All-Optically Controllable Polymer/Liquid Crystal Composite Films Containing the Azobenzene Liquid Crystal

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Polymer/liquid crystal (LC) composite films possessing an azobenzene LC as a photoresponsive molecule (AzoCFs) were prepared by the thermal polymerization-induced phase separation method. The composite films (AzoCFs) showed a strong light-scattering state after polymerization, and their optical properties were strongly affected by the compositional ratio of the liquid crystals in the composite film. Change in the transmittance between a light-scattering and a transparent state could be induced isothermally by photoirradiation. Upon irradiation at 366 nm, AzoCFs changed from the light-scattering state to the transparent state. This is ascribed to nematic (N)−isotropic (I) phase transition due to *trans*−*cis* isomerization of the azobenzene molecules in the LC domains within the polymer matrix. Furthermore, restoration of the initial state could be achieved by visible-light irradiation (>420 nm), resulting from the I−N phase transition induced by cis−trans back-isomerization of the azobenzene guest molecules.

Introduction

Composite films containing micrometer-sized domains of liquid crystal (LC) dispersed in a polymer matrix have considerable potential for electrooptical applications such as light shutter, information display, and optical nonlinear materials.[1−9] In comparison with the conventional LC devices, polymer/LC composite films show a high transmittance and a wide viewing angle because polarizers are not needed. In addition, the composite films are flexible and possess a high processability, since they require no alignment substrates. These films can be generally switched between a light-scattering state and a transparent state through electrical control of the refractive index similar to the other LC devices. In the absence of the applied electric field, the composite films show an opaque or translucent state because of mismatch of the refractive index between the LC domains and the polymer matrix. If an electric field is applied between the electrodes of the substrates, the director, which is assigned as the average orientation of the LCs in the domain, is aligned along the direction of the applied electric field and the composite films become transparent due to matching of the ordinary refractive index of the LC domains with that of the polymer matrix. When the electric field is removed, the composite films return to an initial state with the random orientation of the LC domains.

Recently, many studies have been performed on optically controllable composite films which are attractive for applications in photonics or optoelectronics.[8−23] Change in the transmittance of the composite films can

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be achieved by two approaches. One is due to laser heating (i.e., heat-mode processes): the change in transmittance results from nematic (N) to isotropic (I) phase transition in the LC domains[8−15] and reorientation of the LC domains.[19−22] The other is due to photochemical reaction of photochromic molecules such as azobenzene and stilbene derivatives incorporated into the LC domains in the polymer matrix (i.e., photon-mode processes).[16−18] These chromophores can undergo reversible *trans*−*cis* isomerization by light with appropriate wavelength. The change in transmittance occurs by change in their molecule shape which leads to phase transition[16] or orientational change in director of the LC domains.[17,18]

We have performed so far systematic studies on photonic control of light by means of the photochemical phase transition of azobenzene LCs.[23−36] The *trans*−*cis* photoisomerization of the azobenzene brought about the LC−I phase transition as demonstrated by the complete loss of birefringence. Such photochemical phase transition behavior was evaluated by monitoring a polarized probe light through a pair of crossed polarizers with the sample between them. In this study, we attempted photonic control of light by the use of light-scattering phenomena. Polymer/LC composite films containing an azobenzene derivative as a photochromic guest molecule (AzoCFs) were prepared by in-situ thermal polymerization, and the photoresponse of AzoCFs was evaluated on the basis of the photochemical phase transition.

Experimental Section

Materials. The chemical structures of materials used in this study are shown in Figure 1. We used 1,6-hexanediol diacrylate as a monomer which was optically isotropic and showed a transparent state even after the polymerization. 2,2′-Azobis(isobutyronitrile) (AIBN) and benzil were used as initiators for thermal polymerization and photopolymerization, respectively. Host LC, which is a four-component mixture of substituted cyanobiphenyls and a cyanoterphenyl (E7, Merck Japan Ltd.), was used without further purification. The smectic−N phase transition temperature and the N−I phase transition temperature (T_{NI}) were −20 and 61 °C, respectively. 4-Butyl-4′-methoxyazobenzene (BMAB) as a guest photoresponsive dopant was prepared as reported previously.[37] The trans form exhibits an N phase between 35 and 45 °C, while the cis isomer shows no LC phase at any temperature.

