

Photochemical Phase-Transition Behavior of Polymer Liquid Crystals Induced by Photochemical Reaction of Azobenzenes with Strong Donor–Acceptor Pairs

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The photochemical phase-transition behavior of polymer liquid crystals (LCs) containing azobenzene moieties with strong donor–acceptor substituents has been investigated. Copolymers of a mesogen and a donor–acceptor azobenzene were prepared. Photoirradiation of a thin film of the polymer LCs (100–200 nm thickness) in the nematic (N) phase caused an N-to-isotropic (I) phase transition due to trans–cis photoisomerization of the azobenzene moiety, and the N phase recovered rapidly when photoirradiation was ceased because of cis–trans thermal back-isomerization. Time-resolved measurements with a laser pulse (532 nm; 10 ns, fwhm) revealed that the N–I phase transition took place in 300 μ s. The thermal recovery of the N phase in the polymer LC with a donor–acceptor azobenzene, which stabilized the LC phase, occurred in 8 ms at 146 °C. This response of the recovery is 10^3 times faster than that of non-donor–acceptor azobenzene LCs. In a sample that showed a smectic (S) phase, however, no photochemical phase transition was observed. These phenomena are interpreted in terms of the stability of the LC phase.

Introduction

Liquid crystals (LCs) show large optical anisotropy, and one can control the optical anisotropy by changing the alignment of the LC molecules with an electric field. Thus, nematic (N) LCs have been used widely as active media in display devices. Recently, control of alignment of LC molecules with light instead of an electric field has been studied intensively because the photoresponsive LC systems are of interest in view of their potential for optical switching and image-storage materials.^{2–9}

We have reported that we could control the phase structure of low-molecular-weight and polymer LCs by photochemical reaction of photochromic molecules such as azobenzene and spiropyran derivatives.^{10–13} For example, the trans form of the azobenzene derivatives stabilizes the LC phase when dispersed in the LC phase because their molecular shape (rodlike) is similar to that of the host LC molecules. On the other hand, the cis isomer shows a bent shape and destabilizes the LC phase. When we induced the trans–cis photoisomerization of the azobenzenes, we observed the LC-to-isotropic (I) phase transition induced isothermally. Recently, we found that the photochemical N–I phase transition took place in 200 μ s with a single laser pulse in low-molecular-weight and polymer LCs with an azobenzene moiety in each mesogen.^{14–18} When the irradiated sample was kept in the dark, the initial N phase was restored thermally because of the cis–trans thermal back-isomerization of the azobenzenes. Hence, we can expect that the photochemical phase transition of the azobenzene LCs may be utilized for all-optical switching and real-time holography. However, the response time of the thermal recovery of the N phase is not satisfactory: the thermal recovery of the N phase took place in

several seconds above 100 °C and this response of the recovery was 10^4 time slower than that of the photochemical phase transition.

The thermal I–N phase transition is composed of two processes: thermal cis–trans back-isomerization of the azobenzene moieties and reorientation of the mesogens.¹⁵ We found that the thermal recovery of the N phase took place quickly in a polymer azobenzene LC with an alkoxy group as an electron donor and a cyano group as an acceptor,¹⁹ since the cis–trans isomerization process was accelerated with the donor–acceptor pair.²⁰ It is known that the thermal cis–trans isomerization of the azobenzene with stronger donor–acceptor pairs becomes faster.^{21,22} If we provide the azobenzene moiety with a stronger donor–acceptor pair in polymer LCs, the thermal I–N phase transition may occur more quickly. In this article, we report the photochemical N–I phase-transition behavior and the thermal I–N phase-transition behavior of polymer LCs containing azobenzene moieties with strong donor–acceptor pairs.

