

Photochemical Switching Behavior of Liquid-Crystalline Networks: Effect of Molecular Structure of Azobenzene Molecules

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Two types of photoresponsive liquid-crystalline (LC) networks with macroscopic uniaxial molecular orientation were prepared by polymerizing mixtures of a LC monoacrylate, a LC diacrylate and an azobenzene compound in a homogeneous glass cell at a nematic phase: one was the LC networks doped with azobenzene molecules and the other was those copolymerized with azobenzene monomers. The optical switching behavior of the LC networks was examined with respect to the molecular structure of the azobenzene molecules by using a Xe lamp and a single pulse light from a Nd:YAG laser as light sources. The LC networks doped with 4-butyl-4'-dodecyloxylazobenzene showed the fastest response time and decay time in the range of about 1.0 and 15 μ s among the LC networks synthesized. The lateral intermolecular interaction as well as interaction through bonds affects significantly the optical switching behavior.

Introduction

Recently, photoresponsive liquid-crystalline (LC) polymers have become of interest in recent years because of their self-organizing properties, responsiveness to external stimuli, and large anisotropy in physical properties.^{1–11} One of the preparing methods for such photoresponsive LC polymer systems is polymerization of LC monomers^{10–17} containing photoresponsive molecules. In particular, LC polymer networks with macroscopic uniaxial molecular orientation can be easily synthesized by the polymerization of LC monomers in a unidirectional orientation.

It has been reported that the properties of LC polymer networks are affected by a cross-linking density.^{12–15,18–23} We also reported the preparation and properties of LC networks by polymerization of mono- and difunctional LC monomers with respect to the cross-linking effect.^{16,17} Lightly cross-linked LC networks with an appropriate amount of difunctional LC monomers showed stable macroscopic molecular orientation as well as a reversible phase transition, indicating liquid crystallinity and responsive ability to external stimuli. Actually, the lightly cross-linked LC networks containing azobenzene molecules were found to show rapid optical switching with respect to the change in the birefringence by means of photoisomerization of azobenzene molecules.^{10,11} The change in the birefringence is closely related to the photochemical change in the molecular shape. It is well-known that the azobenzene compounds can isomerize from the *trans* to *cis* form by ultraviolet irradiation and return by visible light irradiation or by thermal means. The *trans*-azobenzene dissolves in the host LCs without a disorganizing effect on the molecular orientation of the host LC molecules. On the other hand, the *cis*-azobenzene disorganizes the molecular orientation of the host LC molecules because of its bent molecular shape. Therefore, it is expected that the photochemical change in the birefringence is dependent on the molecular structure of the azobenzene compounds.

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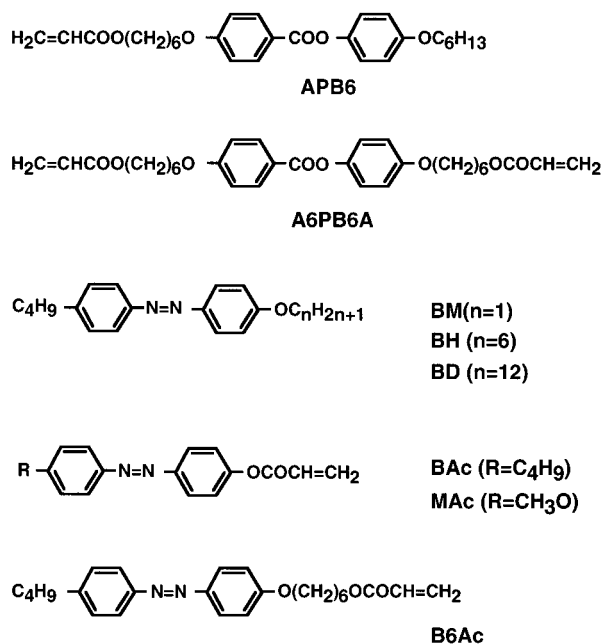


Figure 1. LC mono- and diacrylates and azobenzene compounds.

In this study, we describe the preparation of macroscopic uniaxial LC networks containing various azobenzene molecules, and the effect of the molecular structure of the azobenzene compounds on the optical switching behavior of the LC networks.

Experimental Section

Materials. LC mono- and diacrylates, **APB6** and **A6PB6A**, were synthesized according to the method reported earlier.^{23,24} Azobenzene compounds shown in Figure 1 were synthesized.