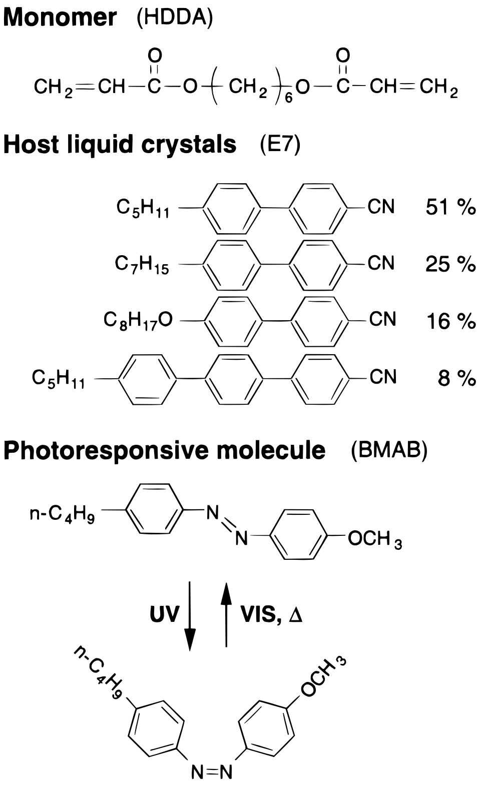

Figure 1. Chemical structures of compounds used in this study and the isomerization of BMAB.

Preparation of Samples. Homogeneous mixtures were prepared by dissolving E7 and BMAB in the diacrylate monomer solution containing a small amount of the initiator (2 mol %). The mixtures were injected into two glass substrates separated with a 13 μm silica spacer by capillary action. In this study, we adopted thermal and photopolymerization-induced phase separation to obtain the composite films showing a light-scattering state. The thermal polymerization-induced phase separation was performed in a Mettler hot stage, Models FP-82 and FP-90. In the photopolymerization, the samples were irradiated with 366 nm light isolated from a mercury lamp (1.0 ∼ 20 mW/cm^2).

Measurement. To investigate the optical behavior of the composite films, we used the experimental setup shown in Figure 2. Photoirradiation was performed with a 500 W high-pressure mercury lamp, in which 366 or >420 nm light was isolated with glass filters. Transmittance of a probe light at 633 nm from a He−Ne laser was measured with a photodiode. We defined the 100% transmittance as the transmittance of the probe light in the absence of the sample.

Results and Discussion

Characterization of Composite Films. In general, polymer/LC composite films can be prepared by emul-

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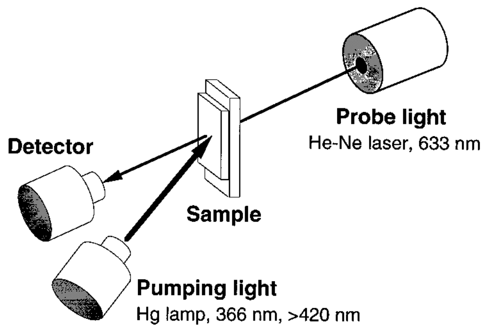

Figure 2. Schematic representation of an experimental setup. The 100% transmittance was defined as the transmittance in the absence of the sample.

Table 1. Characterization of Composite Films with Different Composition Ratios

sample[a]	monomer[b]:LCs (wt %)	LCs[c] BMAB: E7 (wt %)	T_{NI}[d]
AzoCF-1	14:86	0:100	61
AzoCF-2		5:95	60
AzoCF-3		10:90	59
AzoCF-4		13:87	58
AzoCF-5		16:84	56
AzoCF-6		20:80	54
AzoCF-7		23:77	51
AzoCF-8		26:74	55

[a] All samples were prepared by thermal polymerization at 90 °C for 90 min. [b] The monomer contains 2 mol % of AIBN as an initiator. [c] LCs are a mixture of BMAB and E7, and the composition ratio of two LCs was varied within the LC content of 86 wt %. [d] T_{NI} of the samples was measured with a polarizing microscope.

sification or phase separation methods.[1−7,38−41] In contrast with the emulsification method using aqueous polymer, the phase separation method starts with a one-phase mixture. The phase separation is induced through the film formation due to polymerization, solvent evaporation, or cooling. Among all of these methods, photopolymerization-induced phase separation is the most common because low-viscosity materials are used and processing is very simple. Thus, we attempted the photopolymerization to obtain the composite films. However, this method could not induce the phase separation even under any condition. This results from the large extinction coefficient of the sample ($\epsilon > 10^4$). Namely, photons were absorbed only by the azobenzene molecules in the mixtures, and photopolymerization was not initiated. On the other hand, samples showing a light-scattering state were easily obtained by the thermal polymerization-induced phase separation method. The samples with different composition ratios were prepared by the thermal polymerization at 90 °C for 90 min (Table 1). The mixing ratio of the monomer to the LCs (E7 plus BMAB) was fixed at 14:86 wt %, and the ratio of E7 to BMAB was varied within the LC content of 86 wt % as shown in Table 1. The T_{NI} of AzoCFs was determined by monitoring the light intensity passed through the sample between crossed polarizers on the hot stage, and T_{NI} was defined as the temperature at which the LC phase disappeared completely.

