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Photochemical Switching Behavior of Liquid Crystalline Polymer Networks Containing Azobenzene Molecules

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ABSTRACT: Photoresponsive liquid crystalline polymer networks with macroscopically uniaxial molecular orientation were prepared by polymerizing mixtures of liquid crystalline mono- and diacrylates and an azobenzene compound in a homogeneous glass cell at a nematic phase. The polymer networks showed an enantiotropic phase transition from an anisotropic phase to an isotropic phase as well as high transparency. The photoisomerization of the azobenzene compound resulted in a change in a birefringence. The photochemical change in the birefriengence was investigated by using a Xe lamp and a single pulse light from a Nd:YAG laser as light sources. We observed a response time in the range of a few microseconds and a decay time in the range of a few hundred microseconds. The optical switching behavior depended on the cross-linking density of the liquid crystalline polymer networks.

Introduction

Many studies have been focused on photoresponsive liquid crystals (LCs) and liquid crystalline polymers (LCPs) with azobenzene molecules in the field of optical devices.[1−12] The azobenzene molecules are well-known to show reversible photoisomerization between the trans form and cis form: the *trans*-azobenzene molecules with a rod shape can convert into the cis form with a bent shape by ultraviolet irradiation and return thermally or photochemically to the trans form. The trans-to-cis photoisomerization of the azobenzene molecules disorganizes a structure of a LC phase and causes a depression of a phase transition temperature from a LC phase to other phases. Consequently, an isothermal phase transition can be induced photochemically, which is called the photochemical phase transition. Time-resolved measurements have revealed that the photochemical phase transition was induced in 50−200 ms when a small amount of azobenzene compound was dispersed in low molecular weight nematic LCs and LCPs.[8,9] In addition, it was recently found that the monomeric LCs having an azobenzene moiety in each mesogen caused the photochemical phase transition in 100 μs explored by means of reflection-mode analysis.[11,12] The fast response will enable us to use the LC systems not only for display devices but also for various optical devices such as optical switching and optical computing.

On the other hand, we expect that we do not need to induce complete phase transition of LC systems photochemically for applying to the optical devices. Namely, if we can detect enough signal based on the photochemical change in the physical properties of the LC systems such as transparency and birefringence, we will be able to use the LC systems for the optical switching and optical computing. To demonstrate such systems, we have recently reported an optical switching of a slightly cross-linked uniaxial LCP containing azobenzene molecules.[13] The slightly cross-linked uniaxial LCP showed excellent transparency and high birefringence due to stable macroscopically uniaxial molecular orientation. Fast change in the birefringence of the slightly cross-linked LCP was achieved by pulse irradiation: the pulse irradiation experiments have revealed that the LCP showed the response time and decay time in the ranges of a few tens of microseconds and a few hundred microseconds, respectively. The decay time was faster by 1 order of magnitude than those reported previously.[11,12] The cross-linking of the LCP results in the depression of motion of network chains in the LCP.[14] Thus, the cross-linking affects the stability of macroscopic molecular orientation and the response of the LCP to the external stimuli such as the perturbation effect of the photoisomerization of the azobenzene molecules. In this study, we describe the preparation of macroscopically uniaxial LCP networks containing azobenzene molecules and the effect of the cross-linking on a photochemically induced optical switching behavior of the LCP networks by the photoisomerization of the azobenzene molecules.

Experimental Section

Materials. Two monomers, **APB6** and **A6PB6A**, and azobenzene compound, **BHAB**, were synthesized and used in this study.[15−19]

Monoacrylate, **APB6**, was synthesized by reacting 4-(6-(acryloyloxy)hexyloxy)benzoic acid with 4-*n*-hexyloxyphenol in the presence of *N*,*N*′-(dimethylamino)pyridine (**DMAP**) and dicyclohexylcarbodiimide (**DCC**) in methylene chloride. Purification was carried out by recrystallization from ethanol (yield: 45%). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.0−1.9 (m, 16H, methylene), 3.9 (t, 2H, ArOCH$_2$−), 4.22 (t, 2H, COOCH$_2$−), 5.8−6.5 (m, 3H, vinyl), 6.8−8.2 (m, 8H, aromatic). IR (KBr) (cm^{-1}): 1630 ($\nu_{C=C_{vinyl}}$), 1725 ($\nu_{C=O}$). Anal. Calcd for $C_{28}H_{36}O_6$: C, 71.7; H,7.74. Found: C, 70.9; H, 7.87.