BM, BH, and BD. 4-Butyl azobenzenes having three different alkyl groups at the 4'-position, **BM**, **BH**, and **BD**, were synthesized by the diazo-coupling reaction between 4-butylaniline and phenol in the presence of sodium nitrite and hydrochloric acid and following alkylation with three alkyl halides, methyl iodide, hexyl bromide, and dodecyl bromide. The purification was carried out by recrystallization from ethanol. Yield: 79% for **BM**, 68% for **BH**, and 67% for **BD**. The compounds were identified by NMR, IR, and elemental analysis.

BAc, B6Ac. 4-Butyl azobenzenes having an acryloyl group attached to the 4'-position directly and via a hexamethylene spacer, **BAc** and **B6Ac**, were synthesized by the diazo-coupling reaction between 4-butylaniline and phenol in the presence of sodium nitrite and hydrochloric acid and following reaction with acryloyl chloride or following reaction with 6-chloro-1-hexanol and acryloyl chloride. **BAc** and **B6Ac** were purified by column chromatography (silica gel; eluent: chloroform) and recrystallization from ethanol. Yield: 46% for **BAc** and 24% for **B6Ac**. Identification was carried out by NMR, IR, and elemental analysis.

MAc. 4-Methoxy-4'-acryloyloxyazobenzene, **MAc**, was synthesized by the diazo-coupling reaction between 4-methoxyaniline and phenol in the presence of sodium nitrite and hydrochloric acid and following reaction with acryloyl chloride in the presence of triethylamine. Purification was carried out by column chromatography (silica gel; eluent: chloroform) and recrystallization from ethanol/acetone mixture. Yield: 71%. Identification was carried out by NMR, IR, and elemental analysis.

Thermotropic Properties. Thermotropic phase transition behavior of the compounds was examined by means of differential scanning calorimetry (DSC, Seiko I&G SSC-5020) and polarizing optical microscopy (POM, Olympus BHSP polarizing optical microscope; Mettler FP80 and FP82 hot stage and controller). Scanning rate of DSC measurements was 5 °C/min, and the peak temperatures obtained were taken as the phase transition temperatures.

Characterization. Mixtures of **APB6**, **A6PB6A**, and azobenzenes containing 3 mol % of benzoyl peroxide as a radical initiator were injected into the homogeneous glass cell with a 5- μ m cell gap at the isotropic phase. The polymerization of the mixtures was carried out by heating for 2 h at the temperatures at which the mixtures existed in the nematic phase.

To examine the phase transition temperature of the resulting networks, the transmittance of the samples was measured. Each network in the homogeneous glass cell was thermostated and placed between two crossed polarizers. The polarizing direction of the two crossed polarizers was set at an angle of 45° with respect to the orientation axis of the cell. Then the transmitted light intensity of a probe light from a laser diode (Suruga Seiki Co.; 670 nm; 5mW) was measured with a laser power meter (Neo Ark, PM-221). The reference for the transmittance was defined as the transmitted light intensity through the sample between two parallel polarizers. In addition, the transmittance of the samples without polarizer was also measured to examine the stability of a uniaxial molecular orientation of the networks. In this case, the reference for the transmittance was defined as the transmitted light intensity without the sample.

Optical Switching Behavior. The network in the homogeneous glass cell was thermostated and placed between two crossed polarizers. The polarizing direction of the two crossed polarizers was set at an angle of 45° with respect to the orientation axis of the cell in the same way for determining the phase transition temperature. The photochemical switching behavior was examined by using a 500-W high-pressure Hg lamp (Ushio SX-UI 500) equipped with a cut filter (Sigma UTVAF-35U) for ultraviolet irradiation (366 nm) to cause trans-cis photoisomerization of azobenzene compounds. The laser diode was used as a probe light source. The change in the transmitted light intensity of the probe light was monitored with the laser power meter. In addition, photochemical change in the birefringence (Δn) was estimated by measuring the transmitted light intensities of the samples between two crossed polarizers (I_{\perp}) and between two parallel polarizers (I_{\parallel}), (I_{\perp}/I_{\parallel}) = $\tan^2(\pi \cdot \Delta n \cdot d/\lambda)$ before and under light irradiation, where d and λ are the cell gap and the wavelength of the probe light, respectively.²⁵

Time-resolved measurements of photochemical change in the birefringence were carried out by means of a pulse irradiation. The networks were thermostated and set between two crossed polarizers. Then, the networks were irradiated with a single pulse of a Nd:YAG laser (Continuum NY 60; the third harmonic, 355 nm; 10 mJ/cm²; 15 ns, full width at half-maximum (fwhm)). The transmitted light intensity of the probe light from the laser diode through two crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded on a Phillips PM3350A storage scope.

