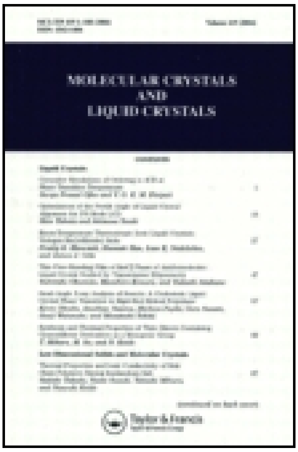

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Photochemical Control of Switching Behaviors of Ferroelectric Polymer Liquid Crystals: Poly(2-methylbutyl 4′-(10-acryloyloxydecyloxy)-biphenyl-4-carboxylate)

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Photochemical Control of Switching Behaviors of Ferroelectric Polymer Liquid Crystals: Poly(2-methylbutyl 4′-(10-acryloyloxydecyloxy)-biphenyl-4-carboxylate)

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Switching behaviors of ferroelectric polymer liquid crystal (FPLC), poly(2-methylbutyl 4′-(10-acryloyloxydecyloxy)biphenyl-4-carboxylate), were successfully modulated reversibly by photochemical reaction of photochromic guests (azobenzene derivatives) doped in the FPLC. Chiral azobenzene (AB_{chi}) possessing the same structure as the host FPLC at the chiral part was found to enhance the transmitted light intensity through a pair of crossed polarizers on the trans to cis photoisomerization, while the other achiral azobenzene derivatives reduced the transmitted light intensity on photoisomerization. This difference in photoresponsiveness has been attributed to the different effect of the trans-cis photoisomerization on the host mesogens, the change in molecular shape for the achiral azobenzenes and the change in dipole moment for AB_{chi}.

Keywords: ferroelectric liquid crystal, photochemical control, photochromic, azobenzene, chiral, trans-cis photoisomerization

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INTRODUCTION

In visual cells, photons are absorbed by photoreceptors called retinal in rhodopsin and cis-trans photoisomerization results.[1] This photochemical reaction then induces a conformational change of the whole protein (opsin), and subsequent reactions take place.[1] In these successive processes, the photons act only as a trigger to bring about a change in molecular shape of a single chromophore in the macromolecular protein, but this change in the small, local site results finally in tremendous *physical amplification* in terms of the conformational change of the whole protein. This has been regarded as the origin of the high sensitivity of the visual cells.[1]

These processes occurring in the visual cells may be translated into *chemical terms* and the extracted principle may be applied to devices for photonics. The working principle of vision translated into *chemical terms* is *photochemically triggered physical amplification* of photosignals with the aid of molecular aggregates as matrices. Namely, photoresponsive molecules are incorporated into molecular aggregate systems at a very low concentration, and photochemical reactions are brought about by exposure to light, inducing physical changes of the whole system. In this way, the photosignals are converted with amplification into the change in the physical properties of the matrices (molecular aggregates). The merits of this way of image storage devices are evident. Since the photosignals are converted into the physical change of the system, a variety of methods can be used for nondestructive readout of the stored information. We applied this principle to a variety of molecular aggregate systems such as micelles,[2] vesicles[3] and liquid crystals (LCs),[4] aiming at highly sensitive image storage systems.

Although the micellar and vesicular systems were useful to verify the principle, their poor processability clearly prevented these systems from practical applications. We, then, used LCs as matrices and found that an isothermal phase transition of the photoresponsive guest/LC mixtures could be induced by photochemical reaction of the guest molecules.[4] Furthermore, by the use of polymer liquid crystals (PLCs) as hosts, the optical image could be stored in the form of the induced isotropic phase and could be kept stable for a long period below the glass transition temperature (Tg) of PLCs.[4(b),(c)] Unlike the response against an electric field, PLCs were found to exhibit a similar photoresponse to low-molecular-weight LCs and the write-in process was completed within ~50 ms.[4(f)]

Optical image recording systems based on PLCs have been satisfactory in terms of high stability of stored information, high resolution (<2 μm) and relatively quick response (50 ms). However, for a quicker response to be achieved, systems based on the photochemical phase transition of photoresponsive guest/PLC mixtures are to be replaced by those with a new working principle. We, in the present paper, report the first example of the photochemical control of ferroelectric switching behaviors of ferroelectric polymer liquid crystals (FPLCs) with the aid of photochromic guest molecules. Ferroelectric LCs (FLCs) show a much quicker response to applied electric fields than conventional LCs with a nematic phase because of aligned permanent dipoles (spontaneous polarization, Ps) spatially oriented perpendicular to the long axis of each mesogenic molecule when placed in cells with a small gap.[5,6] Use of PLCs as hosts is expected to provide the guest/host mixtures with a high stability owing to Tg of the PLCs, and the ferroelectric properties of FPLC will enable the guest/FPLC mixtures to show a quicker response. This study will provide a basis for the photochemical image storage devices with a new working principle.

