

Photochemical Control of Properties of Ferroelectric Liquid Crystals: Photochemical Flip of Polarization

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Received July 21, 1993. Revised Manuscript Received November 9, 1993*

Abstract: A novel principle for photochemical control of optical properties of ferroelectric liquid crystal (FLC) is presented, which is based on photochemically induced switching of polarization of FLC triggered by photoisomerization of azobenzene derivatives doped in FLC. At the irradiated sites of the azobenzene/FLC mixtures, flip of polarization was induced, causing the change of the optical properties. The process was found to be fast, reversible, and repeatable.

Introduction

Ferroelectric liquid crystals (FLCs) have attracted great interest from both fundamental and practical viewpoints.^{1,2} The development of bistable fast switching displays exhibiting response times in the range of some microsecond has created considerable interest in the synthesis and investigation of new ferroelectric materials with large spontaneous polarization (P_s). The attractive feature of FLCs is that they exhibit the phenomena so called electrooptic effect. FLCs are usually chiral smectic C (SmC^*) LCs with unique phase structure when sandwiched between two glass plates (surface-stabilized state).¹ At this state, if one applied alternating voltage across the two glass plates, FLC molecules show flip-flop movement and cause the switching of the light transmittance through a pair of crossed polarizers placed in front and behind the FLC sample. This switching behavior of FLC is known to be very fast, so that the research for the application to display devices is intensively under way. Beside the efforts for displays, some ideas have been proposed to utilize FLCs for devices in electronics and photonics.³ However, there were many difficulties in utilizing FLCs, because of the restrictions in exhibiting fine electrooptic effects.⁴⁻⁶ In order to construct optical FLC devices, one must obtain fine, thinly gapped ($\sim 2 \mu$) cells with well treated surfaces in addition to the preparation of appropriate FLCs. Thus, if photoresponsive functions are provided with FLC itself, construction of photoresponsive FLC devices becomes much simpler, and the applications of FLCs will be quite widened.

We have already reported several attempts to provide LCs with photofunctional properties⁷ and have demonstrated that

introduction of photoresponsive molecules (such as azobenzene, spiroxan, etc.) into LCs is a powerful method. When photoresponsive molecules like azobenzenes were doped in nematic LCs at the concentrations of several mol % and irradiated to cause trans \rightarrow cis photoisomerization, the phase transition temperature decreased. If the system was held at a temperature close to T_{NI} (nematic-isotropic phase transition temperature) and irradiated, the isothermal N-I phase transition took place. This phenomenon can be explained in terms of molecular shape of the photoresponsive guest molecules: the trans forms of azobenzene are favorable for LC phase because of the rod-like shape, while the cis forms are bent, unfavorable for LC phase, thus, the LC phase is destabilized in line with the accumulation of the *cis*-azobenzene. Although such a photochemically induced phase transition might be exploited in optical image recording systems, the response time and working temperature are disadvantageous.

Standing on these results, we propose a new application of FLCs which works on the new principle. We already reported a brief communication on the first successful example recently.⁹ In this article, we present a detailed description of the example of the photochemical control of FLCs.

Principle. FLCs possess bistable states with opposite orientations of P_s and distinct critical values of electric field (coercive force, E_c) on switching between the two states. These ferroelectric properties of FLCs result from the specific structure of the SmC^* phase; thus, when azobenzenes are doped in the SmC^* phase and isomerized to cis form, the structure of the SmC^* phase is disorganized with concomitant lowering of the E_c value. The device with the novel principle is based on this property and works in the following sequences of events (Figure 1). (1) The polarization of FLC is aligned into one direction with the aid of an external electric field. (2) Electric field (E) is applied in the opposite direction to the polarization, which should be small enough to retain the initial polarization unchanged ($E < E_c$). (3) The cell is irradiated with a light which causes a photoisomerization of photoresponsive guest molecules (e.g., azobenzene derivatives). (4) The photochemical reaction of the guest molecules simultaneously lowers the critical value (E_c) of the guest/FLC mixture, and when the E_c value is lowered below E , the polarization will flip into opposite direction. In this way, image can be stored in the guest/FLC mixtures, since the irradiated and the unirradiated sites show opposite direction of polarization and hence different optical properties.

