Photochemical Control of Properties of Ferroelectric Liquid Crystals. 3. Photochemically Induced Reversible Change in Spontaneous Polarization and Electrooptic Property

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Received: June 1, 1995[®]

The photochemical control of spontaneous polarization (Ps) and the electrooptic properties of ferroelectric liquid crystals (FLCs) was studied. The photoisomerization of photochromic molecules (azobenzene and spiropyran derivatives) in FLCs caused the disorganization of the liquid crystalline phase with concomitant change in the interaction of FLC molecules and alignment layer and induced a reversible change in physical properties of the FLC. The rate and efficiency of the change in properties are discussed in connection with the structures of FLCs.

Introduction

In the last decade, considerable experiments and theoretical efforts have been put forth on ferroelectric liquid crystals (FLCs) because of their potential use as new types of displays. A characteristic of FLCs is the existence of spontaneous polarization (Ps). The appearance of Ps in specific structures of LCs was discovered by Meyer in 1975.¹ When the LC phase, which consists of molecules possessing dipoles normal to the molecular long axis, loses its symmetry to C_2 , polarization of the LC phase appears spontaneously. In this way, FLC molecules were designed to exhibit the SmC* phase, which belongs to the C_2 symmetry.² The attractive feature of FLCs lies in the so-called electrooptic effect they exhibit. When FLCs are sandwiched between two glass plates, a unique phase structure appears (surface-stabilized state). At this state, if one applies alternating voltage across the two glass plates, FLC molecules show flipflop movement and cause the switching of the light transmittance through a pair of crossed polarizers placed in front and behind the FLC sample. Ths switching behavior of FLC is known to be very fast, so that the research for the application to display devices is intensively under way. $^{3-6}$ Thus, the ferroelectric properties of FLCs arise from the phase structure; then, if the structure of the ferroelectric phase is changed by means of photochemical processes, the magnitude of the Ps will be controlled isothermally by light irradiation.7-9

In this paper, we tried to control the value of Ps and the switching behavior of FLCs by photochemical processes. Photoresponsive molecules were incorporated into FLCs and photoisomerized to perturb the structure of the LC phase. The change in the Ps and the switching behavior thus induced are discussed in connection with the disorganization of the phase structure as well as the interaction between the FLC molecules and alignment layer.

Experimental Section

Samples. The structures of FLCs and photoresponsive molecules are shown in Figure 1. These FLCs are known to possess a large value of Ps.¹⁰ FLC 1 and FLC 2 have a very similar structure except for the existence of a carbonyl group

Ferroelectric Liquid Crystals





Photoresponsive Molecules



$$C_{6}H_{13} \longrightarrow N=N \longrightarrow O \cdot CH_{2} - C \cdot O - CH_{2} \cdot CH_{2} - C_{2}H_{5}$$

$$O \cdot CH_{2} - C \cdot O - CH_{2} \cdot CH_{2} - C_{2}H_{5}$$

$$C_{6}H_{13} \longrightarrow N=N \longrightarrow O \cdot CH_{2} - C \cdot O - CH_{2} \cdot CH_{2} - C_{2}H_{5}$$

$$H_3O = O + N = N + O + OCH_3$$
(8)

$$C_8H_{17}O - OC_8H_{17}$$
 (9)

Figure 1. Structures of the FLC and photoresponsive molecules used in this study.

at the end of the biphenyl group. Because of the introduction of the polar group, FLC 1 was expected to show a high viscosity compared to FLC 2. In fact, FLC 1 showed a larger critical voltage for the change in the direction of polarization than FLC 2. Phase transition temperatures of these FLCs are listed in Table 1. The azobenzene derivatives and the spiropyran derivative were used as photoresponsive molecules. Azobenzene derivatives show *trans* \rightarrow *cis* photoisomerization reaction, and spiropyran derivatives photoisomerize to merocyanine forms by irradiation at 360 nm. These photoresponsive molecules

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^{*} Abstract published in Advance ACS Abstracts, August 1, 1995.