EXPERIMENTAL SECTION

Materials

Structures of a ferroelectric polymer liquid crystal (FPLC) and photochromic azobenzene derivatives used in this study are shown in Figure 1. An acrylate with a side-chain chiral cyanobiphenyl moiety (3) was prepared by the method reported by Hashimoto *et al.* with some modification.[7]

(S)-(+)-2-Methylbutyl 4′-hydroxybiphenyl-4-carboxylate (1)

4′-Hydroxybiphenyl-4-carboxylic acid (5.0 g; 23 mmol) and (S)-(−)-2-methyl-1-butanol (3.9 g; 45 mmol) were dissolved in dehydrated n-butyl ether (80 ml), and to this solution concentrated sulfuric acid (0.5 ml) was added dropwise with stirring. The resulting mixture was then refluxed for 24 h and left at room temperature. The mixture was poured into an excess of water and the precipitate was extracted with ether. The ether layer was washed with aqueous sodium bicarbonate and

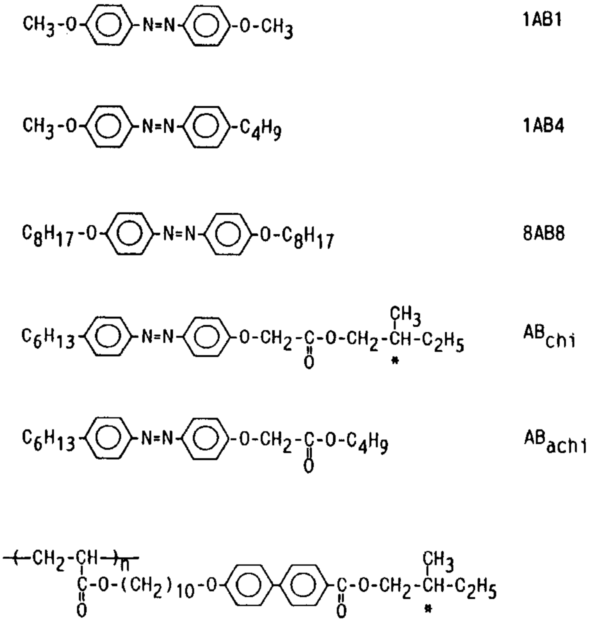

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FIGURE 1 Structures of FPLC and azobenzene derivatives used in the present study.

water, successively, and dried over magnesium sulfate. The product was finally recrystallized from toluene/hexane (1:1) mixture: yield 91%; mp 115-116°C; IR (KBr) 3400, 2960, 1690, 1600, 1500, 1420, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0 (m, 6), 1.2-2.1 (m, 3), 4.2 (dd, 2), 6.9 (d, 2), 7.6 (t, 4), 8.1 (d, 2). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.15; H, 6.95.

10-Bromodecyl acrylate (2)

To a solution of acrylic acid (6.0 g; 83 mmol) and tetramethylammonium hydroxide pentahydrate (17 g; 18 mmol) in 90 ml of dimethylformamide, 1,10-dibromodecane (50 g; 0.15 mol) was added in small portions at room temperature, and the resulting mixture was left for 20 h with stirring. The mixture was then poured into 300 ml of water and the product was extracted with ether, dried over magnesium sulfate and purified by column chromatography on silica gel with benzene/hexane (1:2) as an eluent: yield, 41%; IR (KBr) 2950, 1720, 1415, 1295 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3 (s, 8), 1.5-2.0 (m, 8), 3.4 (t, 2), 4.2 (t, 2), 5.8 (m, 1), 6.2-6.5 (m, 2).

