Photochemical Control of Properties of Ferroelectric Liquid Crystals. 2. Effect of the Structure of Guest Photoresponsive Molecules on the Photochemical Switching of Polarization

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The photochemical switching of polarization of ferroelectric liquid crystals (FLCs) was investigated for various structures of guest photoresponsive molecules. The structure of the photoresponsive molecules affected significantly the efficiency of inducing the switching of polarization. It was found that azobenzenes with a structure similar to the host FLC induced the photochemical switching of polarization quite effectively.

Introduction

Ferroelectric liquid crystals (FLCs) doped with a few mole percent of photochromic compounds show photochemically induced switching of polarization.[1-3] Photoisomerization of the photochromic molecules in the LC phase disturbs the orientation of mesogens and causes the change in the properties of the LC phase.[4] In previous research, the magnitude of the spontaneous polarization (Ps) and the switching threshold of FLCs were controlled by the photochemical reaction of the dopants.[1-3,5]

Structures of both host FLCs and guest photoresponsive molecules are considered to affect the efficiencies of the photochemical switching of polarization. The effect of the structures of host FLCs was investigated in the previous paper.[3] The structure of the core mesogen and the length of the flexible tail were found to strongly affect the efficiency of the photochemical control of ferroelectric properties. The structure of the guest photoresponsive molecules is also supposed to affect the efficiency of inducing photochemical switching of polarization. A series of works have been reported on the effect of the structure of guest molecules on the photochemical nematic (N) to isotropic (I) phase transition.[6] The efficiency of inducing the photochemical phase transition was discussed in connection with the miscibility, photoreaction rate, and the order parameter of the guest molecules in the LC matrices. In this study, various photochromic azobenzene derivatives were used as guests in the FLC host and their ability to induce a change in properties of the guest/host mixtures was examined.

Experimental Section

The structures of FLC and azobenzene derivatives are shown in Figure 1. Phase transition temperatures and Ps values are listed in Table 1. FLCs with α-chloro acid derived from L-isoleucine are known to exhibit large spontaneous polarization.[7,8] The α-chloro acid, (2*S*,3*S*)-2-chloro-3-methylpentanoic acid, was synthesized by means of a nucleophilic substitution of the amino group of L-isoleucine by the chlorine atom via the diazonium salt.[9] The measurement of photochemical switching of polarization was performed as described in part 1 of this series.[3]

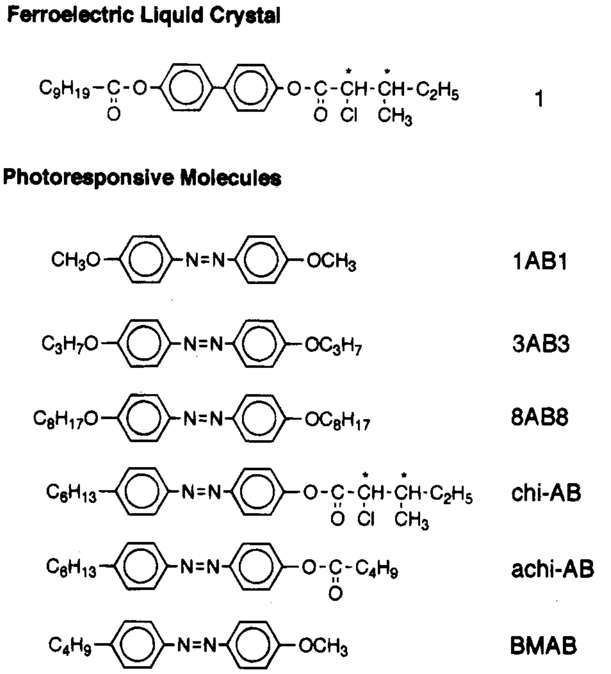

Figure 1. Structures of FLC and azobenzene derivatives used in this study.