Diacrylate, **A6PB6A**, was synthesized by reacting 4-(6-(acryloyloxy)hexyloxy)benzoic acid with 4-(6-(acryloyloxy)hexyloxy)phenol in the presence of **DMAP** and **DCC** in methylene chloride. Purification was carried out by column chromatography (silica gel, CHCl$_3$/methanol as eluent) and recrystallization from 2-propanol (yield: 51%). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.4−1.9 (m, 12H, methylene), 3.9−4.2 (m, 8H, methylene), 5.8−6.5 (m, 6H, vinyl), 6.8−8.2 (m, 8H, aromatic). IR (KBr) (cm^{-1}): 1630 ($\nu_{C=C_{vinyl}}$), 1715 ($\nu_{C=O}$). Anal. Calcd for $C_{31}H_{38}O_8$: C, 69.1; H,7.11. Found: C, 68.9; H, 7.06.

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The azobenzene compound, **BHAB**, was synthesized by the diazo coupling reaction between 4-butylaniline and phenol in the presence of sodium nitrite and hydrochloric acid, following alkylation with hexyl chloride. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.9−1.8 (m, 18H), 2.7 (t, 2H), 4.0 (t, 2H), 6.8−7.9 (m, 8H, aromatic). Anal. Calcd for $C_{22}H_{30}N_2O$: C, 78.1; H, 8.9; N, 8.3. Found: C, 77.8; H, 9.1; N, 8.2.

Thermotropic Properties. Thermal phase transition behavior of the compounds was examined by means of differential scanning calorimetry (DSC, Seiko I&G SSC-5020) and polarizing optical microscopic observation (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.

Bulk Photopolymerization. Polymerizable mixtures were prepared by adding 2 or 3 mol % of benzoyl peroxide (**BPO**) to mixtures of **APB6**, **A6PB6A**, and **BHAB** as a radical initiator. The mixtures were injected into two glass plates. Polymerization was carried out by heating at 57 °C. After polymerization, the samples were removed from the glass plates and were subjected to gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-80M; eluent, tetrahydrofuran; standard, polystyrene) and infrared spectroscopy. The conversion of the mixtures was determined by comparing the peak corresponding to polymers to that corresponding to **APB6** in the GPC chromatograms.

Optical Properties. Mixtures of **APB6**, **A6PB6A**, and **BHAB** containing 3 mol % of **BPO** were injected into the homogeneous glass cell with 5 μm cell gap or the Cano-wedge cell (E.H.C. Co., Ltd.) at the isotropic phase. The Cano-wedge cell is a wedge-shaped cell with a homogeneous planar alignment. The polymerization of the mixtures was carried out by heating at 57 °C for 1 h.

The birefringence (Δn) of samples before and after polymerization was determined by observing interference lines of the samples in the Cano-wedge cell between two crossed polarizers with a probe light from a laser diode (Suruga Seiki Co.; 670 nm; 5 mW): $\Delta n = \lambda/(d_1 - d_2)$, where λ is the wavelength of the probe light and d_1 and d_2 are the cell gaps at adjacent interference lines. Transmittance was measured by using homogeneous glass cell with 5 μm cell gap with the probe light from the laser diode.

Optical Switching Behavior. The sample polymerized in the homogeneous glass cell with 5 μm cell gap 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. The photochemical switching behavior were examined by using a Xe lamp (ILC Technology, ILC-201, 175 W) equipped with a cut filter (Sigma UTVAF-35U) for ultraviolet (UV) light irradiation as an excitation lamp to cause trans−cis photoisomerization of **BHAB**. The laser diode was used as a probe light source. The change in the transmitted light intensity of the probe light from the laser diode was monitored with a laser power meter (Neo Ark, PM-221). In addition, the photochemical change in Δn was estimated by measuring the transmitted light intensities of the samples between two crossed polarizers ($I_\perp$) and between two parallel polarizers ($I_\parallel$): $I_\perp/I_\parallel = \tan^2(\pi\Delta nd/\lambda)$, where d and λ are the cell gap and the wavelength of the probe light, respectively.[20]