2-Methylbutyl 4'-(10-acryloyloxydecyloxy)biphenyl-4-carboxylate (3)

A mixture of 1 (5.1 g; 18 mmol), 2 (5.6 g; 18 mmol) and potassium carbonate (10 g) in 150 ml of acetone was refluxed for 9 h, and the precipitate formed was removed by filtration. The product was recovered from the filtrate and purified by recrystallization from ethanol: yield, 43%; mp 40–41°C; $[\alpha]_D = +2.80°$ ($CHCl_3$); IR (KBr) 2900, 1700, 1600, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.1 (m, 6), 1.1-1.45 (m, 8), 1.45–2.0 (m, 11), 3.9–4.3 (m, 6), 5.7–5.9 (m, 1), 6.1–6.5 (m, 2), 7.0 (d, 2), 7.5–7.8 (q, 4), 8.1 (d, 2). Anal. Calcd for $C_{31}H_{42}O_5$: C, 75.27; H, 8.56. Found: C, 75.26; H, 8.75.

Polymerization of 3 was conducted in tetrahydrofuran (THF) by the use of azobis(isobutyronitrile) (AIBN) as an initiator. The polymer (4) was purified by repeated precipitation from chloroform solution into methanol.

Azobenzene derivatives

4,4'-Dimethoxyazobenzene (1AB1), 4-butyl-4'-methoxyazobenzene (1AB4) and 4,4'-dioctyloxyazobenzene (8AB8) were prepared and purified as reported previously.[8]

2-Methylbutyl 4-(4-hexylphenylazo)phenyloxyacetate (AB_{chi})

4'-Hexyl-4-hydroxylazobenzene was prepared by the conventional diazo-coupling reaction between 4-hexylaniline and phenol, and purified by recrystallization from hexane (analytical data agreed). This azobenzene (2.7 g; 9.5 mmol) and ethyl bromoacetate (1.9 g; 11 mmol) were dissolved in acetone (25 ml) and potassium carbonate (2 g) was added to the mixture. The mixture was then refluxed for 1 h, and a crystalline product was obtained by evaporation of the solvent after removal of the precipitate by filtration. The crystalline product was dissolved in 25 ml of dioxane and KOH (0.8 g) in methanol was added. The hydrolyzed product, potassium 4-(4-hexylphenylazo)phenyloxyacetate, was obtained as a precipitate, and the salt was converted into a free acid by treating with dilute hydrochloric acid. The acid was purified by recrystallization from 2-propanol: yield, 70%; mp 193–194°C; IR (KBr) 3420, 2860, 1750, 1710, 1600, 1500 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.85 (m, 3), 1.1–1.9 (m, 8), 2.65 (t, 2), 4.8 (s, 2), 7.1 (d, 2), 7.4 (d, 2), 7.8 (t, 4). Anal. Calcd for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.11; N, 8.23. Found: C, 70.56; H, 6.94; N, 8.41.

The acid (2.0 g; 5.9 mmol) was mixed with oxalyl chloride (7.5 g; 59 mmol) in THF/benzene (1:1; 30 ml) and the resulting mixture was heated to 60°C for 1 h in order to obtain an acid chloride. The acid chloride was recovered by evaporation of the excess oxalyl chloride, then dissolved in dehydrated THF (25 ml), and to this solution (S)-(−)-2-methyl-1-butanol (0.62 g; 7.1 mmol) and triethylamine (0.6 g) in THF were added dropwise. After addition, the mixture was refluxed for 3 h, allowed to stand overnight with stirring, and poured into sodium bicarbonate solution. The product was obtained by extraction with chloroform and finally purified by recrystallization from ethanol/water (4:1): yield, 45%; mp 35–37°C; $[\alpha]_D$ = +2.28° ($CHCl_3$); IR (KBr) 2860, 1760, 1735, 1600, 1500, 1240 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.85 (m, 9), 1.0-1.8 (m, 18), 2.65 (t, 2), 4.0 (d, 2), 4.9 (s, 2), 7.1 (d, 2), 7.4 (d, 2), 7.8 (t, 4). Anal. Calcd for $C_{25}H_{34}N_2O_3$: C, 73.14; H, 8.35; N, 6.82. Found: C, 73.06; H, 8.38; N, 6.79.