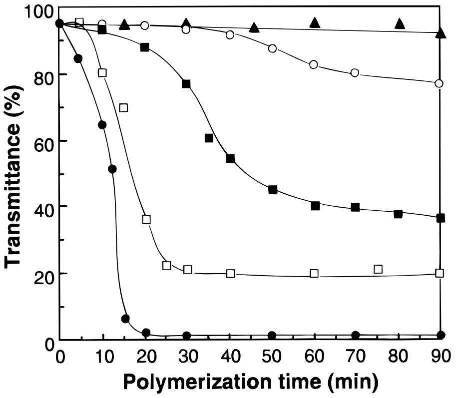

Figure 3. Change in transmittance of AzoCF-4 induced by thermal polymerization at various temperatures. The transmittance was measured at room temperature: ▲, 60 °C; ○, 70 °C; ■, 80 °C; □, 85 °C; ●, 90 °C.

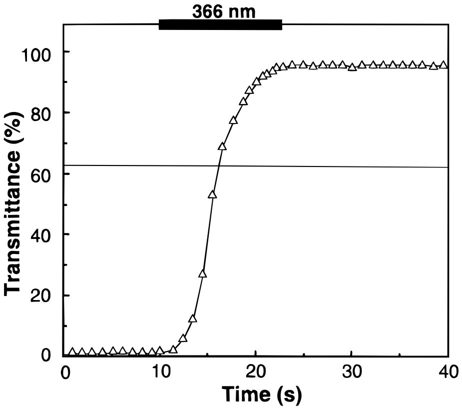

Figure 4. Optical behavior of the composite films induced by irradiation at 366 nm (20 mW/cm^2) at room temperature: △, AzoCF-4; —, AzoCF-1.

Figure 3 shows the effect of polymerization temperature on the optical property of the AzoCF-4 film. Before polymerization, the probe light could transmit through the sample because the homogeneous ternary mixture showed a clear state (i.e., no LC phase). The transmittance of probe light gradually decreased during polymerization irrespective of the polymerization temperature. This result indicates that the phase separation was induced by polymerization and the sample showed the light-scattering state. The phase separation process was found to be affected by the polymerization temperature. When the polymerization was performed at 90 °C, the sample showed the highest light scattering. Although an opaque light scattering occurred at 90 °C within 20 min, the polymerization time was elongated for 90 min to prepare a completely cross-linked polymer matrix.

Change in Transmittance Induced by N−I Phase Transition. Figure 4 shows the change in the transmittance induced by photoirradiation in AzoCF-4. The sample film was irradiated at 366 nm (20 mW/cm^2) at room temperature. Before irradiation, the initial state showed a strong light scattering in which the probe light did not pass through the sample. When AzoCF-4 was photoirradiated, the transmittance of the probe light remarkably increased and reached the saturated state after 15 s irradiation. In the saturated state, AzoCF-4 was completely transparent. The photographs of AzoCF-4 before and after photoirradiation are shown in Figure 5. A sheet of "bar code" print was placed

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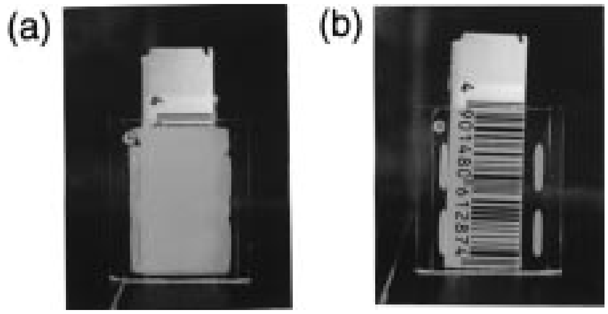

Figure 5. Photograph of AzoCF-4: (a) the sample in the initial opaque state; (b) the sample after irradiation at 366 nm (20 mW/cm^2) for 15 s.