Results and Discussion

Synthesis and Characterization of LC Networks. Thermotropic properties of LC monomers and azobenzenes are given in Table 1. LC diacrylate was used as a cross-linking agent to hold macroscopic uniaxial molecular orientation. We have reported that the photochemical switching behavior depended strongly on the cross-

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Table 1. Properties of LC Monomers and Azobenzene Compounds

compound	λ_{\max} (nm) in MeOH	$\epsilon_{\max} \times 10^{-4}$ in MeOH	phase transition ^a temperature (°C)
APB6			K 32 S 53 N 61 I
A6PB6A			K 33 S 47 N 50 I
BM	345	3.1	K 33 N 48 I
BH	350	3.0	K 45 N 73 I
BD	355	2.1	K 65 S 76 I
BAC	336	4.0	K 47 N 52 I
MAc	352	3.1	K 46 N 117 I
B6Ac	355	3.1	K 64 I

^a K, crystalline phase; S, smectic phase; N, nematic phase; I, isotropic phase. Transition temperatures were measured upon cooling.

linking density, and the network cross-linked with 5 mol % of **A6PB6A** showed rapid optical switching.¹¹ Therefore, to explore the structural effect of the azobenzenes on the switching behavior, the networks with uniaxial molecular orientation were prepared by polymerization of the mixtures of **APB6** (90 mol %), **A6PB6A** (5 mol %), and azobenzenes (5 mol %) in the 5- μm homogeneous glass cell. All mixtures before polymerization showed a nematic phase, and the polymerization was carried out by heating for 2 h at the nematic phase (50–60 °C). After polymerization, the samples became insoluble in any solvents because of cross-linking with diacrylate, **A6PB6A**. Therefore, to determine the conversion of monomers, residual monomers were extracted with tetrahydrofuran and subjected to gel permeation chromatography. The conversion was found to be higher than 75%. In addition, a peak corresponding to vinyl stretching around 1630 cm^{-1} disappeared after the polymerization for 2 h at the nematic phase.

To explore the stability of the uniaxial molecular orientation and phase transition behavior of the samples polymerized, transmittance of the samples without polarizer and between two crossed polarizers were measured as a function of temperature. Figure 2a shows the temperature dependence of the transmittance of the poly(**APB6/A6PB6A/BH**) (90:5:5) network between two crossed polarizers. The transmittance was found to decrease rapidly above 120 °C and became almost zero due to a phase transition to an isotropic phase. To discuss temperature effect on the optical switching behavior, the isotropization temperature, T_i , was defined as the temperature to reduce the transmittance between two crossed polarizers to 10% of the maximum value. Then, the reduction temperature (T_{red}) was defined as T/T_i , where T is the experimental temperature. The isotropization temperatures of the samples are given in Table 2. The isotropization temperatures of the networks containing **BM**, or **BH**, **BD**, were lower than those of the networks prepared by the polymerization with azobenzene monomers. It is likely that the doping of azobenzene molecules in the networks disorganizes the anisotropic molecular orientation more or less. Figure 2b shows the transmittance of the poly(**APB6/A6PB6A/BH**) (90:5:5) network without polarizer. The transmittance kept over 90% in the temperature range between 30 and 120 °C by heating and cooling. The results shown in Figures 2a and 2b indicate that the poly(**APB6/A6PB6A/BH**) network holds the macroscopic uniaxial molecular orientation and shows liquid-crystalline properties.^{10,11} All networks prepared were

found to exhibit almost similar results to the poly(**APB6/A6PB6A/BH**) network.