Experimental Section

Materials. Structures of the polymer LCs used in this study are shown in Figure 1. All the polymers contain azobenzene moieties with a tertiary amine as an electron donor and a nitro group as an acceptor. **P-1** and **P-2** were synthesized as reported by Robello.²³ **P-3**, which contained a piperazine moiety in the donor unit, was prepared through modification of the method reported previously.²⁴ Polymerization was conducted in *N,N*-dimethylformamide (DMF) with 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

Characterization of Polymer LCs. The molecular weight of the polymers was determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 \times 2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. The LC behavior and phase-transition

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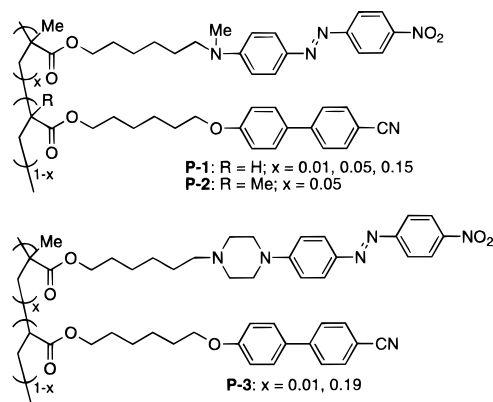
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TABLE 1: Phase-Transition Temperature of LCs and Molecular Weight of Polymers Used in This Study^a

polymer	mole fraction of azobenzene	M_n	M_w/M_n	phase-transition temp, °C	ΔH_{LC-I} , kJ mol ⁻¹	ΔS_{LC-I} , J mol ⁻¹ K ⁻¹
P-1a	0.01	5800	1.8	G 34 N 121 I	0.70	1.8
P-1b	0.05	15000	1.3	G 27 N 110 I	0.53	1.4
P-1c	0.15	9300	1.7	G 35 N 104 I	0.50	1.3
P-2	0.05	31000	1.4	G 33 S 105 I	2.1	5.6
P-3a	0.01	13000	1.4	G 30 N 116 I	0.49	1.3
P-3b	0.19	16000	1.5	G 38 N 156 I	1.0	2.3

^a Abbreviations: G, glass; N, nematic; S, smectic; I, isotropic; M_n , number-average molecular weight; M_w , weight-average molecular weight; ΔH_{LC-I} , change in enthalpy of LC–I phase transition; ΔS_{LC-I} , change in entropy of LC–I phase transition.

**Figure 1.** Structures of polymer LCs used in this study and their abbreviations.

behavior were examined by polarizing microscopy (Olympus model BH-2, Mettler hot-stage models FP-90 and FP-82) and X-ray diffractometry (MAC Science MXP, equipped with a thermal controller, model 5301). The thermodynamic properties of LCs were determined by differential scanning calorimetry (DSC, Seiko I&E SSC-5200 and DSC220C) at a heating and cooling rate of 10 °C/min. At least three scans were performed for each sample to check reproducibility. The thermodynamic properties are given in Table 1.

Photochemical Phase Transition. Polymer LCs were dissolved in tetrahydrofuran (THF, spectroscopic grade) at a low concentration ($\sim 10^{-3}$ mol/L), and a small portion of the resultant solution was cast on a glass substrate that had been coated with poly(vinyl alcohol) (PVA) and rubbed to align mesogens. After the solvent was removed completely under the reduced pressure at room temperature, the LC film was annealed for 12 h at a temperature just below the LC-to-I phase-transition temperature to yield a monodomain of a well-aligned LC phase. The thickness of the LC films was estimated as 100–200 nm by absorption spectroscopy on the basis of molar extinction coefficients of the azobenzene moieties. The LC films were placed in a thermostated block and irradiated with steady light at 488 nm from an Ar⁺ laser (National Laser Co., H210). The intensity of the linearly polarized light at 633 nm from a He–Ne laser (NEC, GLG5370, 1 mW) transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

The time-resolved measurements of the photochemical phase transition of the polymer LCs were performed as follows. The LC film was thermostated and set between two crossed polarizers. The sample was irradiated with a single pulse of a Nd:YAG laser (Spectron, SL805 laser system; the second harmonic, 532 nm; 10 ns, fwhm), and the transmittance of a probe light through crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded with a storage scope (Iwatsu, DS-8631).