Time-resolved measurements of photochemical change in the birefringence were carried out by means of pulse irradiation. The sample polymerized was thermostated and set between two crossed polarizers ($I_\perp$) or two parallel polarizers ($I_\parallel$). The sample was irradiated with a single pulse of a Nd:YAG laser (Continuum NY 60; the third harmonic, 355 nm; 10 mJ/cm^2; 15 ns, full with half-maximum (fwhm)). The transmitted light intensity of the probe light from the laser diode through two polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded on a Phillips PM3350A storage scope. The time-resolved change in Δn on pulse irradiation was estimated by using the above equation, $I_\perp/I_\parallel = \tan^2(\pi\Delta nd/\lambda)$.

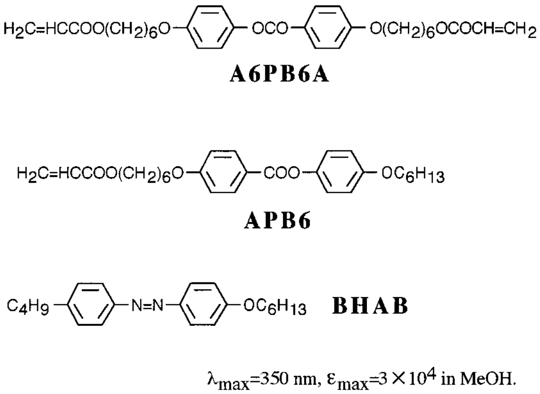

Figure 1. Compounds used in this study.

Results and Discussion

Properties of LC Polymer Networks. Figure 1 shows the structures of the compounds used in this study. The thermal phase transition behavior of the compounds was examined by means of DSC and POM observation. Monoacrylate, **APB6**, shows a nematic (N) phase on heating in a range of 58−64 °C. Diacrylate, **A6PB6A**, is a monotropic liquid crystal; a N phase between 47 and 50 °C is observed only on cooling. Azobenzene compound, **BHAB**, is the N phase in a range of 45−73 °C. Three monomer mixtures, **APB6**/**BHAB** (95:5 mol %) and **APB6**/**A6PB6A**/**BHAB** (90:5:5, 92:3:5 mol %), were prepared. All the mixtures show the N phase between 49 and 60 °C for the (**APB6**/**BHAB**) (95:5) mixture, between 51 and 60 °C for the (**APB6**/**A6PB6A**/**BHAB**) (92:3:5) mixture, and between 49 and 59 °C for the (**APB6**/**A6PB6A**/**BHAB**) (90:5:5) mixture.

Figure 2 shows the photoisomerization behavior of **BHAB** in 4-cyano-4′-pentylbiphenyl (**5CB**) at 45 and 125 °C by UV irradiation with the Xe lamp. The UV irradiation caused clearly the trans−cis photoisomerization of **BHAB** at 45 °C, whereas no significant trans−cis photoisomerization was recognized by the irradiation at 125 °C, because of rapid cis−trans thermally reverse isomerization of **BHAB** at higher temperature.

Figure 3A shows time course of conversion of the (**APB6**/**BHAB**) mixture determined by GPC measurements. The polymerization was carried out by heating at 57 °C, at which temperature the mixture is in the N phase. The conversion was increased by increasing **BPO** content as well as polymerization time and became higher than 75% by heating for 1 h. However, the polymerization behavior of the (**APB6**/**A6PB6A**/**BHAB**) mixtures could not be examined by GPC measurement, because of the insolubility of the samples due to cross-linking with **A6PB6A**. To confirm the polymerization of the (**APB6**/**A6PB6A**/**BHAB**) mixtures, infrared spectra of the mixtures before and after heating at 57 °C for 1 h were measured (Figure 3B). The peak at 1630 cm^{-1} corresponding to vinyl stretching disappeared after the polymerization at 57 °C for 1 h, indicating proceeding of the polymerization of **APB6** and **A6PB6A**.