Experimental Section

Samples. The structures of FLC and an azobenzene derivative used in this study are shown in Figure 2. FLC possesses two chiral centers

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* Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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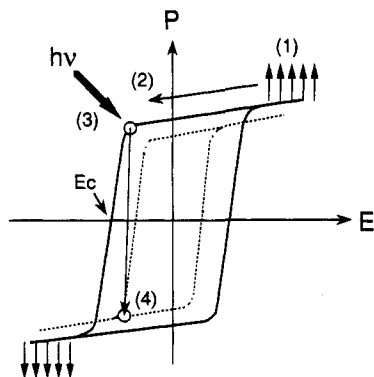


Figure 1. Schematic illustration of photochemical flip of polarization in FLC. Explanation of this figure is described in the text.

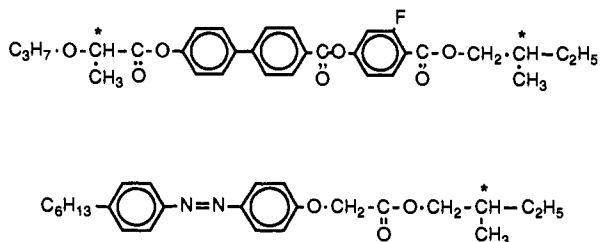


Figure 2. Structures of FLC and photoresponsive molecule used in this study.

Table 1. Physical Properties of FLC Used in This Study

phase transition temp (°C)	Ps (nC/cm ²)	tilt angle (deg)
C 38 SmC* 64 SmA 110 N 112 I	82	20.1

at both ends of mesogen and is fluorinated in the biphenyl moiety. Introduction of a halogen substituent into a mesogenic part decreases the melting point and widens the temperature range of ferroelectric phase (SmC* phase).^{10,11} Phase transition temperatures and Ps of this FLC are listed in Table 1. The azobenzene derivative with the same chiral group as the matrix FLC was employed as a photoresponsive molecule.

FLC was dissolved in chloroform solution of the azobenzene derivative, and the resulting solution was evaporated to dryness. Next the mixture was heated under vacuum for several hours to remove chloroform. The concentration of the azobenzene guest molecule was 3 mol %. At higher concentrations than 10 mol %, aggregation of the guest molecule was observed in the polarizing microscope. Thus, the concentration of the azobenzene derivative was kept dilute enough to disperse the azobenzene freely in the FLC matrix. In fact, no aggregation of the photoresponsive molecule was observed in the UV absorption spectrum and also under microscopic observation in the 3 mol %-doped sample. The sample was then injected into a 2- μ -gap glass cell equipped with ITO electrodes of 1 cm² and polyimide-coated. The sample was heated until it showed an isotropic phase completely and then cooled gradually at a rate of 1 °C/min to give fine alignment of FLC. The sample was annealed at 50 °C overnight before measurement. Absorbance of the azobenzene guest at the maximum (362 nm) was 0.4 in the sample film.

We should also note here the choice of polyimide. In order to align the FLC into one direction, the surface of the cell was coated with polyimide followed by rubbing treatment.¹⁴ In this experiment, the polyimide must not absorb the irradiation light (wavelength for trans-cis photoisomerization of the azobenzene derivative), because we must avoid the problem of photoreaction at FLC-polyimide interface or occurrence of photoelectric effect such as photoconductivity. For this reason, we examined the absorptions of several polyimides and chose one with no absorbance at the irradiation wavelength.

Measurements. Phase transition temperatures of FLC were determined by DSC (Seiko I&E SSC-5000), and Ps were measured by the triangular voltage method (50 Hz, 10 V p-p). Figure 3 shows the experimental setup used for the time-resolved observation of the flip induced by the laser irradiation. A Spectron HL-21 Nd:YAG laser (the third harmonic,

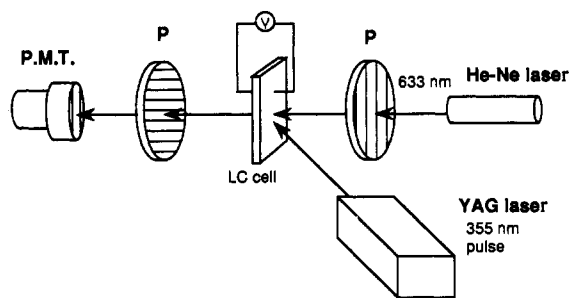


Figure 3. Schematic diagram for the time-resolved measurements of photochemical flip of polarization of FLC.