Butyl 4-(4-hexylphenylazo)phenyloxyacetate (AB_{achi})

This achiral azobenzene was prepared similarly from the acid chloride just described (1.3 g; 3.7 mmol) and n-butanol (0.55 g; 7.4 mmol) in dehydrated THF: yield, 74%; mp 52-53.8°C; IR (KBr) 2950, 1730, 1600, 1500 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.75-1.1 (m, 6), 1.1-1.9 (m, 12), 2.7 (t, 2), 4.2 (t, 2), 4.7 (s, 2), 8.0 (d, 2), 8.3 (d, 2), 8.4 (t, 4). Anal. Calcd for $C_{24}H_{32}N_2O_3$: C, 72.69; H, 8.13; N, 7.06. Found: C, 72.50; H, 8.12; N, 7.25.

Characterization

Molecular weight (Mn) of FPLC (4) was determined by gel permeation chromatography (GPC; Jasco 880-PU, column, Shodex KF800FP + KF80M + KF8025; eluent, chloroform) calibrated with standard polystyrenes. Mn and polydispersity (Mw/Mn) of 4 used in the present study was 3300 and 1.3, respectively. Liquid-crystalline phase behaviors and phase transition behaviors were examined on an Olympus model BH2 polarizing microscope equipped with Mettler hot-stage models FP-80 and FP-82. Thermotropic properties were determined with a differential scanning calorimeter (Seiko I&E SSC-5000) at a heating rate of 10°C/min. At least four scans were performed for each sample to check reproducibility.

Sample preparation

For examination of liquid crystalline and ferroelectric liquid crystalline behaviors of 4 alone and 4/azobenzene mixtures, they were placed in LC cells with ITO electrodes. The cell gaps ranged from 2 to 20 μm, and constituent glass plates were coated with polyimide and rubbed to obtain parallel orientation.

Orientation of mesogens in FPLC depended on the cell gap. When 4 was placed in a cell with a 2-μm gap, parallel orientation of mesogens seemed to be achieved as evidenced by microscopic observation, while it exhibited textures arising from defects in a cell with a larger gap than 2 μm. Therefore, the ferroelectric as well as photochemical behaviors of 4/azobenzene mixtures were examined exclusively in the cells with the 2-μm cell gap.

Ferroelectric liquid-crystalline behavior

Ferroelectric LC phase behaviors were evaluated by applying triangular or square waves across the cells at various temperatures. Trials to determine the Ps values of 4 alone or 4/azobenzene mixtures by such conventional methods[5,6] as hysteresis loop method, square-wave method and triangular-wave method were all unsuccessful. This was mainly due to the difficulty of preparing uniformly oriented samples of the present FPLC.

Photochemical behaviors

Photochemical behaviors of azobenzene alone 4/azobenzene mixtures were explored as reported previously with some modification.[4(b),(c)] The 4/azobenzene mixtures in cells with 2-μm gaps were placed in a thermostated block and irradiated with a monochromatic light on applying square waves (Iwatsu SG-4101 function generator and Kikusui POW 35-1A amplifier), and the switching behaviors of the 4/azobenzene mixtures were evaluated by measuring the transmitted light intensity across the cells through a pair of crossed polarizers. Photoisomerization of azobenzene guests was confirmed by absorption spectroscopy.

RESULTS AND DISCUSSION

Ferroelectric LC behaviors

For the observation of the helical structure of spontaneous polarization (Ps) associated with the SmC* phase, cells with a 10-μm gap were used. Since the formation of the helical structure of Ps in the SmC* phase is strongly dependent on the aging of samples and the SmC* phase of the present FPLC appeared only in the cooling process (monotropic), special precautions were taken for the regulation of the cooling rate. Namely, the FPLC samples were heated at ~120°C which was higher than the SmA-isotropic phase transition temperature (T_{SI}) of the present sample by 20°C. After the sample melted, it was placed on a piece of glass preheated at the same temperature. A trace amount of glass spacers (10 μm) was applied and covered with another piece of glass. These cells containing samples were aged at 120°C for several minutes and then shear was applied to the sample by gently moving the cover glass. The cells were gradually cooled below T_{SI} by 5–10°C and kept at this temperature for 30 min. The characteristic fan-shaped texture of SmA was observed as shown in Figure 2 (a). The cells were further cooled at a cooling rate of 1.0–1.5°C/min, then fan-shaped textures with a stripe pattern were observed, indicating the existence of the helical structure (Figure 2 (b)). The helical pitch was calculated by the direct observation of the stripe pattern as 5.0 μm (average).