TABLE 1: Phase Transition Temperatures[a] **and Absorption Coefficients**[b] **of Azobenzene Derivatives**

abbreviation	phase transition temperature (°C)	λ_{max} (nm)	ϵ_{max}
1AB1	C 163 I	369.5	28 000
3AB3	C 148 I	369.5	28 000
8AB8	C 99 N 113 I	369.5	28 000
chi-AB	C 35 I	333.0	27 000
achi-AB	C 41 I	332.5	27 000
BMAB	C 32 N 42 I	352.0	27 000

[a] C, crystal; N, nematic; I, isotropic. [b] Absorption spectra were measured in ethanol.

Results and Discussion

Photochemical Switching of Polarization of Guest/Host Mixtures. The response times of the photochemical switching of polarization of FLC **1** were measured with 1AB1, 3AB3, 8AB8, and chi-AB as guest molecules at a temperature 1 °C below the SmC*–SmA phase transition temperature. Two types of light sources were employed: a Spectron HL-21 Nd:

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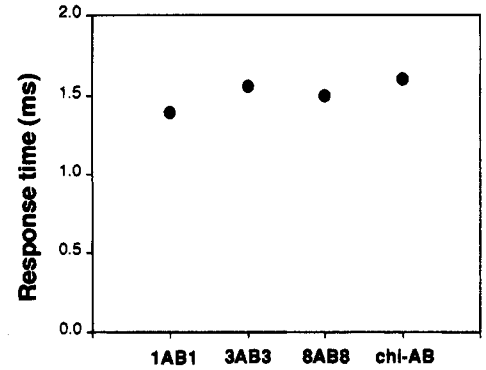

Figure 2. Response times of photochemical switching of polarization in azobenzene derivatives/FLC 1 mixtures induced by pulsed laser irradiation. Irradiation was performed at 355 nm with an intensity of 100 mJ/cm^2.

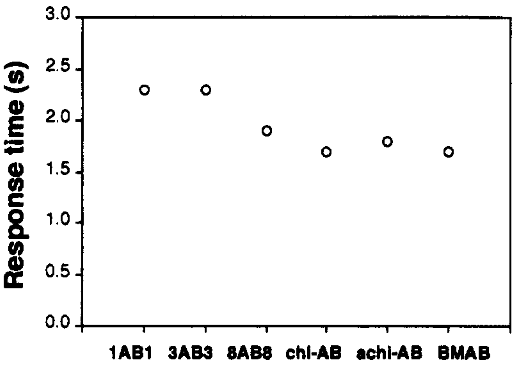

Figure 3. Response times of photochemical switching of polarization in azobenzene derivatives/FLC 1 mixtures induced by steady-state irradiation. Irradiation was performed at 366 nm with a light intensity of 36 mW/cm^2.