Photochemical Switching Behavior. Figure 3 shows photochemical change in the transmittance of the poly(**APB6/A6PB6A/BH**) (90:5:5) networks by turn on and off UV irradiation at T_{red} of 0.98. The intensity was decreased by the irradiation and restored in the dark. The reversible change in the transmittance can be interpreted in terms of perturbation effect due to *trans*–*cis* photoisomerization of **BH** molecules on the macroscopic uniaxial molecular orientation and rapid *cis*–*trans* thermal back reaction. The perturbation effect is closely related to the difference in the molecular shape between *trans*- and *cis*-azobenzene molecules. Namely, the *cis*-azobenzene with a bent shape formed by UV irradiation disorganizes the molecular orientation of LC molecules, resulting in the decrease in the birefringence. On the other hand, in the dark, the rapid *cis*–*trans* thermal back reaction occurs, and the transmittance restores the initial value due to recovery of the macroscopic uniaxial molecular orientation.

Figures 4 and 5 show changes in Δn of the LC networks containing azobenzene molecules by UV irradiation. The results shown in Figures 2a and 2b revealed that the LC networks have liquid-crystalline properties as well as stable macroscopic uniaxial molecular orientation. The birefringence (Δn) is one parameter that measures the uniaxial molecular orientation. In a comparison of Δn of three LC networks prepared by doping **BM**, **BH**, and **BD**, Δn in the dark tends to decrease with the length of alkoxy groups at the 4'-position of 4-butyl azobenzene (Figure 4). The longer the molecular shape of the azobenzenes, the larger the influence on the macroscopic molecular orientation in the dark. The values of Δn of the LC networks prepared by copolymerization with **MAc**, **BAC**, and **B6Ac** were higher than those of the LC networks doped with azobenzene molecules. It is clear that the UV irradiation causes a decrease in the value of Δn for both types of the LC networks, doped type and copolymerized type. In addition, the photochemical decrease in Δn depends on the irradiation temperature.

To clarify the temperature dependence of the optical switching, change in Δn before and after UV irradiation ($\Delta(\Delta n)$) is plotted as irradiation temperature in Figure 6. The value of $\Delta(\Delta n)$ increased with irradiation temperature, but it decreased rapidly near the isotropization temperature. The maximum $\Delta(\Delta n)$ values are roughly in the range of 0.02–0.04 at T_{red} of 0.98 for the doped-type LC networks. On the other hand, the copolymerized-type LC networks gave the maximum $\Delta(\Delta n)$ in a temperature range from 0.94 to 0.96 of T_{red} . In addition, at lower temperatures, the copolymerized-type LC networks show larger $\Delta(\Delta n)$ than the doped-type LC networks. Although the different temperature dependencies of $\Delta(\Delta n)$ between the doped-type and copolymerized-type LC networks is not clear at the present time, one of the factors may be an interaction through the bonds between azobenzene molecules and mesogenic molecules formed by copolymerization.

The value of $\Delta(\Delta n)$ is enough to detect, although the photochemical phase transition of the LC networks cannot be induced completely. The switching rate is an important property of optical materials. Therefore, to

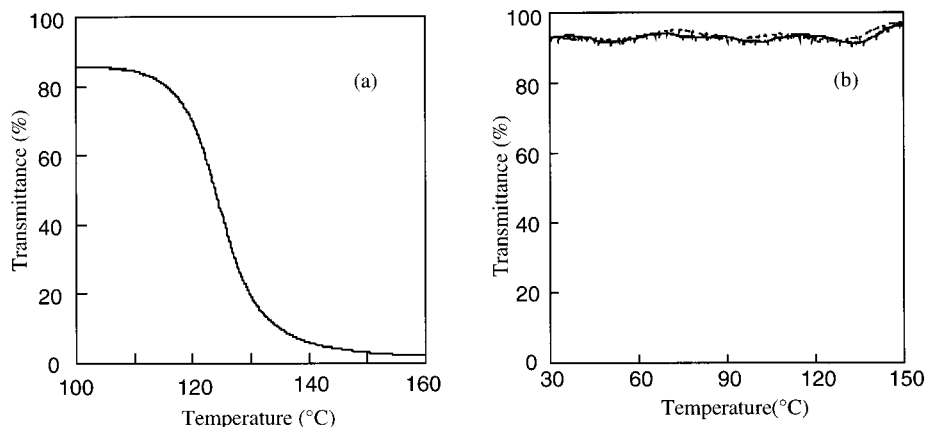


Figure 2. Change in transmittance of the poly(APB6/A6PB6A/BHAB) (90:5:5 mol %) network between two crossed polarizers (a) and without polarizer as a function of temperature.