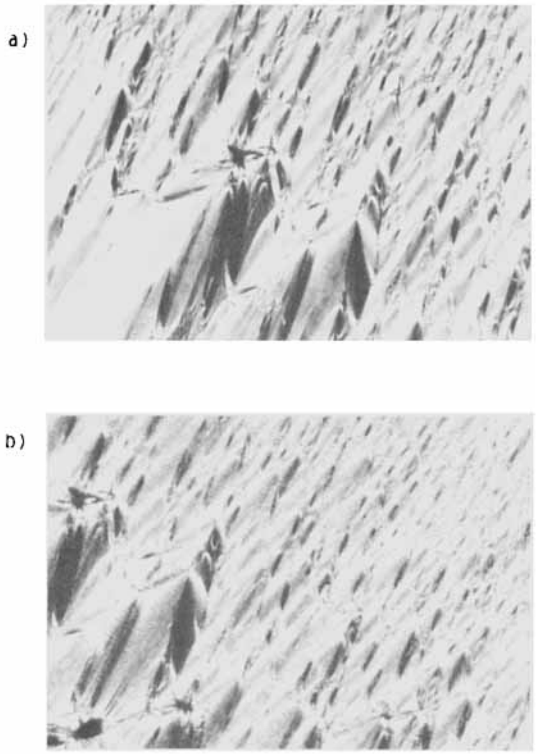

FIGURE 2 Fan-shaped textures observed for 4. (a) SmA phase at 80°C; (b) SmC* phase at 35°C. Note the existence of stripe pattern in (b). See Color Plate III.

As described in the experimental section, measurements of Ps values of 4 or 4/azobenzene mixtures were unsuccessful because of the difficulty in the preparation of uniformly oriented samples. We, therefore, explored the ferroelectric LC behaviors by an optical method in the presence of an applied electric field.

The switching behaviors of 4 alone on the application of the square wave (20 $V_{p\text{-}p}$, 1.0 Hz) are shown in Figure 3, in which a change in transmitted light intensity of a cell with the 2-μm gap containing 4 through a pair of crossed polarizers on the application of the square wave (lower half) is indicated as a function of time in the upper half of the figure. It is clearly observed that the transmitted light intensity changes 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). We define this change in the transmitted light intensity as Δ I as shown in Figure 3.

The Δ I values were determined at various temperatures and the results are plotted as a function of temperature in Figure 4. The Δ I values increased with temperature and gave a maximum at around 40°C, and then decreased again. At temperatures where large values of Δ I were obtained (25~50°C), the stripe patterns arising from the SmC* phase were observed. Although an exothermic peak due to a SmA-SmC* phase transition could not be observed in DSC on cooling in the

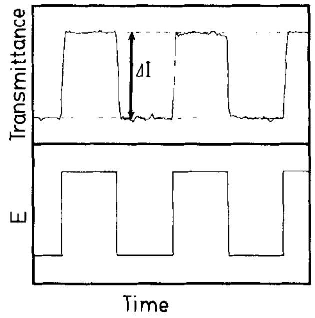

FIGURE 3 Switching behavior of 4. Change in transmitted light intensity of a cell with a 2-μm gap containing 4 through a pair of crossed polarizers on application of rectangular ac wave (10 V_{p-p}, 1.0 Hz, lower half, indicated by E) is shown as a function of time (upper half).

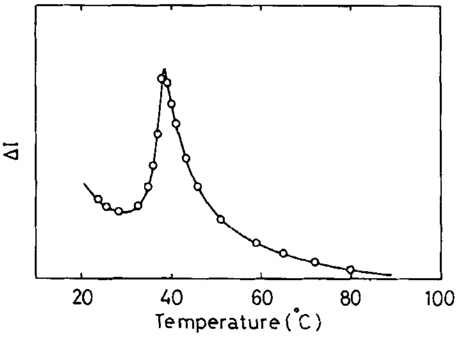

FIGURE 4 Transmitted light intensity (Δ I) of the FPLC cell at various temperatures.

present study,[7] the clear correspondence between the appearance of the stripe patterns by the microscopic observation and the large values of Δ I strongly suggests that the change in the transmitted light intensity on the application of the electric field arose from ferroelectric properties of 4. Namely, the flip-flop of Ps was brought about by the change in polarity of the applied electric field, which, of course, is accompanied by the change in direction of the mesogens. This change in n-director of the mesogens results in the change in optical properties of the cell, leading to the observed change in the transmitted light intensity.