To explore the stability of macroscopic molecular orientation of the samples polymerized, the birefrigence (Δn) and the transmittance were measured as a function of temperature. The value of Δn was determined by measuring the width of interference lines of the samples in the Cano-wedge cell between two crossed polarizers. Figure 4 shows the temperature dependence of both Δn and transmittance for the poly(**APB6**/**A6PB6A**/**BHAB**)

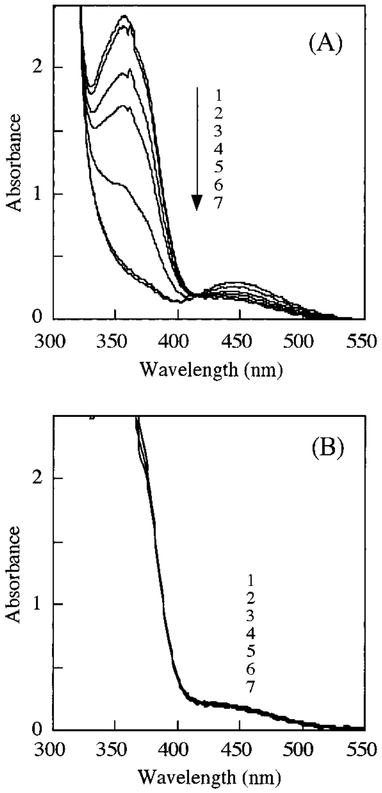

Figure 2. Changes in absorption spectra of **BHAB** in 5CB upon UV irradiation at 45 (A) and 125 °C (B): 1, before irradiation; 2, 1 min; 3, 3 min; 4, 5 min; 5, 10 min; 6, 20 min; 7, 30 min.

(90:5:5) network. The polymerization caused no significant change in Δn. The values of Δn of the poly(**APB6**/**A6PB6A**/**BHAB**) network were around 0.1 and kept constant up to 120 °C. Above 120 °C, Δn decreased due to the phase transition to the isotropic (I) phase. By subsequent cooling, Δn was increased and restored to the initial level of Δn as shown in Figure 4 (open and solid circles). In addition, no change in the transmittance was induced by polymerization, and it was kept about 90% by heating to 120 °C and following cooling (open and solid triangles). The results clearly demonstrate that the poly(**APB6**/**A6PB6A**/**BHAB**) network not only holds the macroscopically uniaxial molecular orientation but also shows the reversible phase transition between the uniaxial LC phase and the I phase. Contrary to the poly(**APB6**/**A6PB6A**/**BHAB**) network, Δn of poly(**APB6**/**BHAB**) without cross-linking was not restored by cooling after the phase transition to the I phase once, as shown in Figure 5. Furthermore, the polymerization caused a significant decrease in the transmittance. Poly(**APB6**) was reported to show S phase as a LC phase.[19] Thus, it was likely that a transformation from the N phase to the S phase took place during the polymerization. Actually, POM observation revealed that the uniaxial monodomain structure before the polymerization transformed into a multidomain structure by the polymerization and following heating. The decrease in the transmittance is related to the light scattering, arising from the transformation to the S phase and the multidomain structure.