YAG laser (the third harmonic, 355 nm; pulse width, 10 ns fwhm) and a 500 W high-pressure Hg lamp. Transmittance of linearly polarized light from a He-Ne laser (633 nm) through the crossed polarizers between which the sample was placed, I_t, was measured as a function of time. When the azobenzene guest molecule was isomerized from the *trans* to the *cis* form by photoirradiation (355 nm), the magnitude of the coercive force of the guest/host mixture was reduced, and the switching of polarization was induced. The response time of the photochemical switching was defined as the time required to reduce I_t to 10% of the initial value. The response times of FLC **1** containing 3 mol % of azobenzene guest molecules in the pulsed laser experiment are shown in Figure 2, where the voltage $E =$ 0.9 Ec (here Ec is the optically determined switching threshold) was applied to the samples. No significant difference was observed in the response times of the photochemical switching of polarization among the azobenzene guest molecules examined in this study. However, when the high-pressure Hg lamp was employed as a light source so as to induce the photochemical switching of polarization under steady-state irradiation (366 nm), a clear difference was observed in the response time (Figure 3). Samples of FLC 1 doped with 8AB8, chi-AB (chiral-AB), achi-AB (achiral-AB), and BMAB showed faster responses than those with 1AB1 and 3AB3. The difference between the pulsed laser measurement and the steady-state irradiation measurement lies in the number of processes involved in the observed results. In the pulsed laser experiment, only the switching process of FLC **1** was observed in the millisecond time scale after a sufficient amount of *cis* form was produced within ~10 ns with a single pulse of the laser. On the other hand, both the accumulating process of the *cis* form and the switching process of the host FLC were included in the observed results under the steady-state irradiation. Thus, the steady-state experiment reflects the efficiency of each guest molecule to induce the photochemical switching of polarization. Namely, small values of the response time mean a high rate of photoisomerization of the azobenzene to produce a sufficient amount of the *cis* form to induce the switching of polarization in a short period or a high efficiency of the azobenzene to disorganize the phase structure on isomerization. At the present stage, it is not clear which is predominantly responsible for the observed results; however, the response time in the steady-state experiment is a measure of the overall efficiency of the azobenzene guest to induce the switching of polarization in any event. It can be observed in Figure 3 that chi-AB, achi-AB, and BMAB can induce the photochemical switching of polarization in a shorter time than 1AB1 and 3AB3. Absorption wavelength and the absorption coefficient of these azobenzenes are listed in Table 1. 1AB1, 3AB3, and 8AB8 absorb 355–366 nm light more effectively than chi-AB and BMAB. Thus, it can be safely concluded that the efficiency of inducing photochemical switching of polarization was higher in chi-AB, achi-AB, and BMAB.

The efficiency of inducing the photochemical phase transition was studied in detail on various azobenzene derivatives in the nematic LCs. It was revealed that the efficiency of perturbing the nematic phase was largely affected by the affinity of photoresponsive molecules with LC matrices. The molecular size of chi-AB, achi-AB, 8AB8, and BMAB is similar to that of the FLC **1** molecule. They are expected to possess high affinity with the host FLC **1**.

Solubility of Azobenzene Guest Molecule in Matrix FLC. *1AB1, 3AB3, and 8AB8.* The phase diagram of guest molecule/FLC **1** mixtures was investigated. The phase transition temperatures of FLC **1** containing various amounts of 1AB1, 3AB3, and 8AB8 are shown as a function of the concentration of the azobenzene guests in Figures 4, 5, and 6, respectively. Very similar diagrams were obtained for 1AB1/FLC **1** and 3AB3/FLC **1** mixtures. The phase transition temperatures of the LC phase decreased as the concentration of the guest molecules increased, while the melting point was not affected by the addition of the azobenzenes up to 20 mol %. These results indicate that 1AB1 and 3AB3 could not form mixed crystals with FLC **1**. Azobenzenes and FLC **1** molecules were separated in the crystalline phase. Furthermore, the decrease in the phase transition temperature was rather small, which indicates that 1AB1 and 3AB3 were at least partly miscible with FLC **1** in the LC phase. On the other hand, when 8AB8 was doped into FLC **1**, the temperature range of the SmA phase was much affected. As the concentration of 8AB8 increased, the temperature range of the SmA phase was narrowed and the SmA phase finally vanished at concentrations higher than 10 mol %. It seems that the miscibility of 8AB8 with FLC **1** was relatively high.

This different behavior of the 8AB8/FLC **1** mixture from those of the 1AB1/FLC **1** and the 3AB3/FLC **1** mixtures may be attributed to the difference in the molecular size of those guest molecules. The length of the 8AB8 molecule was very similar to that of FLC **1**, while 1AB1 and 3AB3 were rather small. If FLC and the azobenzene guest molecules were molecularly miscible and azobenzene molecules were intercalated into the SmC* layer, the azobenzene with a molecular size similar to that of the FLC molecule may produce a larger perturbation to the phase than those with a smaller size. This is because the interlayer interaction of azobenzene and the FLC molecule is larger for the azobenzenes with a molecular size similar to that of the host.