The switching behaviors were examined at various applied fields and it was found that Δ I was proportional to the applied voltage. This proportionality seemed to indicate that the well-aligned surface-stabilized state (SS state)[5] of 4 was not established in the whole area of the cell, but domains existed in which the SS state was achieved, and the number of the domains increased with the strength of the applied electric field.

It is worth considering the physical meaning of Δ I here. In each temperature, the direction of the polarizers was adjusted first by rotating the sample table in the polarizing microscope so as to reduce the transmitted light intensity to the minimum for either polarity of the applied square wave with a lower frequency than 1.0 Hz. Then, the Δ I values were measured on applying the square wave

(1.0 Hz) on the sample. If the well-aligned SS state is established, Δ I reflects the tilt angle of the present FLC, and the larger the Δ I value, the larger is the tilt angle. This is true for the range of the tilt angle up to 22.5°, since the transmitted light intensity should become maximum when the angle between the direction of the mesogens and that of one of the polarizers is 45°, and up to this angle, the transmitted light intensity increases monotonously as the relevant angle increases. In the present FPLC, however, it seems likely that Δ I is not directly related to the tilt angle, but rather reflects the number of domains in which the SS state is established. Thus, the large values of Δ I seem to indicate the large number of domains in which the mesogens alter their direction according to the applied electric field.

It is generally recognized that FLCs show bistability in the SS state with two opposite orientations of the spontaneous polarization, and opposite voltages applied across the plates select between two orientations.[6] The n-director orientations corresponding to these two states of Ps can be toggled by reversion of the sign of the applied electric field, being retained as they were even after removal of the external electric field.[6] This memory effect was examined for the present FPLC. After the n-directors of 4 were aligned as much as possible by the electric field, a pair of polarizers were set so as to reduce the transmitted light intensity through the cell to a minimum. The external field was then removed and the optical properties were examined. It was found that the transmitted light intensity increased when the external electric field was removed. The same result was obtained on applying the electrical field with an opposite sign, indicating that the n-directors relaxed to a less-ordered state when the external field was removed.

Photochemically induced change in optical properties of azobenzene/4 mixtures

Mixtures of 4 and azobenzenes (3 mole% on the basis of the monomer repeat unit) were prepared by dissolving both components in cosolvent, chloroform, and by removing the solvent thoroughly. The azobenzene guests were homogeneously mixed with host 4 as evidenced by microscopic observation. Examination of the ferroelectric properties of the 4/azobenzene mixtures revealed that the mixtures showed very similar properties to those of 4 alone.

Photoisomerization behaviors of azobenzene guests in solution (ethanol) and in the FPLC host were also examined. It was found that all azobenzene derivatives showed a trans to cis photoisomerization on irradiation at 360 nm and restored their trans forms by irradiation at 450 nm both in solution and in 4. The 4/azobenzene mixtures were irradiated to bring about the trans-cis photoisomerization of the guests and then the switching behaviors of the mixtures were explored by the same method described above. The results for the 1AB4/4 mixture are shown in Figure 5 in which Δ I is plotted as a function of temperature for the trans form of 1AB4 (○) and the cis form of 1AB4 (●). It must be mentioned here that after photoirradiation at 360 nm a photostationary state was reached where 80% of the azobenzene was in the cis form. It is clearly observed that the Δ I values for the cis-1AB4/4 mixture were lower than those of the trans-1AB4/4 mixture in the SmC* range.

The photochemical phase transition behaviors of azobenzene/polymer liquid crys-

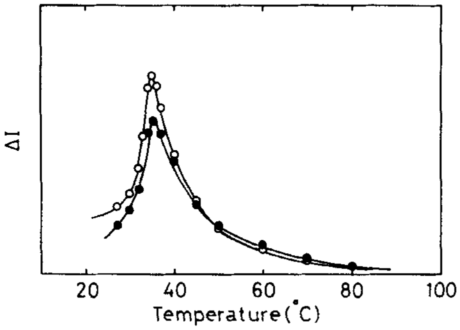

FIGURE 5 Effect of photoisomerization on Δ I of the 1AB4/4 mixture at various temperatures. (○), trans form; (●), cis form.