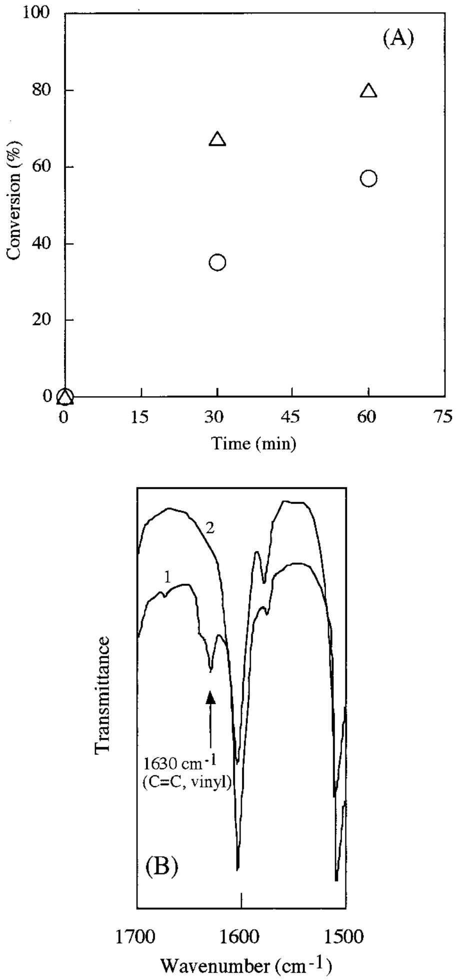

Figure 3. Changes in conversion (A) of **APB6**/**BHAB** mixture (95:5 mol %) by heating at 57 °C and IR spectra (B) of **APB6**/**A6PB6A**/**BHAB** mixture (90:5:5 mol %) before (curve 1) and after (curve 2) 57 °C for 1 h: (○), BPO 2 mol %; (▲), BPO 3 mol %.

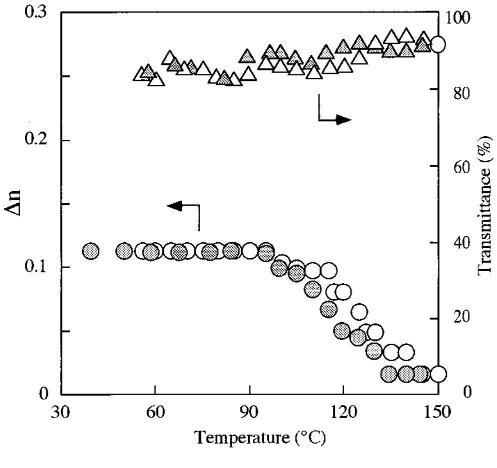

Figure 4. Changes in the birefringence (Δn) (○, ●) and transmittance (△, ▲) of poly(**APB6**/**A6PB6A**/**BHAB**) (90:5:5 mol %) as a function of temperature: (○, △), heating; (●, ▲), cooling.

The stability of the macroscopic molecular orientation is also considered to depend on conditions such as film thickness and strength of the anchoring effect. As the anchoring effect forcing the macroscopic molecular orientation increases, the stability of the macroscopic molecular orientation increases; e.g., uniaxially oriented films of LCP having submicron thickness could be achieved by only casting the LCP diluted solution on a rubbed polymer substrate.[7,21] In this case, the anchoring effect is enough to force the uniaxial molecular orientation, because of the thin film thickness. The temperature

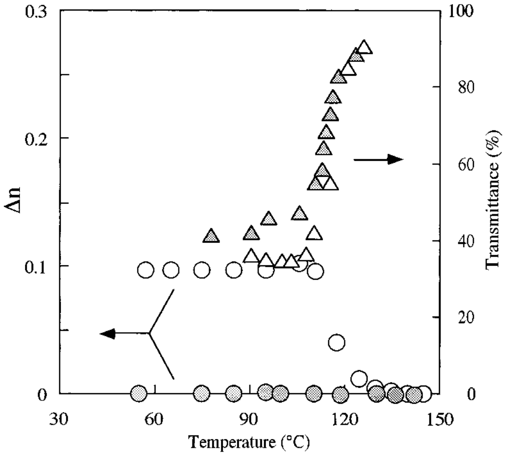

Figure 5. Changes in the birefringence (Δ*n*) (○, ●) and transmittance (△, ▲) of poly(**APB6**/**BHAB**) (95:5 mol %) as a function of temperature: (○, △), heating; (●, ▲), cooling.

dependence of Δ*n* shown in Figures 4 and 5 was examined by using the Cano-wedge cell, which is a wedge-shaped cell having a cell gap in the range of submicrometers to a few hundred micrometers. The irreversible change in Δ*n* shown in Figure 5 may be related to the thick cell gap. However, the comparison with results shown in Figures 4 and 5 implies that the slight cross-linking of the LCPs is responsible for the stability of the macroscopically uniaxial molecular orientation of the LCP networks, resulting in both excellent transparency and reversible change in Δ*n*.