Table 2. Phase Transition Temperatures of the (APB6/A6PB6A/Az) (90:5:5 mol %) Networks

Az	phase transition temperature (°C) ^a	Az	phase transition temperature (°C) ^a
BM	LC 136 I	BAc	LC 142 I
BH	LC 135 I	MAc	LC 139 I
BD	LC 136 I	B6Ac	LC 143 I

^a Phase transition temperature was defined as the temperature to reduce the transmittance intensity through crossed polarizers to 10% of the maximum value.

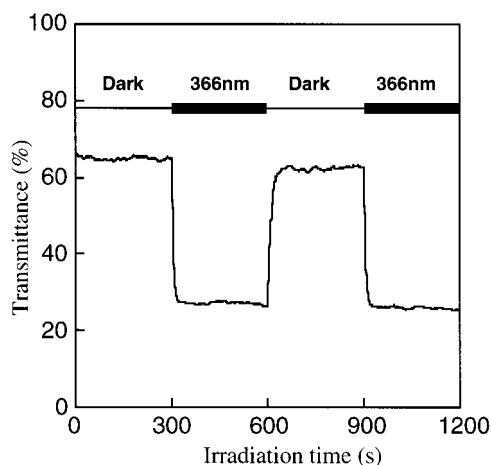


Figure 3. Change in the transmittance of the poly(APB6/A6PB6A/BH) (90:5:5 mol %) network between two crossed polarizers by UV (366 nm, 10 mW) irradiation at T_{red} of 0.98 (126 °C).

explore the structural effect of azobenzene molecules on the switching rate, time-resolved measurements of the photochemical change in the transmittance between two crossed polarizers was carried out. Figure 7 shows results of the time-resolved measurements of three doped-type LC networks at 126 °C (T_{red} of 0.98). The light intensity (I_{\perp}) through a LC sample between two crossed polarizers is expressed as $I_{\perp} = \sin^2(\pi \cdot \Delta n \cdot d/\lambda)$. Therefore, it can be assumed that the photochemical change in Δn is proportional to the decrease in I_{\perp} by pulse irradiation. The decreases in I_{\perp} were 31% at 15 μ s, 23% at 1.5 μ s, and 18% at 1.0 μ s for the LC networks doped with **BM**, **BH**, and **BD**, respectively. The time to recover the initial transmittance (decay time) are about 5 ms for **BM**, 300 μ s for **BH**, and 15 μ s for **BD**, respectively. It is likely that the time required to reach

minimum I_{\perp} (response time) and decay time become shorter with increasing length of alkoxy groups. However, the change in Δn decreased with increasing length of alkoxy groups; that is, the longer alkoxy groups attached to the same azobenzene skeleton, the lower the disordering effect due to trans–cis photoisomerization. A smectic phase is often observed for the liquid crystals having long side substituents such as alkyl and alkoxy groups. Actually, **BM** and **BH** show the nematic phase, while **BD** shows the smectic phase as liquid-crystalline phases. This means that the lateral intermolecular interaction of **BD** is stronger than those of **BM** and **BH**. Therefore, the trans–cis photoisomerization of **BD** molecules are considered to be influenced strongly by the molecular orientation compared with **BM** and **BH** molecules. Both the smaller change in Δn and the rapid optical switching are closely related to the restriction of trans–cis photoisomerization of **BD** due to strong lateral interaction. Thus, it can be assumed that the amount of *cis*-**BD** produced is smaller than the others, whereas the disorganization effect of *cis*-**BD** molecules is larger than the others due to the longer alkoxy tail. However, the structural effect on the photoisomerization could not be explored experimentally because the trans–cis photoisomerization is extremely rapid and the change in the absorption spectra by a pulse irradiation is very small.