Photoisomerization of Azobenzenes. Photoisomerization behavior of the azobenzenes in the LC phase was evaluated by transient absorption spectroscopy with a spectroscopic multi-channel analyzer (SMA; Princeton, IDPDA-512G/B) as a detector. The film of the polymer LCs was excited with a laser pulse at 532 nm under exposure to an analyzing light from a Xe flash lamp. The analyzing light that passed through the LC film was collimated on a Jobin-Yvon HR-320 monochromator, and its intensity was measured with the SMA (gate width: 800 ns) synchronized with the analyzing light with a delay generator.

Results and Discussion

LC Behavior of Polymers. It was observed with a polarizing microscope that all the polymers used in this study showed the LC phase. Phase structures and phase-transition temperatures are summarized in Table 1. As listed in Table 1, **P-1** and **P-3** exhibited the N phase while **P-2** exhibited the smectic (S) phase. The annealing of the LC films at temperature just below their LC–I phase-transition temperature gave a well-aligned monodomain of the LC phase.

In **P-1**, the temperature range of the N phase becomes narrow with increasing mole fraction of the azobenzene. This suggests that the azobenzene incorporated in **P-1** destabilized the phase structure of the N phase. On the other hand, the temperature range of the N phase in **P-3** increased with an increase of the azobenzene content in the copolymer. Thus, we can consider that the azobenzene in **P-3** stabilized the N phase. The thermodynamic data (change in enthalpy and entropy of LC–I phase transition) supported these assumptions. The *N*-methyl substituent of the azobenzene in **P-1** occupies some pocket in the side of the molecule. In general, introduction of a substituent in such a way that it extrudes from the long axis of the mesogenic core tends to decrease the thermal stability of the N phase.^{25,26} As a result, the N phase in **P-1** was destabilized with increasing azobenzene content. In contrast, the azobenzene in **P-3**, which has a three-ring structure in the core unit, stabilized the N phase because increasing the number of ring units enhances the N–I phase-transition temperature.²⁶ Therefore, **P-3** with a larger amount of the azobenzene shows a higher N–I phase-transition temperature.

Isomerization Behavior of Azobenzenes. Figure 2 shows the time-resolved absorption spectra of the polymer films in the LC phase (at 100 °C). The absorption maximum appeared at around 500 nm in the absorption spectra because of a π – π^* transition of the *trans*-azobenzenes.²⁰ The absorbance at the π – π^* band was reduced (negative transient absorption was observed) by irradiation with a laser pulse at 532 nm in the LC phase owing to *trans*–*cis* photoisomerization of the azobenzene moieties.²¹ After pulse irradiation, the absorbance recovered almost completely in 2 ms at 100 °C because of the *cis*–*trans* thermal back-isomerization. The *trans*–*cis* photoisomerization and the *cis*–*trans* thermal isomerization of the azobenzene

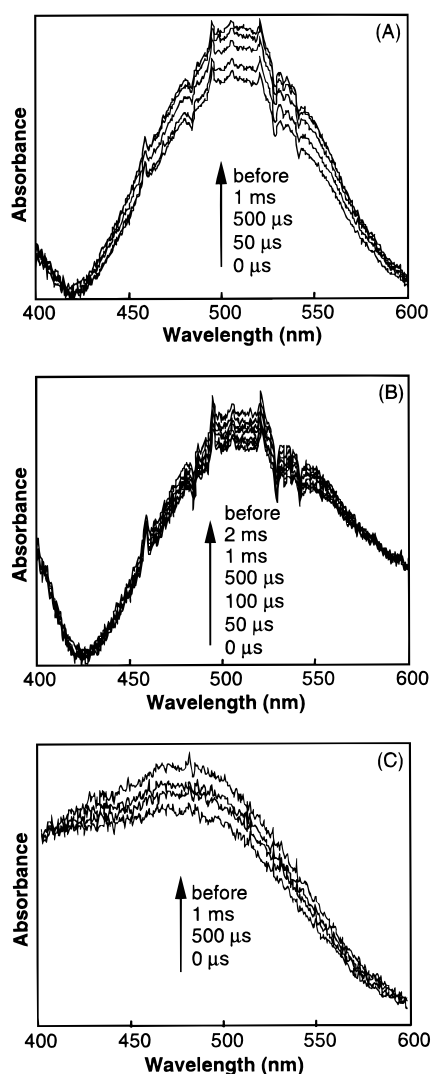


Figure 2. Time-resolved absorption spectra of polymer LC films in the LC phase at 100 °C: (A) **P-1b** in N phase; (B) **P-2** in S phase; (C) **P-3b** in N phase. Delay times after pulse irradiation are indicated in the figure.

moieties were observed in both the N phase (parts A and C of Figure 2) and the S phase (Figure 2B).