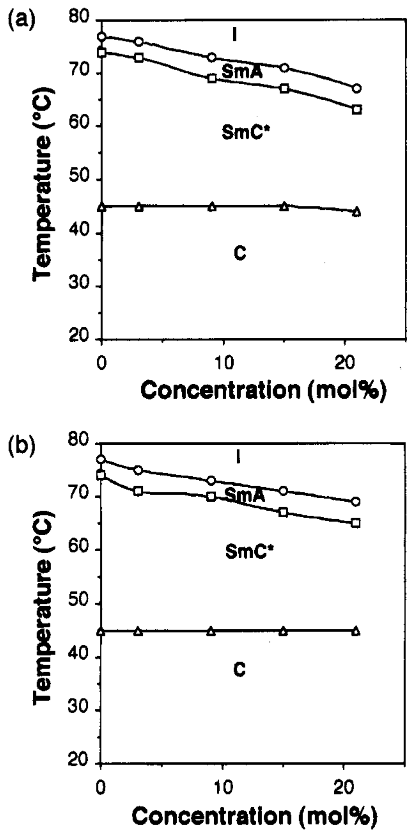

Figure 4. Phase diagram of the 1AB1/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

After the *cis* forms of azobenzenes were produced by irradiation at 366 nm, the phase diagrams were changed to (b) in Figures 4, 5, and 6. In the case of 1AB1 and 3AB3, the phase diagrams were almost the same as those before irradiation (a) and the phase transition temperatures decreased by only 1 °C. Additionally, no change was observed in the melting points. However, in the case of 8AB8, the temperature range of the SmA phase was narrowed after irradiation. These results can be interpreted in terms of the larger perturbation to the phase brought about by the photoisomerization of the molecularly dispersed azobenzene.

Chi-AB, Achi-AB, and BMAB. The phase diagrams of the chi-AB/FLC **1** mixture before and after irradiation are shown in Figure 7. Different from the behavior observed for 1AB1, 3AB3, and 8AB8, both the phase transition temperatures of the LC phase and the melting point were affected by the introduction of the chi-AB molecule. The melting point of this mixture decreased by ~15 °C at a concentration of 20 mol %. This result indicates that chi-AB and FLC **1** formed the mixed crystal. The SmA phase existed at lower concentrations than 15 mol % and vanished at higher concentrations. Thus, chi-AB was soluble in FLC **1** both in the LC phase and in the crystalline phase. The molecular size and the molecular structure of chi-AB are similar to those of the host FLC **1**. Those structural factors (similarity) are supposed to be the origin of the high miscibility of chi-AB to FLC **1**.

The melting point of guest molecules is also considered to affect the miscibility with FLC **1**. The melting points of 1AB1, 3AB3, and 8AB8 were higher than the liquid crystal–isotropic phase transition temperature of FLC **1**, while chi-AB was liquid in the temperature range discussed. To investigate the effect of the melting point of the guest molecules, achi-AB and BMAB, which possess low melting points, were also examined.

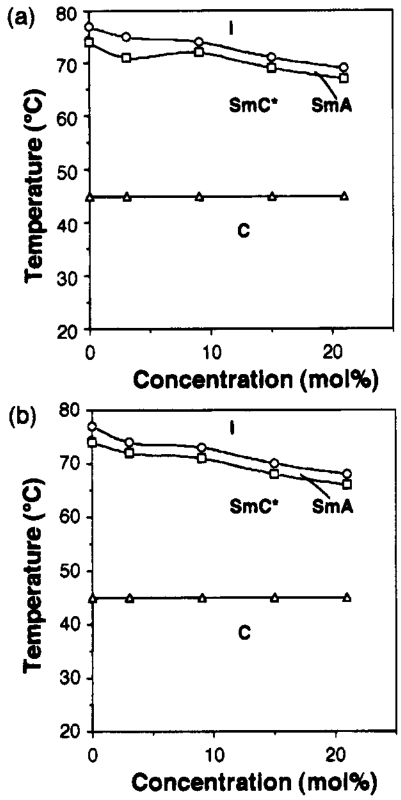

Figure 5. Phase diagram of the 3AB3/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