 TABLE 1: Phase Transition Temperature of FLC Doped

 with Photoresponsive Molecule^a

	phase transition temperature (°C)
FLC 1 (pure)	C 45 SmC* 74 SmA 77 I
azobenzene (4), 3 mol %	C 44 SmC* 69 SmA 73 I
spiropyran (5), 1 mol %	C 45 SmC* 52 SmA 67 I
FLC 2 (pure)	C 33 SmC* 52 SmA 66 I
azobenzene (4), 3 mol %	C 33 SmC* 49 SmA 63 I
FLC 3 (pure)	C 38 SmC* 64 SmA 110 N 112 I
azobenzene (6), 3 mol %	C 38 SmC* 58 SmA 105 N 108 I

^{*a*} C, crystal; SmC*, chiral smectic C phase; SmA, smectic A phase; I, isotropic.



Figure 2. Ps of FLC 1 doped with 3 mol % of azobenzene derivative 4: (O) before irradiation; (•) after irradiation at 360 nm.

were doped into the FLCs at a concentration of 3 mol %. All measurements were performed on the samples with a 2 μ m glass cell (with a 1 cm² ITO electrode, polyimide coated).

Measurements. Phase transition temperatures of FLCs were determined with a differential scanning calorimeter (DSC; Seiko I&E SSC-5000) and by microscopic observation (Mettler FP-90 and Olympus BH2 polarizing microscope). Ps values were measured by the triangular voltage method (50 Hz, $\pm 10 V_{p-p}$). The sample was thermostated and irradiated with monochromatic light from a Jasco CRM-FA irradiator (2 kW Xe arc lamp). The change in Ps induced by the photoisomerization of the photoresponsive molecules was monitored as a function of time. The electrooptic properties were measured with a 500 W high-pressure Hg lamp as an excitation light source and the visible light from a tungsten lamp as an analyzing light. The sample film was thermostated, placed between two crossed polarizers, and connected to a function generator and an amplifier. The switching behavior of the azobenzene/FLC mixtures was evaluated by measuring the transmitted light intensity through the crossed polarizers. The change in transmittance of the analyzing light was monitored with a photodiode and an Iwatsu TS-8123 storage scope. Photoisomerization of azobenzene guests was confirmed by absorption spectroscopy.

Results and Discussion

Photochemically Induced Change in Spontaneous Polarization. The values of Ps of FLC 1 doped with 3 mol % of 4 are plotted as a function of temperature in Figure 2. The Ps of FLC 1 was 35 nC/cm² at a temperature 5 °C below the SmC^{*}-SmA phase transition temperature. The magnitude of the Ps ceased at the SmC^{*}-SmA phase transition temperature. Introduction of 3 mol % of the azobenzene derivative into the LC phase lowered the SmC^{*}-SmA phase transition temperature by 5 °C, as indicated in Table 1. After irradiation at 360 nm, the profile changed as shown in Figure 2. The phase transition



Figure 3. Change in the signal of spontaneous polarization of the 4/FLC 1 mixture in the triangular voltage method under irradiation. 50 Hz, 10 V_{p-p} triangular voltage was applied. Photoirradiation was performed at the temperature T = Tc - 3 °C.

temperature was lowered by 3 °C on irradiation, which agreed with the previously reported results of the photochemical N–I phase transition.^{11,12} The photoisomerization of the *trans* azobenzene in the LC phase destabilized the LC phase and lowered the phase transition temperature. The extent of the photoisomerization was estimated as 72% by a UV absorption spectrum, which indicates that ~2 mol % of the *cis* forms were produced in the LC phase.

The decrease in the phase transition temperature observed for the *trans-cis* photoisomerization of the azobenzene guest molecule in the present system seemed to be too small. Incorporation of the *trans* form of 4 into FLC 1 at the concentration of 3 mol % lowered the SmC*-SmA phase transition temperature by 5 °C, while 2 mol % of the *cis* form produced *in situ* by photoirradiation lowered the phase transition temperature by only 3 °C. The bent shape of the *cis* form is evidently more favorable for the destabilization of the LC phase. Thus, the magnitude of the decrease in the phase transition temperature seemed to be anomalous.