Photochemical Switching Behavior. To investigate the effect of the photoisomerization of **BHAB** on the optical properties of the LCP networks, changes in the birefringence of the poly(**APB6**/**A6PB6A**/**BHAB**) (90:5:5 and 92:3:5) and the poly(**APB6**/**BHAB**) (90:5) networks were examined upon UV irradiation. The LCP networks in the homogeneous glass cell with 5 μm gap were placed between two crossed polarizers and thermostated. The polarizing direction of the two polarizers was set at an angle of 45° with respect to the orientation axis of the cell. The change in the transmitted light intensity through the poly(**APB6**/**A6PB6A**/**BHAB**) (90:5:5) network or the poly(**APB6**/**BHAB**) (90:5) network was monitored with the laser power meter while the sample was irradiated with the Xe lamp, causing the trans−cis photoisomerization of **BHAB** in the LCP networks. The changes in the transmitted light intensity of the probe light by the irradiation at T_{red} ($=T/T_{\mathrm{c}}$) of 0.98 are shown in Figure 6. Both the LCP networks show a clear photochemical change in the transmitted light intensity by the irradiation. The intensity was decreased by the irradiation and restored in the dark as can be seen in Figure 6. The estimated values of Δ*n* before and after the irradiation were 0.034 and 0.027 for the poly(**APB6**/**A6PB6A**/**BHAB**) (90:5:5) network and 0.015 and 0.010 for the poly(**APB6**/**BHAB**) (95:5) network. The reversible change in the transmittance for the poly(**APB6**/**BHAB**) network without cross-linking may be related to the cell gap of 5 μm; namely, the anchoring effect forcing homogeneous alignment contributes to the restoration of Δ*n* in the dark.

It is worth noting here that the changes in the transmittance are enough to detect, although the photochemical phase transition of the LCP networks cannot be induced completely. The initial value of Δ*n* for the poly(**APB6**/**A6PB6A**/**BHAB**) network was higher than that for the poly(**APB6**/**BHAB**) network. In addition, it is likely that the time required for restoration of Δ*n* for the poly(**APB6**/**A6PB6A**/**BHAB**) network is slightly shorter than that for the poly(**APB6**/**BHAB**) network. The results indicate that the cross-linking affects not only the stability of the macroscopic molecular orientation but also the photochemical switching behavior. Therefore, the time-resolved measurements of the photochemical change in the birefringence were carried out by means of pulse irradiation in order to explore the cross-linking effect on the photochemical switching behavior of the LCP networks.

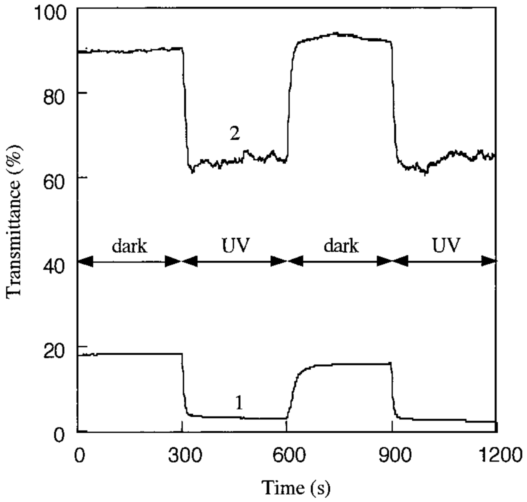

Figure 6. Changes in the transmittance of LCP networks between two crossed polarizers by UV irradiation at T_{red} of 0.98: 1, poly(**APB6**/**BHAB**) (95:5:5 mol %); 2, poly(**APB6**/**A6PB6A**/**BHAB**) (90:5:5 mol %). Reference light intensity (I_0) for the transmittance measurements was defined at the transmitted light intensity through two parallel polarizers.

Both the LCP networks were thermostated and set between two crossed polarizers. Each LCP network was irradiated with a third harmonic single pulse of a Nd:YAG laser. Figure 7 shows the time-resolved measurements of the photochemical changes in the transmittance of both the LCP networks between two crossed polarizers. In the case of the poly(**APB6**/**A6PB6A**/**BHAB**) network, the transmittance was decreased and reached the minimum value upon the pulse irradiation. Subsequently, the transmittance increased and was restored to the initial level. To discuss the optical switching behavior, the response time and decay time were defined as the time required to decrease to the minimum value and as the time required to raise to 90% of the initial value, respectively. The response time was in a range of a few microseconds (curve 1 in Figure 7A). The decay time was much longer than the response time and was in a range of a few hundred microseconds (curve 2 in Figure 7A). On the other hand, only a little change in the transmittance was observed for the poly(**APB6**/**BHAB**) network by the pulse irradiation (Figure 7B), contrary to the change in the transmittance by UV irradiation with a Xe lamp (Figure 6). Poly(**APB6**) shows the S phase at the temperature studied. The transformation from the uniaxial monodomain structure to the multidomain structure was recognized during polymerization. The poor response to the pulse irradiation may be explained as a result of the transformation to the S phase and the multidomain structure of the LCP without the cross-linking, causing strong light scattering. The light scattering interferes with the