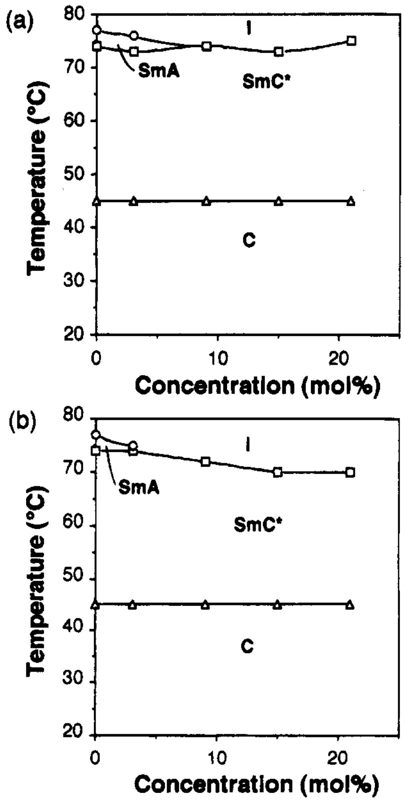

Figure 6. Phase diagram of the 8AB8/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

The phase diagrams of achi-AB/FLC **1** and BMAB/FLC **1** are shown in Figures 8 and 9. The dependence of the liquid

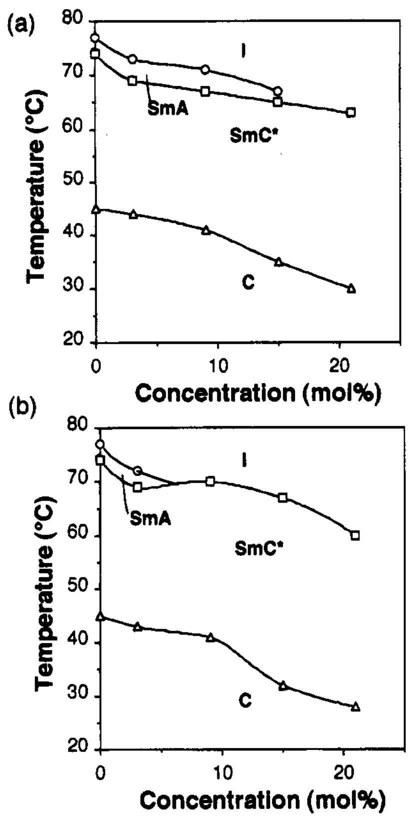

Figure 7. Phase diagram of the chi-AB/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

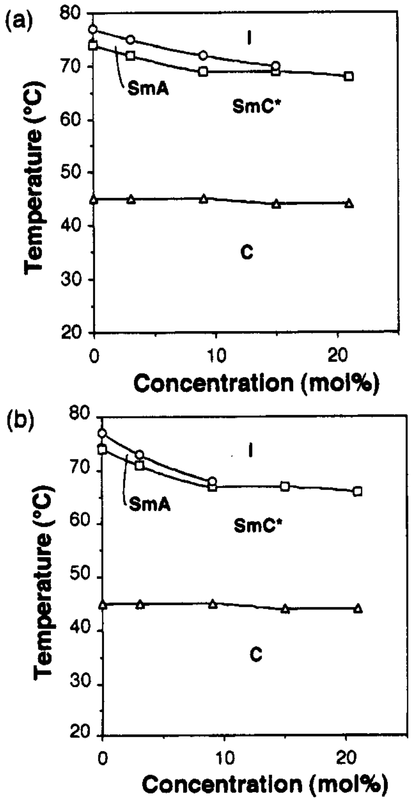

Figure 8. Phase diagram of the achi-AB/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