A change in the texture of the LC phase on irradiation was observed under the polarizing microscope. Homogeneous texture was observed before irradiation. After irradiation, many defects were created at the first stage, and finally a lot of small dark spots appeared. The phase transition temperature of these spots was found to be much lower than that of the other sites. It seems possible that these spots result from the aggregation of the cis forms of the azobenzene derivative. Under photoirradiation, the cis forms of the azobenzene were produced, which possess low miscibility with the host FLC molecules in the SmC* phase; thus, the molecularly dispersed state of the cis forms in the host FLC was energetically unfavorable, and aggregation of the cis forms presumably took place. Phase separation, even though it is partial, leads to a decrease in the effective concentration of the *cis* forms in the bulk of the FLC and tends to diminish the effect of the perturbation imposed on the phase structure of the FLC in the form of the trans $\rightarrow cis$ isomerization, resulting in a small decrease in the phase transition temperature.

Change of Ps Induced by the Photochemical Phase Transition. When the azobenzene/FLC mixture was held at temperatures 2-3 °C below the SmC*-SmA phase transition temperature (Tc) and irradiated to cause the *trans*-*cis* isomerization of the azobenzene, the photochemical phase transition took place isothermally. The SmC* phase was transformed to the SmA phase by accumulation of the *cis* azobenzene. The Ps vanished through this process, since the SmA phase is not a ferroelectric phase. The Ps signal in the triangular wave voltage method uner irradiation of azobenzene 4/FLC 1 is shown in Figure 3. The irradiation was performed at T = Tc - 3 °C.



Figure 4. Time-resolved observation of the photochemically induced change in the Ps of the 4/FLC 1 mixture at T = Tc - 1 °C.



Figure 5. Reversal of the Ps of FLC 1 induced by the $cis \rightarrow trans$ photoisomerization of azobenzene derivative 4.

The values of the Ps under irradiation are plotted as a function of time in Figure 4. The value of the Ps decreased and vanished after 100 s, which indicates that the $SmC^* \rightarrow SmA$ phase transition took place within this period.

The photochemical phase transition has been reported to be a reversible process. The azobenzene derivative used in this study exhibited the *trans* \rightarrow *cis* photoisomerization by irradiation at 360 nm and the *cis* \rightarrow *trans* photoisomerization at 430 nm. After the Ps completely vanished by irradiation at 360 nm, the sample was exposed to 430 nm light. As shown in Figure 5, the Ps was restored to the initial value, demonstrating that this process was also reversible. Thus, the magnitude of the Ps was altered continuously and reversibly from 0 to ~10 nC/cm² by the photochemical reaction.

Effect of Temperature. The photochemical phase transition is induced by the lowering of the phase transition temperature, so that the temperature of the FLC under irradiation is important. To discuss the influence of the temperature on the photochemical phase transition, we define the response time of the photochemical phase transition of FLC as the time required to reduce the Ps to 10% of the initial value. In Figure 6, response times are plotted against the irradiation temperature. As seen in this figure, the response time is remarkably influenced by the irradiation temperature: the closer to the phase transition temperature, the shorter the response time. This temperature dependence can be attributed to the stability of the SmC* phase in the initial state. Namely, when the temperature of the LC is close to the SmC*-SmA phase transition temperature, the stability of the SmC* phase becomes low, and the transition from the SmC* phase to the SmA phase can be induced easily.

Effect of Structure of the FLC. 4'-(Octyloxy)biphenyl-4yl (2S,3S)-2-chloro-3-methylpentanoate (2) was also employed as a host FLC. The main difference in properties between FLC 1 and 2 is the magnitude of the coercive force (Ec). The



Figure 6. Temperature dependence of the response time of the photochemical SmC^*-SmA phase transition of 4/FLC 1 monitored by the Ps change.



Figure 7. Ps of FLC 2 doped with 3 mol % of azobenzene derivative 4: (O) before irradiation; (\bullet) after irradiation at 360 nm.

coercive force is the critical value of the applied electric field at which polarization of the FLC is switched to the opposite direction. When the Ec is large, one can apply an electric field of the opposite polarity to the FLC without inducing the switching of polarization. FLC 1 possessed a large Ec of 3 V, and it exhibited a sharp response when polarization reversal took place. On the other hand, FLC 2 possesses a small Ec of <1 V and showed gradual reversal of polarization. These two FLCs were expected to show different properties when they were employed in electrooptical applications.

