

Photochemical Phase Transition Behavior of Nematic Liquid Crystals with Azobenzene Moieties as Both Mesogens and Photosensitive Chromophores

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Modulation of light by light as stimulus has been explored by the use of liquid-crystalline (LC) materials with photosensitive moieties. Azobenzene derivatives with monomeric and polymeric forms were prepared, which show nematic (N) LC behavior in the *trans* form and no LC phase in the *cis* isomer. Photoirradiation of a very thin film of the liquid-crystalline azobenzene derivatives (~ 200 nm) in the *trans* form resulted in the disappearance of the N phase because of *trans*–*cis* photoisomerization of each mesogen, and the N phase recovered quickly when the irradiated sample was kept in the dark in the whole temperature range where the azobenzene LCs showed the N phase because of *cis*–*trans* thermal isomerization. Time-resolved measurements by the use of a laser pulse (355 nm, 10 ns fwhm) revealed that the N-to-isotropic (I) phase transition took place in 200 μ s in both monomeric and polymeric systems. This response is at least 1 order of magnitude faster than the response of nematic LCs previously reported.^{1,2} In the polymer system the N–I phase transition was also induced in 200 μ s even below T_g . The isotropic glass state induced by photoirradiation in the polymer sample below T_g was stable at room temperature for a long period even after the *trans* form was restored by the thermal back-isomerization.

Introduction

Low molecular weight nematic liquid crystals have been extensively used as active media in display devices. However, their time is not satisfactory (greater than several milliseconds). Although ferroelectric liquid crystals show quicker response on a time scale of less than a millisecond to a change in the electric field, cell fabrication needs a cell gap within 2 μ m and no short-circuiting between two electrodes. Owing to this strict requirement, exploitation of ferroelectric liquid crystals in display devices is difficult at present and nematic liquid crystals (NLCs) are still in major use.

Photochromic compounds, such as azobenzene and spiropyran, change their molecular structure on photoirradiation. This property has been widely used to control the orientation of liquid crystals (LCs).^{1–10} For example, the *trans* form of azobenzene derivatives can stabilize the LC phase when dispersed in the LC phase because the shape of the molecule is rod-like. On the other hand, the *cis* isomer destabilizes the LC phase because its shape is bent. Therefore, the *trans*–*cis* photoisomerization of the azobenzene in the LC phase can induce disorganization of the phase structure. This is the basis of the photochemical phase transition of NLCs and of the novel photon-mode response of ferroelectric LCs.^{9,10}

Isothermal phase transition of LCs may be brought about reversibly by a photochemical reaction of photochromic compounds dispersed in the LC phase at concentrations of 1–5 mol %. Time-resolved measurements using a pulsed laser have shown that the photochemical nematic (N)–isotropic (I) phase transition takes place on a time scale of 50–200 ms for the N hosts of low molecular weight and polymeric LCs.^{1,2} Propagation of perturbation in the form of the *trans*–*cis* isomerization

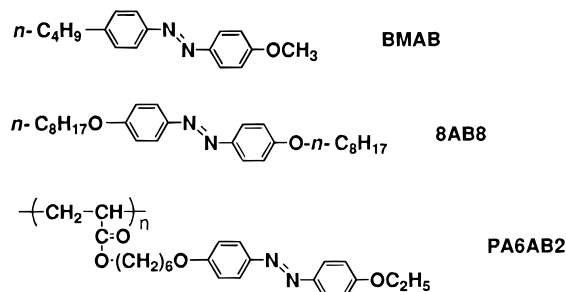


Figure 1. Structures of LCs used in this study and their abbreviations.

of a small amount of the photochromic molecules may require a relatively long time in the LC systems.

Photoisomerization of photochromic molecules is a fast process. The *trans* form of some azobenzene derivatives shows an N phase, while the *cis* form shows no LC phase, and *trans*-azobenzene can be isomerized to the *cis* form instantaneously with the aid of a short pulsed laser. Therefore, the disappearance of the LC phase may be induced in principle on the same time scale as the *trans*–*cis* photoisomerization with the laser pulse.¹¹ In this article, we report the photochemical phase transition behavior of very thin films of low molecular weight and polymeric NLCs composed of photosensitive azobenzenes that also act as mesogens in the *trans* form.

Experimental Section

Materials. Structures of the LCs used in this study are shown in Figure 1. 4-Butyl-4'-methoxyazobenzene (BMAB) and 4,4'-di(4-octyloxyphenyl)azobenzene (8AB8) were synthesized and purified as reported previously.^{6,12} Poly[6-[4-(4'-ethoxyphenylazo)phenoxy]hexyl acrylate] (PA6AB2) was prepared by the method reported by Angeloni et al.¹³ Polymerization was conducted in *N,N*-dimethylformamide (DMF) by the use of 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

Characterization of LCs. The molecular weight (MW) of the polymer was determined by gel permeation chromatography

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TABLE 1: Thermodynamic Properties of LCs and MW of Polymer Used in This Study^a

	M_n	M_w/M_n	phase transition temp, °C	ΔH_{NI} , kJ mol ⁻¹	ΔS_{NI} , J mol ⁻¹ K ⁻¹
BMAB			K 35 N 48 I	0.35	1.1
8AB8			K 99 N 113 I	1.6	4.2
PA6AB2	9100	1.3	G 45 N 155 I	0.84	2.0

^a M_n , number-average molecular weight; M_w , weight-average molecular weight; K, crystal; N, nematic; I, isotropic; G, glass; ΔH_{NI} , change in enthalpy of N–I phase transition; ΔS_{NI} , change in entropy of N–I phase transition.