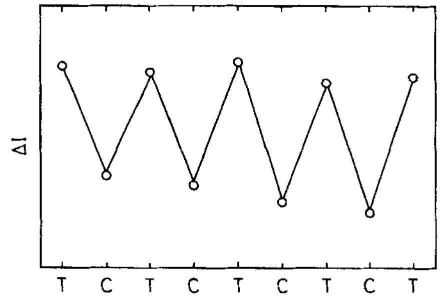

FIGURE 6 Change in Δ I on trans-cis photoisomerization of the guest 1AB4 in 4 at 35°C. Trans-cis isomerization was brought about by photoirradiation at 360 nm and cis-trans isomerization at 450 nm.

tal (PLC) mixtures have been thoroughly investigated under steady-state and pulse irradiations.[4] In principle, rod-like molecules tend to stabilize the LC phase while sphere-like molecules are inclined to destabilize the LC phase. Because of rod- and sphere-like shapes of the trans and the cis forms of azobenzenes, respectively, the trans-azobenzene/LC mixtures exhibit higher nematic to isotropic phase transition temperatures (T_{NI}) than those of the cis-azobenzene/LC mixtures, indicating that the trans-cis isomerization of azobenzene guests disorders the LC phases. This may be true for the present azobenzene/FPLC systems. Photoisomerization of the guest 1AB4 from the trans to the cis form perturbs the host mesogens in FPLC in the vicinity of the guest molecules, making the orientation of mesogens less ordered. This disorganization will reduce the difference in the transmitted light intensity through the cell between states with upward and downward directions of Ps with respect to the glass plane normal, resulting in small values of Δ I.

Reversibility of Δ I on photoisomerization of 1AB4 was examined at 35°C where Δ I gave the maximum value. As shown in Figure 6, the trans to cis photoisomerization reduced the Δ I value and the cis to trans reverse isomerization increased the Δ I to the initial value, and the trans-cis isomerization changed the Δ I values quite regularly.

Photochemical behaviors of other mixtures of the azobenzene guest and 4 were examined similarly and the results are shown in Figures 7–10. As shown in Figure

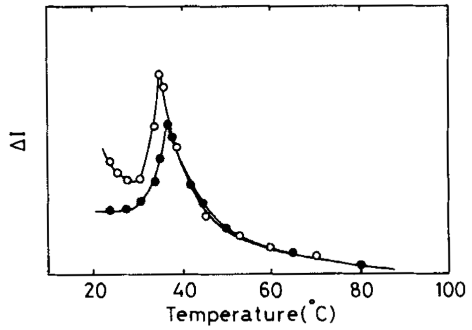

FIGURE 7 Effect of photoisomerization on Δ I of the 1AB1/4 mixture at various temperatures. (○), trans form; (●), cis form.

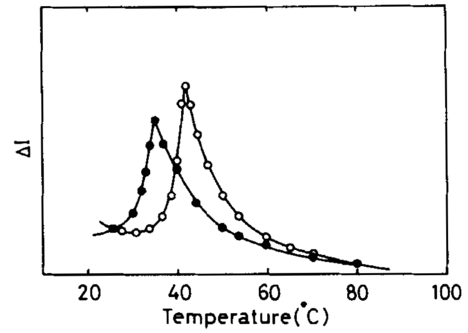

FIGURE 8 Effect of photoisomerization on Δ I of the 8AB8/4 mixture at various temperatures. (○), trans form; (●), cis form.

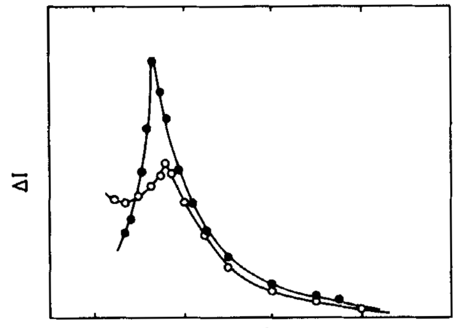

FIGURE 9 Effect of photoisomerization on Δ I of the $\mathrm{AB}_{\mathrm{chi}}$/4 mixture at various temperatures. (○), trans form; (●), cis form.