Photochemical Phase-Transition Behavior of Polymer NLCs. Effect of Mole Fraction of Azobenzene Moiety. Linearly polarized light at 633 nm from a He–Ne laser could transmit through a pair of crossed polarizers, with the LC film between them, owing to the birefringence of the polymer LC. As shown in Figure 3 for **P-1b**, the transmittance of the probe light decayed immediately upon irradiation at 488 nm in the N phase. This was caused by the photochemical N-to-I phase transition of the polymer LC due to the *trans*–*cis* photoisomerization of the azobenzene moiety.^{14,15} When the irradiated film was kept in the dark, the transmittance recovered completely. Because the *trans*-azobenzene was restored thermally, the initial N phase appeared when photoirradiation was ceased. The photochemical N–I and the thermal I–N phase transitions could be induced repeatedly by irradiation at 488 nm.

Figure 4 shows the time-resolved measurements of the photochemical N–I phase transition in the polymer LCs of the **P-1** series. To discuss the phase-transition behavior quantitatively, the response time of the N–I phase transition was defined as the time necessary to reduce the transmittance of the probe light to 10% of the maximum value. Similarly, we defined the

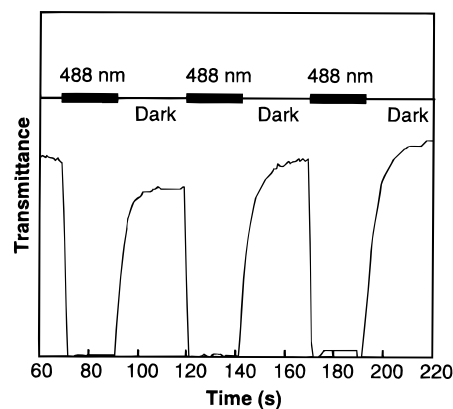


Figure 3. Photochemical N–I and thermal I–N phase transitions of **P-1b**. Photoirradiation at 488 nm (27 mW/cm²) was performed at 100 °C.

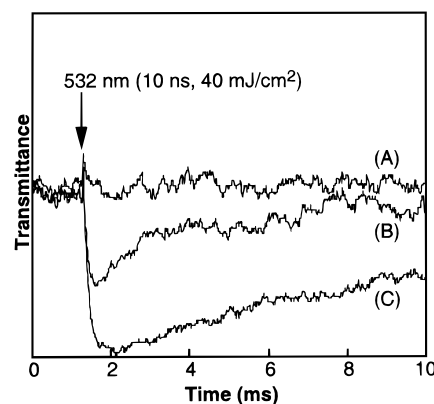


Figure 4. Time-resolved measurements of photochemical N–I phase transition of **P-1**: (A) **P-1a**; (B) **P-1b**; (C) **P-1c**. Laser pulse irradiation at 532 nm (40 mJ/cm²; 10 ns, fwhm) was carried out at 100 °C.

response time of the I–N phase transition as the time required to restore the transmittance to 90% of the maximum value. The N–I phase transition was induced completely in 300 μ s in the polymer with the azobenzene moieties of 15 mol % (**P-1c**). This response in **P-1c** is the same as that in the non-donor–acceptor azobenzene LCs reported previously.^{14,15} In **P-1b** with the azobenzene of 5 mol %, however, the transmittance of the probe light decreased only to about half of the level in the I phase by irradiation with a laser pulse of the same power. This means that the photochemical phase transition was induced only locally in **P-1b**.¹⁸ Furthermore, no change in the transmittance of the probe light was observed in **P-1a**, which contained the azobenzene of only 1 mol %. Thus, the photochemical phase transition could not occur in **P-1a**. The photochemical N–I phase transition of the **P-1** series depended strongly on mole fraction of the azobenzene moiety.