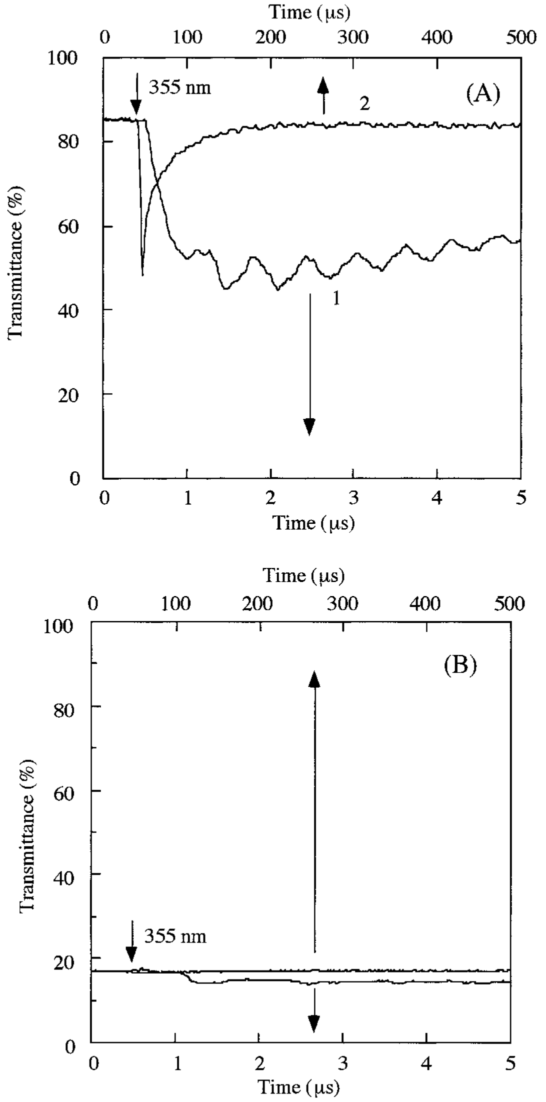

Figure 7. Time-resolved measurements of change in the transmittance of poly(**APB6/A6PB6A/BHAB**) (90:5:5 mol %) (A) and poly(**APB6/BHAB**) (95:5 mol %) (B) networks between two crossed polarizers on pulse irradiation (355 nm, 15 ns fwhm, 10 mJ/cm^2) at T_{red} of 0.98.

photoisomerization of **BHAB**. On the other hand, no transformation to the multidomain structure was recognized for the poly(**APB6/A6PB6A/BHAB**) networks during the polymerization. Therefore, it is expected that the mesogenic moieties in the poly(**APB6/A6PB6A/BHAB**) networks are fixed in the N phase. A difference in the lateral intermolecular interaction between the N phase and the S phase may be one of the factors influencing the photochemical switching behavior of the LCP systems.

Figure 8 shows the time-resolved measurements of changes in Δ*n* of the poly(**APB6/A6PB6A/BHAB**) (90:5:5 and 93:2:5) networks. The conversion of the LC monomers to polymers was estimated to be higher than 75% as shown in Figure 3. Consequently, the cross-linking density of the LCP networks roughly corresponds to the content of **A6PB6A** in the LC monomer mixtures. The optical switching behavior was found to depend on the content of **A6PB6A** moieties in the LCP networks, indicating the effect of cross-linking density. The change in Δ*n* of the LCP network cross-linked with 2 mol % of **A6PB6A** was larger than that of the LCP network cross-linked with 5 mol % of **A6PB6A**. The sensitivity was depressed by the cross-linking. On the other hand, the switching time, which is defined as the sum of the response time and the decay time, was decreased by cross-linking. The decay time is assumed to be related to the thermal cis−trans isomerization.[21] The measurements were carried out at almost the same temperature (120 and 119 °C), so that the temperature dependence of thermal cis−trans isomerization could be neglected. Therefore, the result implies that the cross-linking results in the enhancement of the switching rate.