On the other hand, the cis–trans thermal isomerization of azobenzene molecules is also expected to affect the switching behavior. The cis–trans thermal isomerization behavior of **BM**, **BH**, and **BD** in the LC networks was examined and compared with that in DMSO by using a 500-W high-pressure Hg lamp as a light source. There was little change in the cis–trans rate constants of the three azobenzenes in DMSO, 5.7×10^{-6} for **BM**, 6.7×10^{-6} for **BH**, and 6.5×10^{-6} for **BD** at 30 °C. The rate constants in the LC networks were 3.7×10^{-5} for **BM**, 6.3×10^{-4} for **BH**, and 9.3×10^{-4} for **BD** at 30 °C. Namely, the cis–trans thermal isomerization rate in the LC networks was much higher than that in DMSO and was found to increase with the increase in the alkoxy tail. Therefore, the structural effect on the switching behavior is attributable to the intermolecular interaction between azobenzene molecules and LC network chains, resulting in the difference in the trans–cis photoisomerization behavior as well as the cis–trans

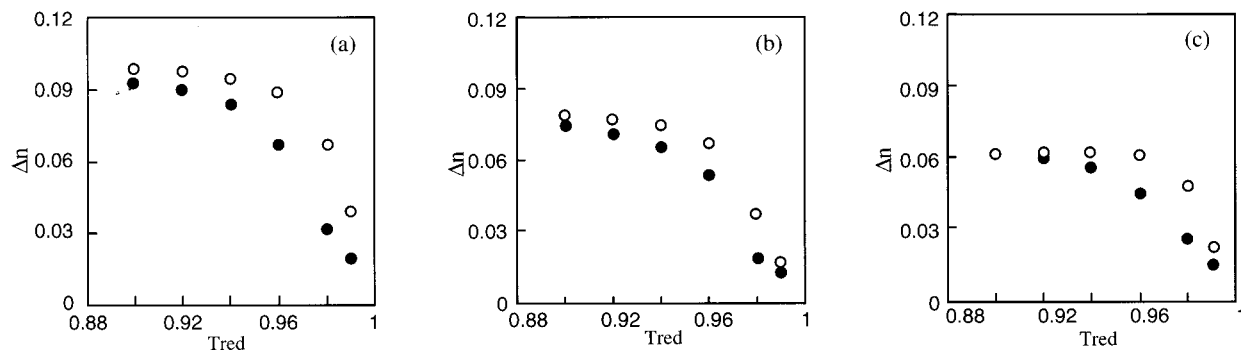


Figure 4. Changes in the birefringence of poly(**APB6/A6PB6A/BM**) (a), poly(**APB6/A6PB6A/BH**) (b), and poly(**APB6/A6PB6A/BD**) (c) networks (90:5:5 mol %) by UV (366 nm, 10 mW) irradiation. (○) and (●), before and after UV irradiation.

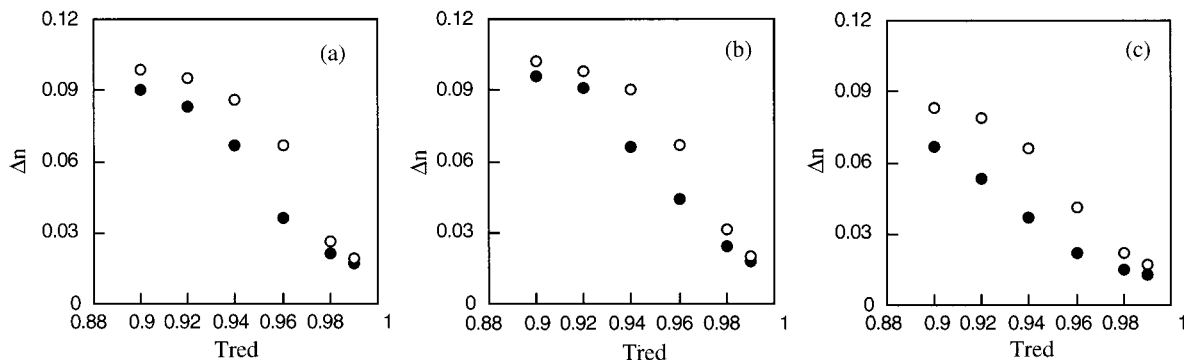


Figure 5. Changes in the birefringence of poly(**APB6/A6PB6A/BAC**) (a), poly(**APB6/A6PB6A/MAC**) (b), and poly(**APB6/A6PB6A/B6Ac**) (c) networks (90:5:5 mol %) by UV(366 nm, 10 mW) irradiation. (○) and (●), before and after UV irradiation.