A similar photochemical N–I phase-transition behavior was also observed in **P-3b** at 146 °C (Figure 5). The photochemical N–I and the thermal I–N phase transitions were also caused repeatedly by laser-pulse irradiation (Figure 6). Moreover, the same dependence on the mole fraction of the azobenzene moiety was observed in the photochemical phase transition of the **P-3** series: the photochemical phase transition was not observed in **P-3a**. We therefore can conclude that there is a threshold concentration of the azobenzenes in the photochemical phase transition of the polymer LCs. In the polymer LCs with the azobenzene moieties of more than 10 mol %, perturbation in the form of the *trans*–*cis* photoisomerization of the azobenzenes was propagated through the LC phase, and the N–I phase-transition temperature was lowered, depending on the concentra-

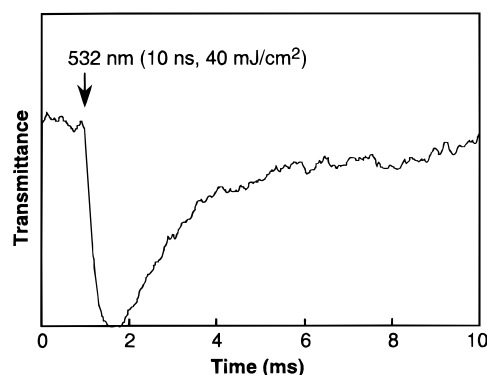


Figure 5. Time-resolved measurement of photochemical phase transition of **P-3b**. Irradiation with a laser pulse at 532 nm (40 mJ/cm^2) was performed at 146°C ($T_{\text{red}} = 0.974$).

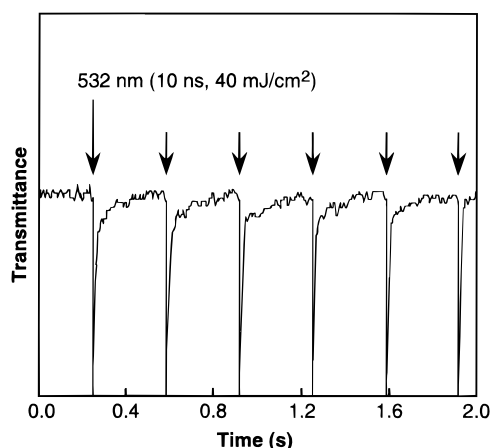


Figure 6. Photochemical N-I and thermal I-N phase transitions of **P-3b** induced by repeated irradiation with laser pulses at 532 nm (40 mJ/cm^2) at 134°C . Repetition rate of the pulse irradiation was 3 Hz.

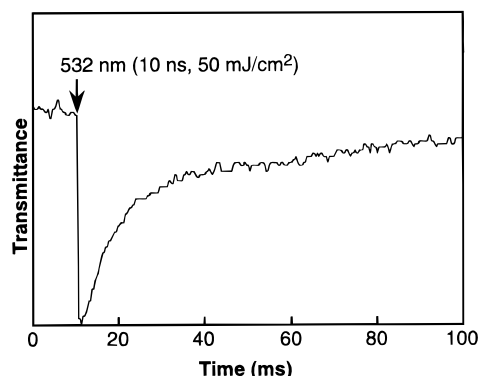


Figure 7. Time-resolved measurement of thermal I-N phase transition of **P-1c** at 95°C ($T_{\text{red}} = 0.974$).

tion of the cis isomer.²⁷ Consequently, orientational relaxation of the mesogens occurred and the N-I phase transition took place completely. In the polymer LCs with the azobenzene moiety of less than 5 mol %, however, the perturbation of the photoisomerization was not enough to bring about the relaxation of the mesogens completely. The photochemical N-I phase transition, therefore, cannot be induced in the polymer LCs with an azobenzene moiety of less than the threshold concentration.