355 nm; pulse width, 12 ns FWHM) was used as an excitation light source and a He-Ne laser (633 nm, 5 mW) was used as an analyzing light source. The sample film was thermostated and placed between two crossed polarizers and connected to a function generator and an amplifier. The He-Ne laser passed through the sample film was focused onto the entrance slit of a Jabin-Ybon HR-320 monochromator. The change in transmittance of the He-Ne laser was measured with an Iwatsu TS-8123 storage scope. The power of the laser pulse was measured with a Scientech 365 power meter. Under the static electric field of +10 V, molecular axis of FLC was aligned into one direction. At this state, the direction of the incident polarizer was adjusted to coincide with the alignment direction, so that the transmitted light intensity was minimum. The electric field was then turned into opposite polarization (-10 V). The molecular axis of FLC changed its direction by twist angle shift from the original orientation, and the transmittance became large (electrooptic effect¹). Thus, the flip of polarization would be monitored by the intensity of the transmitted light through the sample. Then, the electric field was increased slowly (1 V/min) to opposite polarity (+3-6 V). After these procedures, the sample was irradiated with a laser pulse, and the induced flip of FLC was monitored by the transmitted light intensity.

Results and Discussion

Photochemical Flip of Polarization in FLC. A typical example of the pulsed laser experiments is shown in Figure 4. The change in transmittance of the He-Ne laser through the sample on the pulse excitation is indicated as a function of time. The trans-cis photoisomerization of the doped azobenzene occurred on a pulse of the laser, and the flip of polarization of FLC was also induced by the single pulse of the laser. The transmittance through the crossed polarizers changed abruptly by the electrooptic effect. The direction of the polarizer had been adjusted to $-\theta$ (opposite direction of the tilt angle) before the pulse irradiation, so that the transmittance became small after the event. We can see that the photochemical flip of polarization of FLC is a very fast process at least when a sufficient amount of the cis form of azobenzene derivative was produced.

In order to verify that the flip of polarization was in fact induced by the trans-cis photoisomerization of the azobenzene derivative, but not by a heat-mode process nor by other processes, the same measurement was performed on the *p*-hydroxyazobenzene (HO-AB)/FLC mixture and also on the pure FLC. HOAB has very similar electronic properties to those of the other azobenzene derivatives (absorption maximum and extinction coefficients), while it exhibits no photoisomerization behavior even in solution on prolonged exposure to a light which causes the trans-cis photoisomerization of azobenzene.^{7d-f} No change of the transmitted light intensity of the He-Ne laser was observed for the HOAB/FLC mixture and pure FLC after pulse irradiation. It is, therefore, safely concluded that the flip of polarization shown in Figure 4 was induced by the photoisomerization of the azobenzene derivative.

The tilt angle of this FLC before and after irradiation is shown in Figure 5. The change in the tilt angle produced by the trans \rightarrow cis isomerization of the guest molecule was at most $\sim 10^\circ$. This change was too small to induce a large transmittance change like that shown in Figure 4 in the experimental setup used in this

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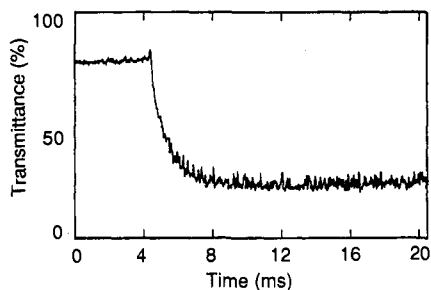


Figure 4. Time-resolved observation of photochemical flip of polarization monitored by electro-optic effect: laser power, 21 mJ/cm²; 60 °C.

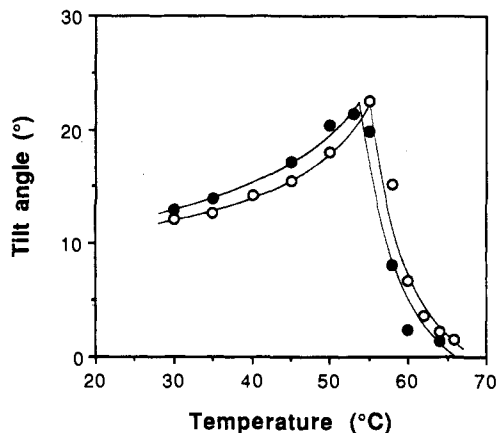


Figure 5. Temperature dependence of tilt angle of azobenzene/FLC mixture used in this study: (O) before irradiation and (●) after irradiation at 355 nm.

study. Thus, the result in Figure 4 can be attributed to the flip of polarization induced by the photochemical reaction of the guest molecule, although the change in the tilt angle produced by the photoisomerization might be one of the origins to alter the coercive force of the mixture.

It is worth referring here to the photoisomerization behavior of the azobenzene derivative in FLC. We tried to follow the time course of the trans-cis isomerization by transient absorption spectroscopy; however, this was unsuccessful. Our laser possesses a pulse width of 12 ns FWHM, and within this period the isomerization was found to be completed. After a single pulse irradiation, the absorption due to the trans form decreased abruptly like a step-function, but no decay of the absorption could be detected even in the shortest time range available for our apparatus (resolution ~ 12 ns) and in the longer time range in which the flip of polarization of FLC was observed.