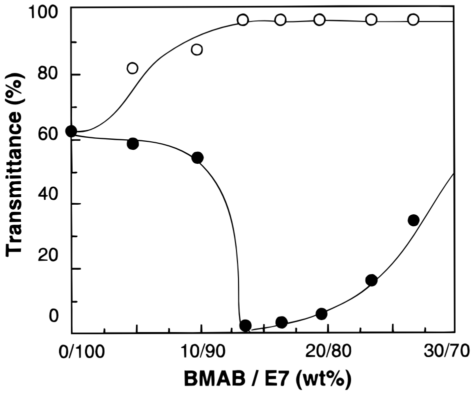

Figure 6. Transmittance of the composite films as a function of the amount of BMAB: before (●) and after (○) photoirradiation at 366 nm. Each point corresponds to each sample listed in Table 1.

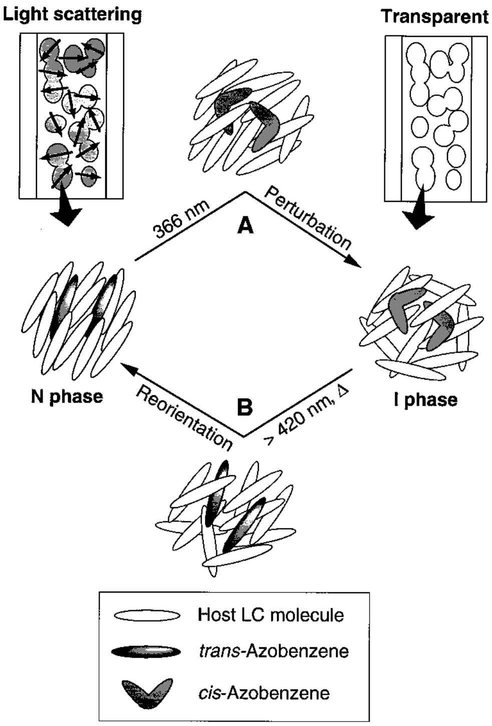

Figure 7. Schematic illustration of the mechanism to control the optical property of AzoCFs between a light-scattering and a transparent state induced by the photochemical phase transition: A, change from a light-scattering state to a transparent state by N–I phase transition of the LC domains triggered by trans–cis photoisomerization of the azobenzene molecules; B, change from a transparent state to a light-scattering state by the I–N phase transition induced by cis–trans back-isomerization of the azobenzene molecules.

behind the sample. Before photoirradiation, the "bar code" could not be observed because incidence light was scattered strongly by the sample. Figure 5b shows the sample after exposure with 366 nm light (20 mW/cm^2) for 15 s. The transparent sample became haze-free at all viewing angles. On the other hand, such phenomena were not observed for AzoCF-1 without azobenzene molecules (the solid line in Figure 4). This result indicates the azobenzene molecules play an important role for the photoresponse of AzoCFs.

In fact, the photoresponsiveness of AzoCFs was strongly dependent on the amount of the azobenzene. Figure 6 shows the transmittance in the initial state (closed symbols) and in the saturated state after photoirradiation at 366 nm (open symbols). Each data point corresponds to each sample listed in Table 1. In the saturated state, the transmittance increased as the azobenzene content increased. On the other hand, the degree of the light scattering in the initial state was largest for the sample with the optimal mixing ratio of BMAB/E7 = 13/87 (wt %). Consequently, AzoCF-4 with this ratio of BMAB/E7 showed the highest contrast on photoirradiation.

The observed optical behavior of AzoCFs may be ascribed to the geometrical change of the guest azobenzene molecules. The azobenzene chromophores can undergo trans–cis photoisomerization on irradiation with light of an appropriate wavelength. In the case of BMAB, the trans form exhibits an absorption maximum at around 360 nm due to the π–π^* transition.[33,36] On irradiation at 366 nm, the absorbance decreased gradually, and the other absorption maximum at around 430 nm was observed due to n–π^* transition. The trans isomer of azobenzene shows an LC phase because the molecule possesses a rodlike shape, while the cis isomer exhibits no LC phase due to its bent shape (see Figure 1). Each isomer produces different environments on the host LC within a polymer matrix as illustrated in Figure 7. The *trans*-azobenzene stabilizes the phase structure of the host LC, so that in the initial state AzoCFs exhibited a light-scattering state due to random orientation of the LC domains. Photoirradiation of AzoCFs results in perturbation of the LC phase with a concomitant decrease of T_{NI} as the amount of *cis*-azobenzene increases. When T_{NI} of the LC is lowered below the irradiation temperature, the isothermal N–I phase transition is induced at the irradiated sites (path A in Figure 7). In AzoCF-4, the increase of the transmittance on photoirradiation is due to the N–I phase transition induced by accumulation of *cis*-BMAB.