Thermal I-N Phase-Transition Behavior of the Polymer LCs. Effect of Structure of Azobenzene Moiety. Figure 7 shows the time-resolved measurement of the thermal I-N phase transition in **P-1c**. It became apparent that the N phase recovered thermally in 50 ms at 95°C in **P-1c**. As shown in

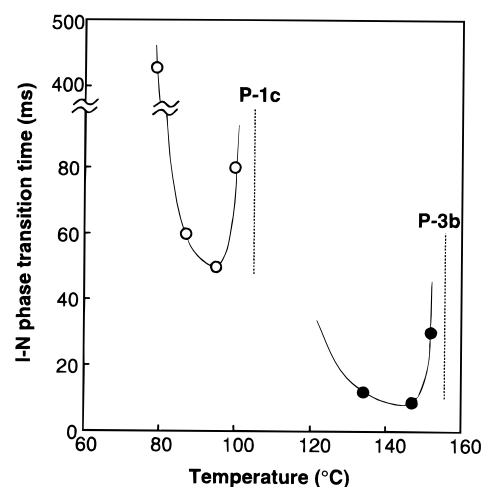


Figure 8. Temperature dependence of the response time of the thermal I-N phase transition: (○) **P-1c**; (●) **P-3b**. Dotted line indicates the N-I phase-transition temperature of the polymer LCs.

Figure 5, however, the thermal I-N phase transition in **P-3b** occurred in 8 ms at 146°C . We reported previously that the thermal recovery of the N phase in the non-donor-acceptor azobenzene LCs took place in 7–8 s at 145°C because the thermal cis-trans isomerization process needed a time scale of several seconds to take place.^{14,15} The thermal cis-trans isomerization of the donor-acceptor azobenzenes, however, proceeded very effectively; it occurred almost completely in 2 ms at 100°C (Figure 2).^{28–34} Thus, the response of the I-N phase transition in the present polymer LCs was faster by 2–3 orders of magnitude than that in the non-donor-acceptor azobenzene LCs. The recovery of the N phase in **P-1c** involved a fast response mode and a slow response mode, while that in **P-3b** involved a single mode. The fast process of **P-1c** may be related to the reorientation of the cyanobiphenyl mesogen, and the slow process may be attributed to the reorientation of the azobenzene moiety that destabilized the LC phase.

Figure 8 shows the temperature dependence of the response time of the thermal I-N phase transition in **P-1c** and **P-3b**. In both **P-1c** and **P-3b**, the photochemical phase transition was not induced completely below about 30°C below their N-I phase-transition temperatures. The N phase appeared more slowly at lower temperatures in both samples. Since the rate of the thermal cis-trans isomerization of the azobenzenes and the mobility of the mesogens decreased with decreasing temperature, the isomerization and reorientation process took place ineffectively. Consequently, the I-N phase transition was slower at lower temperature. In addition, the thermal recovery of the N phase became slower at a temperature just below the N-I phase-transition temperature. At this temperature, although the cis-trans isomerization occurred quickly, the order parameter and the stability of the LC phase decreased because the mobility of the mesogen is similar to that in I phase.¹⁸ Therefore, the reorientation process was depressed and the recovery of the N phase was slow.

It is difficult to compare the thermal I-N phase-transition behavior in **P-1c** and **P-3b** at the same temperature because the temperature range in which the photochemical phase transition took place was different. We therefore discussed it at the same reduction temperatures (T_{red}). T_{red} was defined as the ratio of the measurement temperature divided by their N-I phase-transition temperature. The T_{red} for **P-1c** at 95°C ($T_{\text{red}} = 0.974$) was the same as that for **P-3b** at 146°C . At this temperature, the N phase recovered in 50 ms in **P-1c** (Figure 7) while it