Effect of Applied Voltage. The flip process of FLC is related to the magnitude of the applied electric field. In order to discuss the influence of applied voltage on the photochemical flip of polarization, we define the response time as the time required to reduce the transmittance of the He-Ne laser to 10% of the initial value. As demonstrated in Figure 6, the response time of the photochemical flip is governed by the applied field. The critical voltage for switching the transmittance through FLC was 6 V (optically determined value). Namely, the transmittance of the He-Ne laser completely changed to the dark state at 6 V, thus, we could apply voltages below 6 V. The response time was shortened with increasing the applied voltage, and a value of ~ 500 μ s was obtained at the highest voltage in this experiment. This is very much faster than the fastest response in the photochemical N-I phase transition ever reported.^{7d-g}

Effect of Temperature. The flip of polarization of FLC described in this paper is interpreted as a result from the destabilization of the SmC* phase induced by the appearance of the nonmesogenic cis form in the LC phase, thus the temperature of FLC sample is important. In Figure 7, the response time is

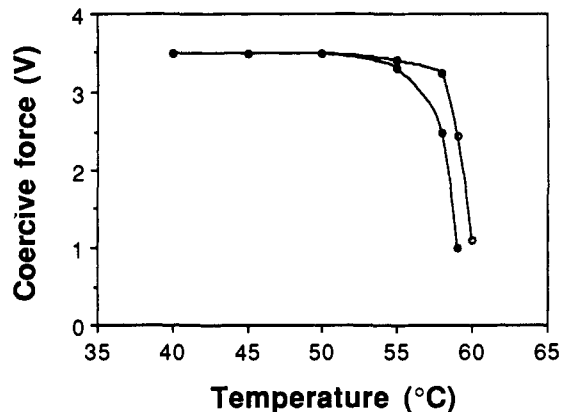


Figure 6. Effect of the magnitude of applied voltage on the response time of photochemical flip of polarization: laser power, 21 mJ/cm²; 60 °C.

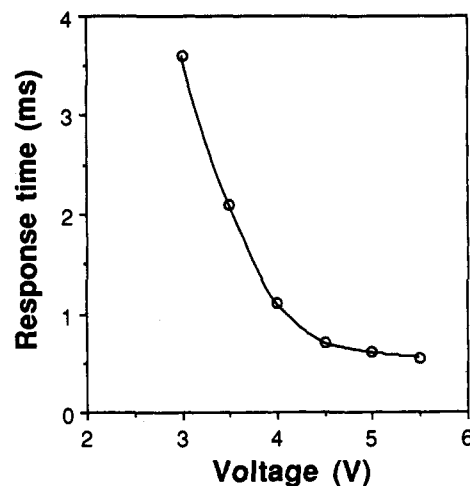


Figure 7. Effect of irradiation temperature on the response time of photochemical flip of polarization: $E = 4.5$ V; laser power, 21 mJ/cm².

plotted against the irradiation temperature. As seen in this figure, the response time was influenced by the irradiation temperature; the closer the irradiation temperature to the SmC*-SmA phase transition temperature, the shorter became the response time. This tendency may be interpreted in terms of the stability of the SmC* phase in the initial state. As the temperature before irradiation approaches the SmC*-SmA phase transition temperature, the stability of the SmC* phase is reduced, and the magnitude of coercive force can be changed easily. In Figure 8, the coercive forces of the azobenzene/FLC determined by Sawyer-Tower bridge¹ before and after irradiation are plotted. After irradiation, the coercive force decreased in the temperature range above 55 °C, and, accordingly, when the azobenzene/FLC was irradiated under the isothermal condition, the coercive force of the azobenzene/FLC was reduced. Particularly, near the SmC*-SmA phase transition temperature, the value of the coercive force changed greatly, so that the difference in magnitude of the coercive force before and after irradiation was very large. The succeeding step (flip of polarization) is a relaxation process; just after irradiation, the FLC is exposed to a larger electric field with an opposite direction of polarization than the coercive force, thus, the polarization relaxes to the direction of the applied field. The response time of this step was shortened with temperature, since as the difference between the applied field and the coercive force after irradiation becomes larger the FLC possesses larger excess energy.