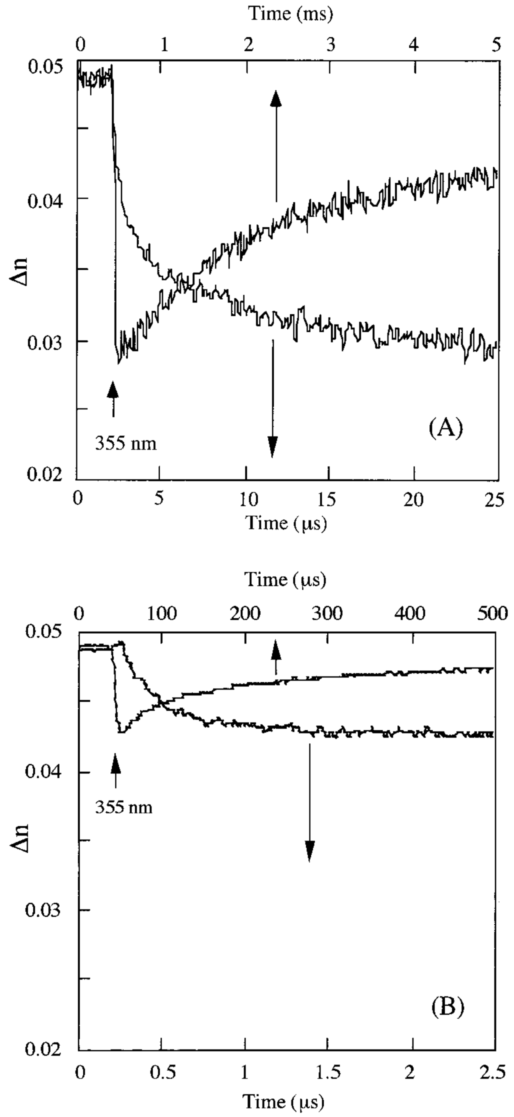

Figure 8. Time-resolved measurements of change in Δ*n* of poly(APB6/**A6PB6A/BHAB**) (93:2:5 mol %) at 120 °C (A) and poly(**APB6/A6PB6A/BHAB**) (90:5:5 mol %) at 119 °C (B) on pulse irradiation (355 nm, 15 ns fwhm, 10 mJ/cm^2).

It has been reported that the thermal motion of the network chains in mesogenic resins was significantly suppressed by cross-linking.[22] In addition, studies on the dynamic thermomechanical behavior of LCP's revealed that the α relaxation of the LCP networks, which was associated with the relaxation of the whole network, was shifted to higher temperatures with increasing cross-linking density.[14,15] The photochemical change in Δ*n* is considered to arise from the transient deformation of uniaxial molecular orientation by the trans−cis photoisomerization. Thus, the motion of the LCP network chains, including mesogenic side chains, is required for the photochemical switching of Δn. The cross-linking effect on the optical switching behavior may be interpreted in terms of the facility of the molecular motion of the mesogenic moieties in the LCP networks. The higher the motion of the network chains increases, the higher the sensitivity becomes. However, the facile motion of the chains gives a negative effect on the restoration of the uniaxially molecular orientation from the transiently disorganized state, resulting in the decrease in the switching rate.

Conclusion

We prepared the slightly cross-linked LCP networks containing the azobenzene compound, poly(**APB6**/**A6PB6A**/**BHAB**), and explored the photochemical switching behavior. UV irradiation resulted in the decrease in the birefringence with respect to the perturbation effect of the photoisomerization of **BHAB** on the molecular orientation. The pulse irradiation experiments revealed that the response and decay times of the LCP networks were in the ranges of a few microseconds and a few hundred microseconds, respectively. In addition, the optical switching behavior was significantly affected by the cross-linking density. The increase in the cross-linking density resulted in the increase in the optical switching rate but decreased the sensitivity of the optical switching.

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