The values of Ps of FLC 2 doped with 3 mol % of 4 of plotted as a function of temperature in Figure 7. The Ps of FLC 2 was 150 nC/cm² at a temperature 10 °C below Tc. Introduction of 3 mol % of the azobenzene derivative into the LC phase lowered the phase transition temperature by \sim 3 °C, as indicated in Table 1. After irradiation at 360 nm, the profile changed as shown in Figure 7. The phase transition temperature was reduced by 1 °C on irradiation. The dark spots were observed under a polarizing microscope after prolonged irradiation. As in the case of the 4/FLC 1 mixture, the cis forms of 4 produced on photoirradiation might be aggregated. A similar tendency was observed in the change of the Ps by the irradiation between FLC 1 and FLC 2; however, the time course of the Ps change was different between the two FLCs. Figure 8 shows the timeresolved observation of the Ps change in the photochemical phase transition for FLC 1 and FLC 2. The Ps values vanished finally in both FLCs. The decay rate of the Ps value was lower in FLC 1. This can be interpreted as a result from the different rates of photochemical phase transition in these FLCs. However, the characteristic parameter of these FLCs, Ec, is related to the intermolecular interaction of the FLC molecules. A large Ec value results from a large intermolecular interaction. The melting point of FLC 1 was also higher than that of FLC 2.



Figure 8. Time-resolved observation of the photochemically induced change in the Ps of FLC 1 (\bullet) and FLC 2 (\odot) brought about by the *trans* \rightarrow *cis* photoisomerization of 4 doped in these FLCs at $T = \text{Tc} - 1 \, ^{\circ}\text{C}$.



Figure 9. Ps of FLC 1 doped with 1 mol % of spiropyran 5: (O) before irradiation; (\bullet) after irradiation at 360 nm.

Thus, the response time for the Ps change resulting from the photochemical phase transition was affected by the intermolecular interaction in such a way that the FLC with a large intermolecular interaction showed a slower response.

The Ps Change Induced by the Photoisomerization of Spiropyran. Spiropyran derivative 5 was also used as a photoresponsive molecule. Spiropyrans are well-known photochromic molecules, which isomerize from the spiropyran to the intensely colored merocyanine form under UV irradiation. While spiropyrans are neutral molecules, merocyanines possess a zwitterionic structure. Thus, the effect of the isomerization of spiropyran to merocyanine on the electric properties of FLC is interesting. The shape of spiropyrans is not favorable for the stabilization of the LC phase because of the bulky structure. On the other hand, merocyanines are planar molecules, so they are favorable for the LC phase. Thus, the phase transition temperature of LCs doped with spiropyrans was raised by the UV irradiation to cause the spiropyran to merocyanine isomerization. The structure of the spiropyrans was too bulky to be dispersed molecularly in the SmC* phase; thus, they aggregated obviously in the concentration range higher than 3 mol %. The Ps values of FLC 1 doped with spiropyran (5) before and after irradiation are shown in Figure 9. Introduction of 1 mol % of spiropyran 5 into FLC 1 lowered the phase transition temperature by ~ 20 °C, as indicated in Table 1. After irradiation at 360 nm, the profile changed as shown in Figure 9. Because of the appearance of the zwitterionic structure and the photodecomposition, the signals observed in the triangular wave voltage method were somewhat distorted after irradiation. The phase transition temperature was raised by 8 °C on irradiation to bring about the spiropyran to merocyanine isomerization. The spiro-



Figure 10. Time-resolved observation of Ps reversal in FLC 1 induced by the spiropyran \rightarrow merocyanine photoisomerization of 5 at 57 °C.



Figure 11. Switching behavior of FLC **3** on the application of the square wave (10 V_{p-p} , 1.0 Hz): (a) transmittance of analyzing light; (b) magnitude of applied voltage as a function of time. The switching intensity, ΔI , is defined as indicated.

pyran in the LC phase destabilized the LC phase and lowered the phase transition temperature, and the merocyanine form stabilized the LC phase to some extent. When the system was held at a temperature 2 °C above the phase transition temperature of the spiropyran/FLC mixture and irradiated at 360 nm, appearance of the Ps signal was observed (Figure 10). This result is in accordance with the result of the $cis \rightarrow trans$ isomerization of the azobenzene in the FLC. Change in the shape of the photoresponsive guest molecule, from spherical to rodlike shape, induced the SmA-SmC* phase transition and the emergence of Ps.