Effect of Light Intensity on Optical Behavior. In AzoCF-4, the effect of light intensity on the change in transmittance was evaluated at room temperature. The light intensity at 366 nm was varied from 1.0 to 20 mW/cm^2 by using neutral density filters. The photochemical phase transition behavior of the LC domains within the polymer matrix was affected by the light intensity as shown in Figure 8. The response time of the N–I phase transition (τ_{N-I}) was defined as the time necessary to increase the transmittance of the probe light to 90% of the saturated value. The transparent state (95% in transmittance) was observed at any light intensity and the response time, τ_{N-I}, decreased with

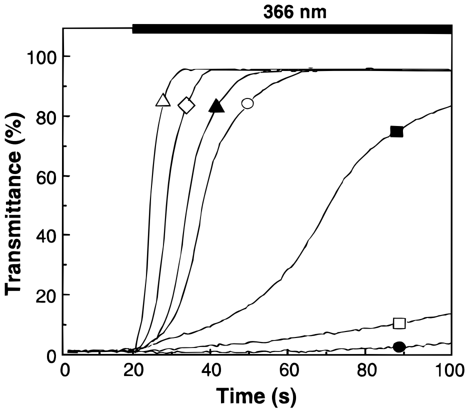

Figure 8. Optical behavior of AzoCF-4 on photoirradiation at 366 nm at various light intensities: ●, 1.0 mW/cm^2; □, 1.5 mW/cm^2; ■, 3.0 mW/cm^2; ○, 6.6 mW/cm^2; ▲, 11 mW/cm^2; ◇, 14 mW/cm^2; △, 20 mW/cm^2.

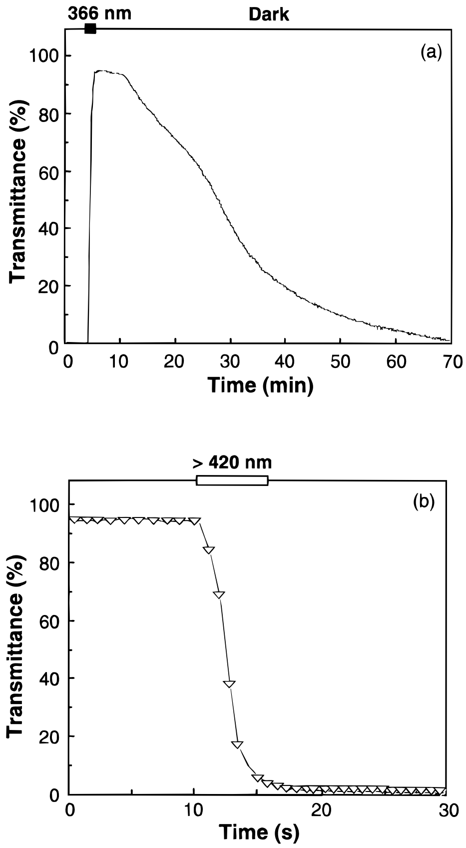

Figure 9. Restoration of the initial light-scattering state of AzoCF-4 thermally (a) and by irradiation at >420 nm (b): ■, irradiation at 366 nm; □, irradiation at >420 nm.

increasing the light intensity. This result may be closely related to the amount of *cis*-azobenzenes photochemically produced. The amount of the *cis*-azobenzenes produced per unit time is dependent on the intensity of the 366 nm light. Therefore, the difference in τ_{N-I} of the composite films would be due to the difference in the amount of the cis form of azobenzene as a function of irradiation time.

Change in Transmittance Induced by I−N Phase Transition. The restoration behavior from the transparent state to the initial light-scattering state was investigated for AzoCF-4. Figure 9a shows a typical example of the change in transmittance of the probe light on thermal recovery. When AzoCF-4 was kept in the dark at room temperature after irradiation at 366 nm, the transmittance of the probe light was recovered thermally to the initial value after 1 h. Figure 9b shows the change in transmittance induced by >420 nm light at room temperature. The transparent sample, induced by irradiation at 366 nm, was restored immediately to the initial light-scattering state on photoirradiation. These recovery processes to the initial light-scattering state are closely related to the cis−trans back-isomerization of the guest azobenzene molecules. The cis−trans isomerization leads to the realignment of the host LCs, i.e., the I to N phase transition, and simultaneously the composite film shows the initial light-scattering state, due to the nonuniform LC director, generated by surface anchoring of the solid polymer matrix (path B in Figure 7). The time required for the I−N phase transition induced by the visible light was much shorter than that for the thermal phase transition. The irradiation at >420 nm, thus, is effective to restore the initial state. Similar results were also observed for the other composite films with the azobenzene.