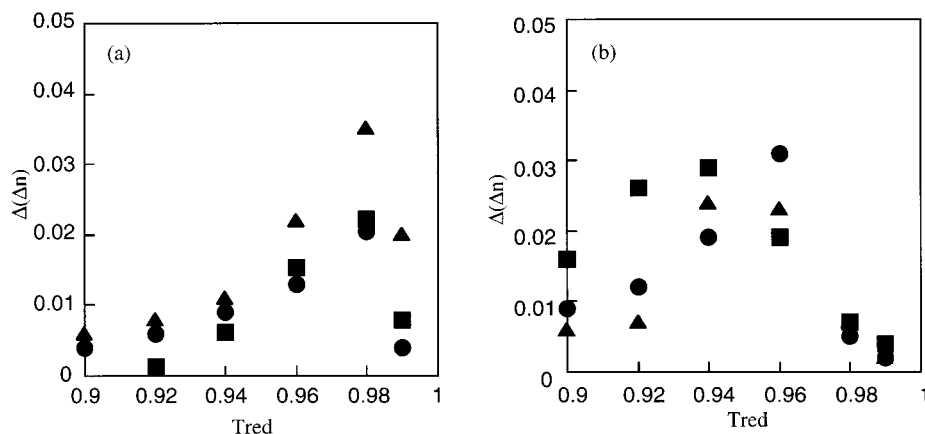


Figure 6. Changes in the birefringence ($\Delta(\Delta n)$) before and after UV irradiation of the doped-type LC networks (a) and the copolymerized-type LC networks (b). (▲), (**APB6/A6PB6A/BM**) (90:5:5 mol %) and (**APB6/A6PB6A/MAC**) (90:5:5 mol %); (●), (**APB6/A6PB6A/BH**) (90:5:5 mol %) and (**APB6/A6PB6A/BAC**) (90:5:5 mol %); (■), (**APB6/A6PB6A/BD**) (90:5:5 mol %) and (**APB6/A6PB6A/B6Ac**) (90:5:5 mol %).

thermal isomerization behavior. As a result, **BD** showed the fastest response and decay times.

Time-resolved measurements of three copolymerized-type LC networks at T_{red} of 0.96 are shown in Figure 8. The decrease in the transmittance and time required for minimum transmittance by single-pulse irradiation were about 16% at 1.5 μ s, 32% at 2 μ s, and 27% at 1.5 μ s for LC networks copolymerized with **BAC**, **MAC**, and **B6Ac**, respectively. Although the LC networks copolymerized with **MAC** required a slightly longer time compared with the others, there is no significant difference in the response behavior. The time to recover the initial transmittance (decay time) are a few ms for **BAC** and **MAC** and about 1 ms for **B6Ac**. Contrary to the response, the decay time of **BAC** and **MAC** was

longer than that for **B6Ac**. Both **BAC** and **MAC** have azobenzene groups directly attached to the polymer backbone, while **B6Ac** has a spacer between the azobenzene group and the polymer backbone. It is known that the length and structure of the spacer between mesogenic groups and the polymer backbone influence the liquid-crystalline properties.²⁶ This is explained in terms of rigidity and steric hindrance. Therefore, it is likely that the spacer influences the switching behavior and contributes to a difference in the switching behavior between the azobenzene-doped and the azobenzene-copolymerized networks as well as between the **BAC**-copolymerized (or **MAC**-copolymerized) and the **B6Ac**-

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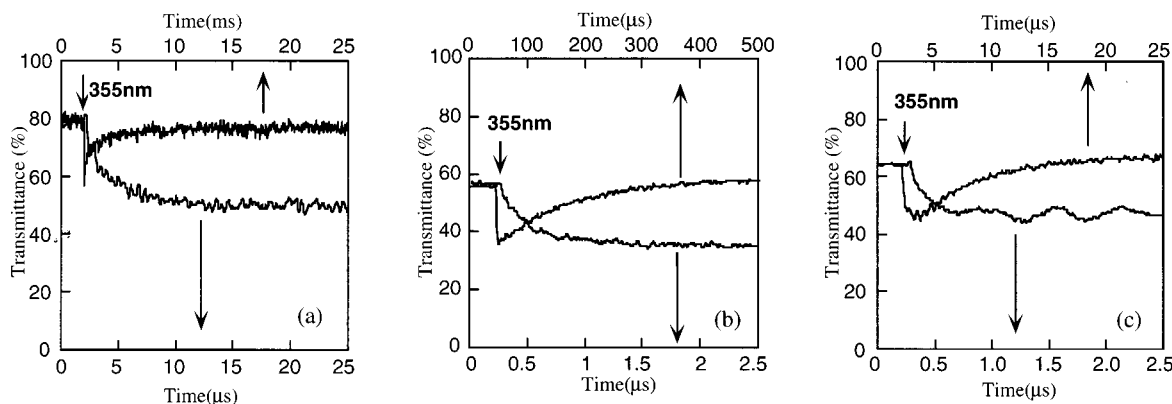


