Azo-AFLC, we can store the pattern in the cell. An example of pattern storage in Azo-CF3 is shown in figure 4. The initial direction of the smectic layer normal was vertical in the figure. When we irradiated the cell with vertically polarized Ar^+ laser light for 30 s, the smectic layer normal in the irradiated part was realigned horizontally. The cell was irradiated at 80 mW cm^{-2} with a 50 V_{pp} triangular wave of 0.5 Hz. Preliminary experiments on recording of an interference pattern revealed that the maximum resolution was about 30 lp mm^{-1}.

4. Conclusion

In conclusion, we have observed the optical switching properties of AFLCs containing an azo group induced by Ar^+ laser light of wavelength 514.5 nm. The optically induced phase in Azo-CF3 using an Ar^+ laser was different from that induced by UV light irradiation. These phase transitions have led to a new form of optical switching. Furthermore, the Azo-AFLCs showed an optically induced alignment effect by linearly polarized Ar^+ laser light irradiation, and we have demonstrated image storage using this optical alignment.

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