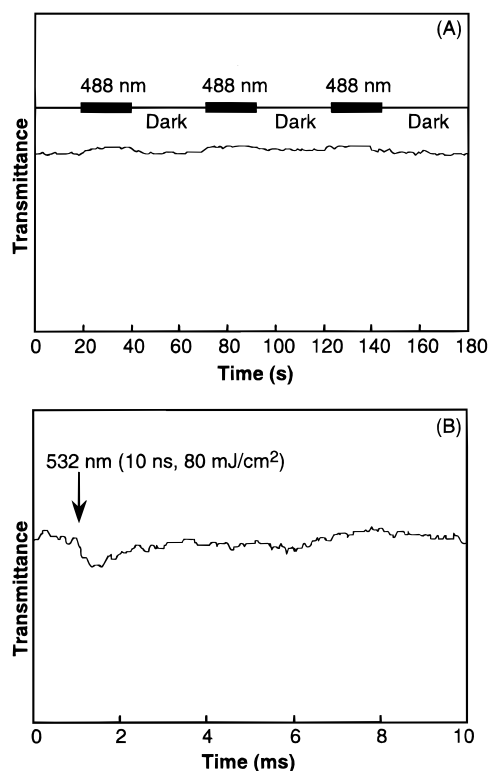


Figure 9. Photoresponse of **P-2** in the S phase: (A) irradiation with steady light at 488 nm (27 mW/cm²) at 100 °C; (B) irradiation with a single pulse of laser at 523 nm (80 mJ/cm²) at 95 °C.

recovered in 8 ms in **P-3b** (Figure 5). As described above, the cis isomer of the azobenzenes in both polymers showed nearly the same lifetimes: it disappeared almost completely in 2 ms. Hence, the difference in the response time of the thermal I–N phase transition between these polymers may be interpreted as the reorientation process of the mesogens, which plays a crucial role in the phenomena. Although the isomerization process took place in 2 ms, the N phase recovered in 50 ms in **P-1c**. This suggests that the reorientation of the mesogens in **P-1c** needs a time scale of about 50 ms to take place. This slow reorientation of **P-1c** may be due to the instability of the LC phase. Since the azobenzene introduced in the **P-1** series destabilizes the N phase, the reorientation process was depressed and occurred slowly. The azobenzene introduced in the **P-3** series, however, stabilizes the LC phase, and the reorientation process of **P-3b** may proceed more effectively than that of **P-1c**. As a result, **P-3b** showed a faster response in the thermal I–N phase transition.

Effect of Phase Structure on Photochemical Phase Transition. In the N phase, when the azobenzene moiety stabilized the LC phase, the thermal recovery of the N phase became faster. From these results, we can expect that the thermal recovery of the LC phase may be brought about more quickly when we induce the photochemical phase transition in a more stable LC phase, such as an S phase. Thus, we investigated the photochemical phase-transition behavior of the polymer LC in the S phase. In **P-2**, which showed the S phase, however, no change in the transmittance of the probe light was observed even though the sample was irradiated with a laser pulse of very high power (80 mJ/cm²) (Figure 9). This means that we could not induce the photochemical phase transition of the polymer LC in the S phase under the present experimental condition. In the S phase, the mesogens form a more stable LC phase than in the N phase. In the S phase, therefore, it may need a larger amount of the azobenzene to destroy the phase structure than in the N phase.

Namely, the threshold concentration of the azobenzene was higher in the S phase and the photochemical phase transition could not occur in **P-2**.

Conclusion

The photochemical phase transition of the polymer LCs with donor–acceptor azobenzenes was induced in 300 μ s by irradiation with a laser pulse to bring about the trans–cis photoisomerization of the azobenzene. When the irradiated sample was kept in the dark, the initial N phase was restored immediately owing to the thermal cis–trans back-isomerization. The photochemical phase transition of the polymer LCs depended strongly on mole fraction of the azobenzene; it required a larger amount of the azobenzene than a threshold concentration. Furthermore, the photochemical phase transition was influenced by the phase structure of the LC phase.

The thermal recovery of the N phase was affected by the structure of the azobenzene moiety. When the azobenzene with a strong donor–acceptor pair stabilized the N phase, the cis–trans thermal isomerization and the reorientation of the mesogen proceeded effectively. Thus, the thermal I–N phase transition occurred very quickly; it took 8 ms at 146 °C. The polymer LCs with donor–acceptor azobenzenes, therefore, are potential all-optical-switching and real-time-holography materials.

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