It is worth mentioning here the results obtained at lower temperatures than those indicated in Figure 7 where the response time is plotted only in the range of 4 °C. The photochemical flip of polarization was also observed in the lower temperature range. However, it was observed only through the microscopic observation

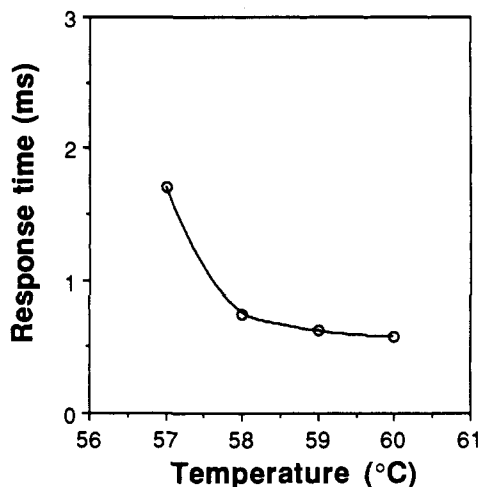


Figure 8. Temperature dependence of coercive force of FLC doped with azobenzene derivative measured by Sawyer–Tower bridge: (○) before irradiation and (●) after irradiation at 355 nm; 50 Hz, 10 V p-p.

and could not be detected by our time-resolved measurements. At lower temperatures than 57 °C, the flip was induced only in the small local area, suggesting that the condition at the interface of FLC and polyimide-alignment layer affected the results.

Effect of Laser Power. The power of the pulsed laser affected the photochemical flip of polarization as shown in Figure 9. The flip of polarization was observed with the laser power higher than 10 mJ/cm², and the response time was shortened with increasing laser power. As shown in Figure 10, the amount of cis isomer produced with a single pulse of the laser increased with the laser power, so that this laser power dependence can be ascribed to the amount of the cis isomer produced by the laser pulse. The photochemical flip of polarization of FLC can be interpreted as the relaxation process from a thermodynamically unstable to a stable state. Thus, the larger the amount of the cis form (destabilizer) in the SmC* phase, the smaller the thermodynamic stability of this phase becomes.

Conclusion

A new application of FLCs based on the novel working principle has been developed. FLC doped with a few mol % of the azobenzene derivative showed photochemically induced switching of polarization (photochemical flip). This process was very fast, and the optical property of flipped area showed sharp contrast against the unirradiated area. However, the performance of this device was strongly dependent on the cell construction, especially on the treatment of glass–FLC interface. This problem may be

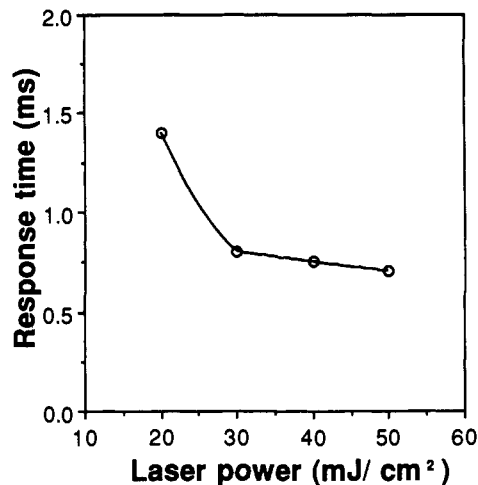


Figure 9. Effect of laser power on the response time of photochemical flip of polarization: $E = 4.0$ V; 60 °C.

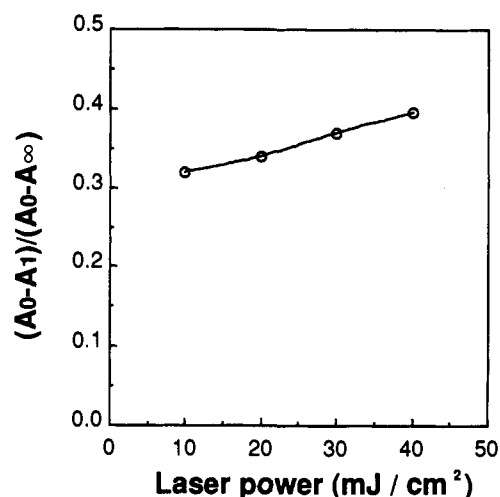


Figure 10. Course of trans → cis photoisomerization of azobenzene derivative in FLC as evaluated by the change in $(A_0 - A_1)/(A_0 - A_\infty)$ as a function of laser power. A_0 , A_1 , and A_∞ are the absorbances at 360 nm before irradiation, after irradiation of a single pulse, and after prolonged irradiation, respectively.

solved by an appropriate choice of combination of FLC molecules and alignment layers.

Acknowledgment. We thank Dainippon Ink and Chemicals, Inc., for a kind gift of the FLC.