7, the mixture of 1AB1/4 exhibited quite a similar behavior to that of the 1AB4/4 mixture in that the Δ I values for the trans form of the guest were higher than those of the cis form, indicating that the trans-cis photoisomerization causes disorganization around the guest molecules in 1AB1/4 mixture. The 8AB8/4 mixture

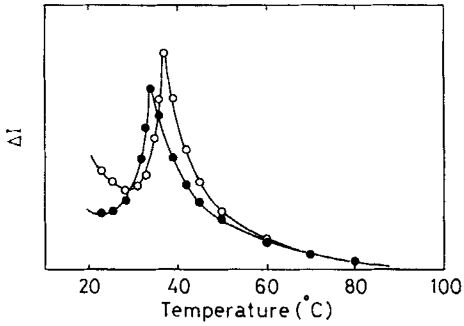

FIGURE 10 Effect of photoisomerization on Δ I of the $AB_{achi}/\underline{4}$ mixture at various temperatures. (○), trans form; (●), cis form.

showed again a similar photochemical behavior to that of $1AB4/\underline{4}$ except for a significant shift of the maximum of Δ I of the trans form toward a higher temperature (Figure 8). The trans form of such a guest molecule as 8AB8 is expected to stabilize the LC phase because of the long alkyl tails attached to both ends of the rigid part, leading to the shift of Δ I to a high temperature, while the cis form disorganizes the LC phase in a similar manner to that of other azobenzene guest molecules.

Quite unusual behaviors were observed in the $AB_{chi}/\underline{4}$ mixture on photoisomerization as shown in Figure 9. Unlike the other azobenzene/$\underline{4}$ mixtures so far described, the $AB_{chi}/\underline{4}$ mixture exhibited larger values of Δ I on the trans-cis photoisomerization. The larger values of Δ I of the cis-guest/$\underline{4}$ mixture than the trans-guest/host mixture were observed nearly at every temperature. It has been pointed out that carbonyl groups spatially oriented nearly perpendicular to the long axis of molecules contribute to a great extent to the ferroelectric properties of FLCs.[5] AB_{chi} possesses a carbonyl group of this kind near the chiral carbon. It was expected, therefore, that on the trans-cis photoisomerization the carbonyl group of the guest molecule would affect the ferroelectric properties of the $AB_{chi}/\underline{4}$ mixture so as to enhance the Δ I values of the cis-guest/host mixture. In order to examine this possibility, the switching behaviors of the $AB_{achi}/\underline{4}$ mixture on photoisomerization were explored under the same condition. AB_{achi} possesses the same structure as AB_{chi} except the chiral part: AB_{achi} has an achiral butyl group in place of (S)-(−)-2-methyl-1-butyl group in AB_{chi}. As shown in Figure 10, the $AB_{achi}/\underline{4}$ mixture showed the same behaviors as the other azobenzene(achiral)/$\underline{4}$ mixtures, indicating that the unusual behaviors observed for the $AB_{chi}/\underline{4}$ mixture are not ascribed only to the carbonyl group in AB_{chi}.

It is well known that trans forms of azobenzene derivatives have only small dipoles (~0.5 D) because of their extended, symmetrical structure, while the relevant cis forms possess large dipoles (~3.5 D).[9] This means that the trans-cis isomerization of azobenzene derivatives is always associated with a large change in dipole moment arising from the change in shape of molecules from rod-like to sphere-like structures. In the achiral azobenzene/$\underline{4}$ mixtures the change in shape of the guest molecules may predominantly affect the switching behaviors of the mixtures and no sign of the effect of the change in dipoles has been recognized. In the $AB_{chi}/\underline{4}$ mixture, on the other hand, because of the similarity of the chiral parts in the molecules between the guest molecule and the host mesogen, it seems possible that the guest molecules are closely and regularly packed in the host mesogens. In these regularly aligned arrangements, it may be possible that induced dipoles brought about by the trans-cis isomerization contribute to the overall dipoles so as to enhance the strength of dipoles, leading to a marked difference in the transmitted light intensity as observed in the $AB_{chi}/\underline{4}$ mixture.

CONCLUSION

In the present study, it has been demonstrated clearly that the switching behaviors of FPLC can be modulated by photoisomerization of photochromic guest molecules. In particular, the chiral azobenzene AB_{chi} has exhibited a characteristic feature in that the trans-cis isomerization has brought about an enhancement of Δ I, which is attributable to a cooperative alignment of mesogens in FPLC, owing presumably to induced dipoles by the photoisomerization. This study will provide a basis for photochemical control of spontaneous polarization (photochemical flip-flop of Ps associated with cooperative alignment of mesogens), which will be a novel working principle for optical memories.

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