Figure 7. Time-resolved measurements of the photochemical changes in the transmittance of poly(**APB6/A6PB6A/BM**) (a), poly(**APB6/A6PB6A/BH**) (b), and poly(**APB6/A6PB6A/BD**) networks (90:5:5 mol %) between two crossed polarizers induced by single-pulse irradiation from a Nd:YAG laser (355 nm; 10 mJ/pulse; 15 ns fwhm) at T_{red} of 0.98 (126 °C).

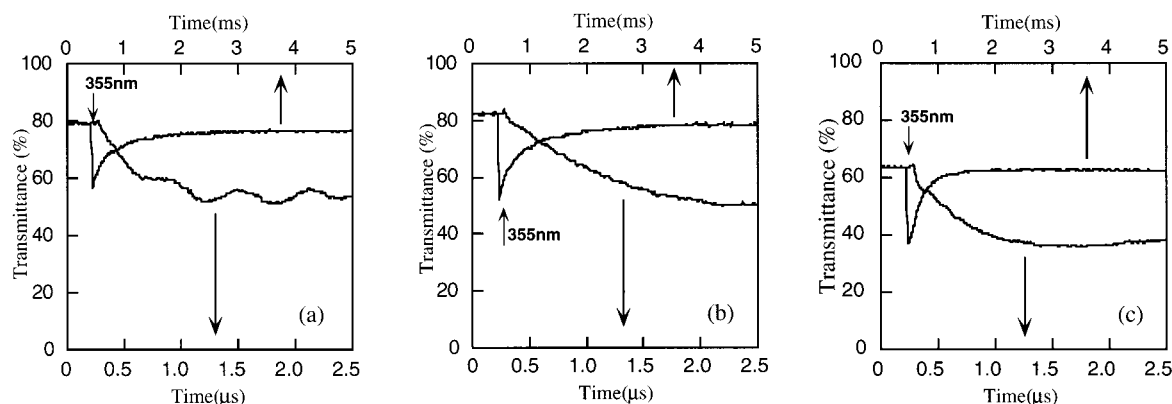


Figure 8. Time-resolved measurements of the photochemical change in the transmittance of poly(**APB6/A6PB6A/BAC**) (a), (**APB6/A6PB6A/MAC**) (b), and (**APB6/A6PB6A/B6Ac**) (c) networks (90:5:5 mol %) between two crossed polarizers induced by single-pulse irradiation from a Nd:YAG laser (355 nm; 10 mJ/pulse; 15 ns fwhm) at T_{red} of 0.96.

copolymerized networks. However, at present, it is difficult to discuss the spacer effect on the switching behavior quantitatively.

Conclusion

We prepared two types of uniaxial LC networks containing the azobenzene compounds: one was the LC networks doped with **BM**, **BH**, and **BD** and the other was those copolymerized with **MAc**, **BAC**, and **B6Ac**. The change in the birefringence of the uniaxial LC networks was induced by UV irradiation to cause trans–cis photoisomerization of azobenzene molecules, resulting in the disorganization effect on the uniaxial molecular orientation. A larger structural effect of the azobenzene molecules was observed on the time-

resolved measurements of the doped-type LC networks. The LC network doped with **BD** showed the fastest optical switching rate: the response time was about 1.0 μ s and the decay was about 15 μ s. These response and decay rates were faster than those of the LC network doped with **BM** and **BH** by 1–2 orders. Lateral intermolecular interaction between azobenzene molecules and mesogenic molecules in the LC networks is an important factor in optical switching behavior.

Supporting Information Available: NMR, IR, and elemental analysis data of the azobenzene compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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