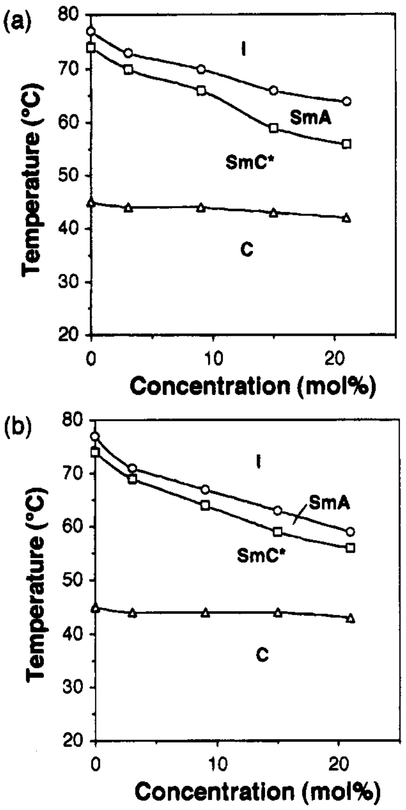

Figure 9. Phase diagram of the BMAB/FLC **1** mixture: (a) before irradiation; (b) after irradiation at 366 nm. The concentration of azobenzene was 3 mol %, and the degree of isomerization after irradiation was estimated as ~80%.

crystalline phase transition temperatures of the achi-AB/FLC **1** mixture on the concentration of achi-AB was almost the same as that of the chi-AB/FLC **1** mixture. However, the melting point of the mixture was insensitive to the concentration of the guest molecule. On the other hand, in the BMAB/FLC **1** mixture, the SmA phase was rather stabilized at high concentrations of BMAB, and the temperature range of the SmC* phase was narrowed. The melting point of the BMAB/FLC **1** mixture was also insensitive to the concentration of BMAB. The photoirradiation at 366 nm caused the destabilization of the SmA phase in both achi-AB/FLC **1** and BMAB/FLC **1**; however, the melting point of the mixtures was not affected by the photoirradiation.

Thus, the solubility of azobenzene derivatives in FLC may be mainly dominated by a structural factor: similarity in molecular size and chemical structure seems to improve the solubility in the FLC. It is worth mentioning here that the aggregation of the guest azobenzene derivatives took place under irradiation. Even though the structure of the guest molecule is similar to that of the host FLC, the aggregation of the *cis* form of azobenzene was observed particularly when the ac electric field was applied to the mixture. The flip-flop movement of the host FLC molecules may be responsible for the phase separation of the nonmesogenic molecules from the LC phase.

Order Parameters of Azobenzene Guest Molecules in Host FLC. The solubility of azobenzene guest in the FLC at the molecular level will reflect the ordering of azobenzene guest molecules in the LC phase of the guest/host mixture. The *trans* forms of azobenzene derivatives used in this study are all rodlike in shape, so that if they are molecularly dissolved in the LC phase, the long axes of the molecules may be aligned parallel to the direction of the long axes of the FLC molecules. Since the transition moment of the $\pi-\pi^*$ absorption of the *trans* form

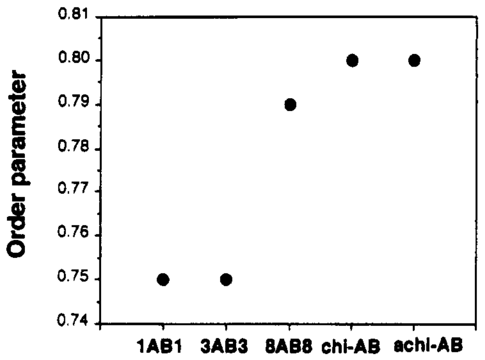

Figure 10. Order parameters of azobenzene derivatives doped in FLC 1. The concentration of azobenzene was 3 mol %. Measurements were performed at 55 °C.