Switching Behavior of the Ferroelectric Liquid Crystal. The switching behavior of FLC 3 alone on the application of the square wave (10 V_{p-p} , 1.0 Hz) is shown in Figure 11: in the upper half of the figure a change in transmitted light intensity of the cell with the 2 μ m gap containing the FLC through a pair of the crossed polarizers on the application of the square wave is indicated as a function of time, and in the lower half is shown the magnitude of the applied voltage as a function of time. It was clearly observed that the transmitted light intensity changed regularly in accordance with the polarity of the applied electric field, and this result indicates that the mesogens alter their orientation by the applied electric field (*E*). The switching intensity (ΔI) is defined as shown in Figure 11.

The ΔI values were determined at various temperatures, and the results are plotted as a function of temperature in Figure 12. The ΔI values increased with temperature and abruptly



Figure 12. Switching intensity (ΔI) of FLC 3 at various temperatures.



Figure 13. Switching intensities of the 6/FLC 3 mixture at various temperatures: (\bigcirc) before irradiation; $(\textcircled{\bullet})$ after irradiation at 366 nm.

decreased at a temperature around 64 °C. The change in ΔI at this temperature agreed with the SmC*-SmA phase transition. In the thinly sandwiched SmC* phase, FLC molecules adopt the surface-stabilized state, in which the long axis of each FLC molecule tilts from the layer normal and changes direction in accordance with the polarity of the applied electric field so as to alter the light intensity through a pair of crossed polarizers. However, when the phase was transformed to the SmA phase, the tilt angle of FLC changed to almost 0°, and the switching intensity became small.

Photochemically Induced Change in Optical Properties of the Azobenzene/FLC Mixture. The ΔI values of 6/FLC 3 are plotted as a function of temperature in Figure 13. Before irradiation, the ΔI value showed a maximum at around 58 °C, which was lower by 6 °C than the maximum exhibited by FLC 3 alone (Figure 12). Thus, 3 mol % of the trans form of 6 lowered the SmC*-SmA phase transition by 6 °C. After irradiation at 366 nm (indicated by ●), the transition temperature decreased to 53 °C. The extent of photoisomerization was estimated as 80% by absorption spectroscopy; thus, 2.4 mol % of cis-6 diminished the phase transition temperature of FLC 3 by 5 °C, which was smaller than the value brought about by the 3 mol % of the trans form. It was found in Figure 13 that the profile of ΔI shifted to lower temperatures on photoirradiation without changing the whole shape. Furthermore, the maximum value of ΔI did not change on production of the *cis* form. The tilt angle of this mixture before and after irradiation is plotted as a function of temperature in Figure 14. The tilt angle also gave a maximum just below the SmC*-SmA phase transition temperature, and a very similar temperature dependence was observed in the ΔI -temperature profile (Figure 13) and in the tilt angle-temperature profile (Figure 14) on photoirradiation. The temperature profile of the tilt angle shifted to lower temperature upon irradiation. The optical properties of FLC are related to the alignment condition and its direction. The similarity observed in the temperature dependence between ΔI and the tilt angle suggests that the change in ΔI induced by



Figure 14. Tilt angle of 6/FLC 3 at various temperatures: (\bigcirc) before irradiation; (O) after irradiation at 366 nm.



Figure 15. Change in switching behavior of the 6/FLC 3 mixture induced by the *trans-cis* isomerization of azobenzene. Photoirradiation was performed at 366 nm. (a) 55 °C; (b) 40 °C.

the irradiation can be attributed to the change in tilt angle. The result in Figure 13 shows that when irradiation is performed in the temperature range 50–60 °C, the switching intensity ΔI decreases in line with the accumulation of the *cis* azobenzene. On the other hand, when the irradiation temperature is lower than 40 °C, ΔI increases on irradiation. The switching behavior of the **6/FLC 3** mixture on irradiation is shown in Figure 15. It was confirmed that irradiation at 55 °C reduced the switching intensity, while irradiation at 40 °C increased the intensity. Thus, it was demonstrated that the switching intensity of the azobenzene/FLC mixture can be either increased or decreased by irradiation of 366 nm light at different temperatures.