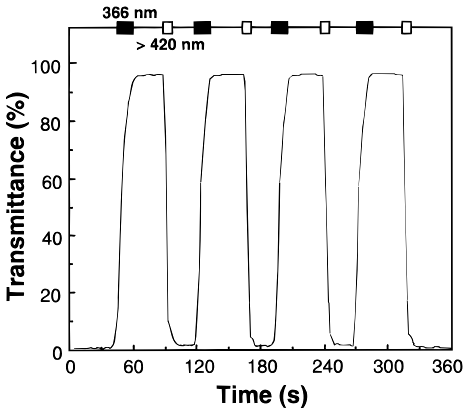

Figure 10. Reversible change in transmittance of AzoCF-4 induced by alternating irradiation at 366 and >420 nm: ■, irradiation at 366 nm; □, irradiation at >420 nm.

Optical Switching Behavior. As mentioned above, the control of the optical property of the composite films between the light-scattering and the transparent states could be achieved by the photochemical phase transition between the LC and the I phases based on the photoisomerization of the azobenzene guest molecules. As shown in the Figure 10, the optical property of AzoCF-4 could be controlled repeatedly between the light-scattering and the transparent states by alternating irradiation at 366 and >420 nm. Such an optical control between the two states was also observed for the other AzoCFs containing the photoresponsive molecule. It was found that AzoCFs act as an optical switching device without polarizers.

Furthermore, we explored the effect of the irradiation temperature on the optical control between the two states. The photochemical phase transition is induced by the lowering of T_{NI} as described before, so that the temperature of AzoCFs under irradiation is important. Similarly to the τ_{N-I}, we define the response time of the I−N phase transition (τ_{I-N}) as the time required to recover the transmittance of the probe light to 10% of the saturated value. In Figure 11, the response times were plotted against the irradiation temperature on AzoCF-4. The response times were considerably influ-

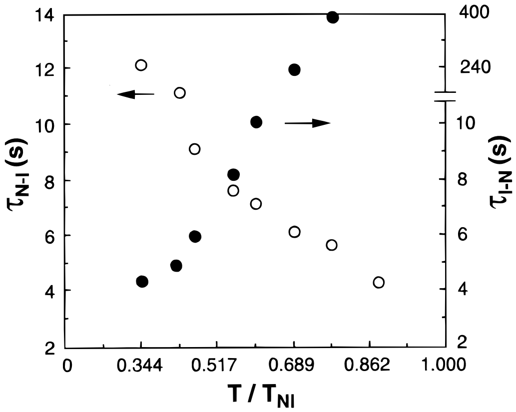

Figure 11. Dependence of irradiation temperature on the response times for AzoCF-4: ○, τ_{N-I}; ●, τ_{I-N}.

enced by the irradiation temperature. The τ_{N-I} decreased while the τ_{I-N} increased as the temperature approached T_{NI}. This optical behavior as a function of the temperature can be interpreted in terms of stability of the LC phase in the initial state before irradiation. The stability of the LC phase decreases as the temperature approaches T_{NI} because an increase in the temperature leads to an increase in heat fluctuation which always accelerates the transition to the disordered state. Thus, the transition from an ordered N phase (a light-scattering state) to a disordered I phase (a transparent state) can be induced more easily when the perturbation by the trans−cis photoisomerization of the guest molecules is applied. On the other hand, the transition from the disordered I phase to the ordered N phase becomes unfavorable under heat fluctuation, which explains the slower recovery of the ordered state (the light-scattering state) as shown in Figure 11.

Conclusion

All-optical control based on photochemical phase transition has been studied in polymer/LC composite films which contain the azobenzene LC as a photochromic guest molecule. The light-scattering state of AzoCFs was obtained by thermal polymerization-induced phase separation, and the optical property of the composite film was governed not only by the polymerization conditions but by their compositional ratio. It was found that the reversible phase transition of AzoCFs was induced photochemically and led to repeatable change between light-scattering and transparent states. The response time was dependent on the light intensity and the irradiation temperature. The degree of the change in transmittance was affected by the amount of the guest azobenzene molecules. AzoCF-4 containing an optimal amount of the azobenzene showed the highest contrast and a complete transparent state on photoirradiation at 366 nm.

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