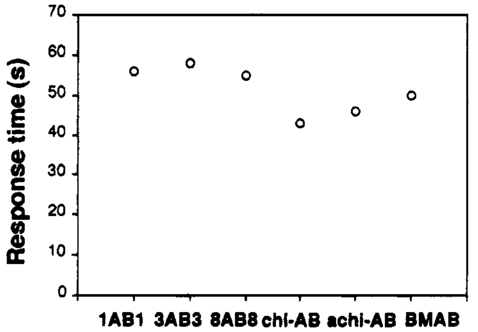

Figure 11. Response times of the photochemical SmC*−SmA phase transition in the azobenzene derivative/FLC **1** mixtures induced by steady-state irradiation at 366 nm. $T = \mathrm{Tc} - 1$ °C.

of azobenzene derivatives is oriented nearly parallel to the molecular long axes, the order parameters of the guest azobenzenes can be determined by the measurement of the UV dichroism.

For a uniaxially symmetrical system, the dichroic ratio, R, can be given by eq 1.[10]

$$R = \frac{A_{\mathrm{para}}}{A_{\mathrm{per}}} = \frac{4\cos^2\alpha\,\langle\cos^2\theta\rangle + 2\sin^2\alpha\,\langle\sin^2\theta\rangle}{2\cos^2\alpha\,\langle\sin^2\theta\rangle + \sin^2\alpha\langle 1 + \cos^2\theta\rangle} \qquad (1)$$

where A_{para} and A_{per} are the absorbances measured by the polarized light with parallel and perpendicular orientation to the optic axis of the molecule, respectively. θ is the angle between the direction of the long axis of the molecule and the optic axis of the uniformly oriented liquid crystal, and α is the angle between the long axis of the molecule and the direction of the transition moment of the chromophore. In the case where the transition moment is oriented parallel to the long axis of the molecule, the order parameter, S, can be written in the form of eq 2.

$$S = (R - 1)/(R + 2) \qquad (2)$$

Figure 10 shows the order parameters of azobenzene derivatives in the host FLC **1**. The order parameters determined for 8AB8, chi-AB, and achi-AB were higher than those of 1AB1 and 3AB3. The higher value of S observed for chi-AB seems to support the assumption that chi-AB is dispersed in the host FLC more molecularly than the other guest molecules.

Effect of Structure of Guest Azobenzene Derivatives on the SmC*−SmA Photochemical Phase Transition. As described above, when the azobenzene/FLC **1** mixture is irradiated with UV light, the phase transition temperature is lowered. If the mixture before irradiation is kept at temperatures near but below the SmC*−SmA phase transition temperature and irradiated, the isothermal SmC*−SmA phase transition takes place. The magnitude of perturbation to the LC phase brought about the *trans−cis* isomerization of guest azobenzene will be reflected in the efficiency of the photochemical phase transition. Thus, the effect of molecular structure on the efficiency of inducing the SmC*−SmA photochemical phase transition was also investigated.

The SmC*−SmA phase transition behavior can be evaluated by the measurements of Ps.[5] The response time of the photochemical SmC*−SmA phase transition, which was defined as the time required to reduce the value of Ps to 10% of the initial value under steady-state irradiation at 366 nm, is shown in Figure 11. The response time was shorter in the chi-AB/FLC mixture than in the other azobenzene/FLC mixtures. Chi-AB induced the photochemical phase transition at a lower concentration of the *cis* form. Thus, the azobenzene with a structure similar to that of the host FLC is suitable as a guest molecule in the photoresponsive FLC materials.

Conclusion

The difference in the efficiency of inducing a photochemical change in th properties of host FLC **1** among various azobenzene derivatives was investigated. The magnitude of the changes in properties of FLC **1** induced by the isomerization of the guest azobenzene derivatives was related to the solubility of azobenzene derivatives in the FLC **1** matrix. The azobenzene with a structure similar to that of the host FLC showed high solubility and large change in the properties of the host LC.

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