Also, a reversible change was observed by irradiation at 360 and 420 nm. As shown in Figure 16, when 6/FLC 3 was irradiated at 360 nm with a 2 kW Xe lamp at 58 °C, the photochemical SmC*-SmA phase transition was induced and the switching intensity became small, and when the irradiation wavelength was changed to 420 nm, the switching intensity recovered.

Effect of Structures of Azobenzene Derivatives. The azobenzene derivatives 7, 8, and 9 were also employed as guest photoresponsive molecules. The obtained profiles were similar to those shown in Figure 13. The SmC*-SmA phase transition temperature was lowered by incorporation of the azobenzene and reduced further by irradiation at 366 nm. However, the extent of lowering of the phase transition temperature was



Figure 16. Photochemically induced change in switching behavior of the 4/FLC 3 mixture. 360 and 420 nm light from a Xe lamp was irradiated at the time indicated by arrows. Irradiation temperature was 58 °C.

smaller than that observed when 6 was used as a guest molecule. The SmC^{*}-SmA phase transition temperature of the 6/FLC 3 mixture was 58 °C for the trans form of 6 and 53 °C for the cis form, while in the 7/FLC 3 mixture, the phase transition temperature was 62 °C for the trans form of 7 and 56 °C for the cis form. The difference in lowering of the phase transition temperature may be attributed to the difference in the solubility of the azobenzene guest molecules. 6 might be more soluble in FLC 3 than 7. 7 may be aggregated to some extent in FLC 3, so that the concentration of the molecularly dispersed guest molecules in the LC phase may be lower than that in the 6/FLC 3 mixture. The structures of 6 and 7 are almost the same except for the chiral unit. The structures of 6 and FLC 3 are very different; however, 6 has the same chiral unit as FLC 3. Thus, it seems that the chiral recognition by the host SmC* phase works very strongly. The chiral recognition by the SmC* phase has been known: the SmC molecules with pure R and pure Schiral structure exhibit a helicoidal SmC* phase; however, when the R form and the S form were mixed in equal portions, the mixture did not show the SmC* phase. Thus, it is possible that the host FLC molecules recognized the chiral part of 6.

The azobenzene derivative 8 was also used as a photoresponsive molecule. It was observed that the profile of the *trans*-8/FLC 3 mixture was almost the same as that of the pure FLC. Very few changes were observed after irradiation. 8 has a much smaller molecular size than the host FLC without the chiral part, so that it is very difficult for 7 to be dispersed molecularly in the host FLC even in the *trans* form. In fact, aggregation of 8 was recognized in the 7/FLC 3 mixture as needles under microscopic observation at 120 °C, where the host FLC showed an isotropic phase. Thus, the addition of 8 to FLC 3 resulted in a very small effect on the phase transition temperature of the guest/host mixture.

On the other hand, when 9 was incorporated into FLC 3 as a photoresponsive molecule, the switching intensity was clearly reduced by the irradiation even though the ΔI -temperature profile before photoirradiation was almost the same as that of the 8/FLC 3 mixture. The solubility of 9 in the SmC* phase of FLC 3 might be the same as that of 8; however, the long tail unit of 9 seemed to affect the SmC* phase structure effectively enough to produce a large change in ΔI on photoirradiation.

The results obtained for the azobenzene guest molecules with different structure clearly indicate that the effect of the *trans* to *cis* isomerization is different, depending on the structure of the guest molecule; however, the guest molecules with structure similar to the host FLC tend to affect the phase behavior of the host to the greatest extent on irradiation.

Conclusion

The magnitude of Ps and the switching properties of FLC were controlled by the photochemical reactions. FLC doped with a few mole percent of azobenzene or spiropyran derivatives showed a photochemically induced change in those properties. Those phenomena were considered to be attributed to the occurrence of photochemically induced disorganization of the liquid crystalline phase. The aggregation of the *cis* form of azobenzene and the spiropyran might be a problem when repeatability is required.

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