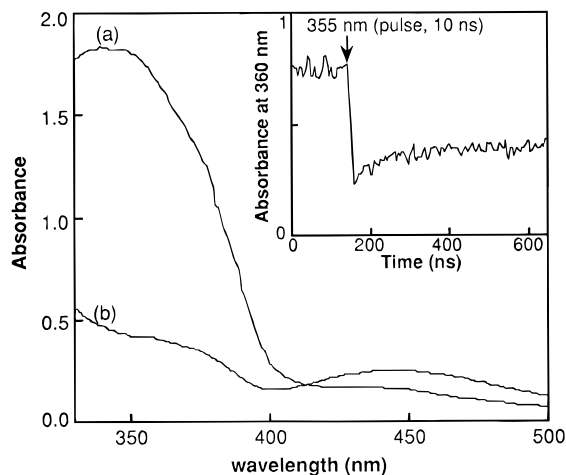


Figure 2. Absorption spectra of BMAB film (a) before irradiation and (b) after irradiation at 366 nm from mercury lamp. The inset contains the time-resolved measurement of the change in absorbance of the BMAB film at 360 nm by laser pulse irradiation (355 nm; 10 ns, fwhm). Measurement was performed at 35 °C where BMAB showed an N phase.

(GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. Liquid-crystalline behavior and phase-transition behavior were examined on an Olympus Model BH-2 polarizing microscope equipped with Mettler hot-stage Models FP-90 and FP-82. Thermotropic properties of LCs were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. At least three scans were performed for each sample to check reproducibility. The thermodynamic properties of the LCs and MW of the polymer are given in Table 1.

Absorption spectra were recorded with a Shimadzu UV-200S absorption spectrometer.

Photoinduced Phase Transition. Azobenzene derivatives were dissolved in chloroform (spectroscopic grade) at a low concentration ($\sim 10^{-3}$ mol/L), and a small portion of the resultant solution was cast on a glass plate that had been coated with poly(vinyl alcohol) and rubbed to align mesogens. After the solvent was removed, the LC film was annealed at a temperature (at 45, 110, and 150 °C for BMAB, 8AB8, and PA6AB2, respectively) just below the N-to-I phase transition temperature (T_{NI}) to yield a monodomain of a well-aligned N phase. The thickness of the LC films was estimated as ~ 200 nm by absorption spectroscopy on the basis of molar extinction coefficients of the azobenzene moieties. The LC films thus prepared were placed in a thermostated block, and photoinduced phase transition behavior of the LC films was followed by means of an apparatus already reported.¹⁴ The films were irradiated at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35 + IRA-25), and the intensity of the linearly polarized light at 830 nm from a diode

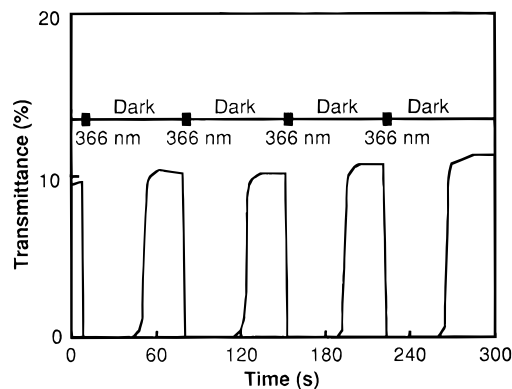


Figure 3. Photochemical N–I phase transition and thermal I–N transition of 8AB8. Photoirradiation was performed at 110 °C.

laser transmitted through a pair of crossed polarizers, between them the sample film was placed, was measured with a photodiode.

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 third harmonic, 355 nm; 40 mJ/cm²; 10 ns, fwhm), and the transmittance of the probe light (NEC, GLG5370 He–Ne laser; 633 nm; 1 mW) through crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded using a storage scope (Iwatsu, DS-8631).

For the time-resolved observation of the *trans*–*cis* photoisomerization of azobenzene derivatives, the laser pulse at 355 nm was also used as an excitation source. The analyzing light from a Xe flash lamp was irradiated synchronously on the LC film. The analyzing light passed through the LC film and was collimated on a Jobin-Yvon HR-320 monochromator. The intensity of the analyzing light at 360 nm was measured using a photomultiplier and recorded using the storage scope.

Results and Discussion

***Trans*–*Cis* Photoisomerization Behavior of Azobenzene LCs.** The absorption spectra of *trans*-azobenzenes exhibit their absorption maxima at around 350 nm due to a π – π^* transition and at around 450 nm due to an n – π^* transition. It was observed that irradiation at 366 nm induced *trans*–*cis* isomerization of the azobenzene moiety in the N phase (Figure 2). Time-resolved measurement of the change in absorbance at 360 nm showed that the *trans*–*cis* photoisomerization occurred within 20 ns in the N phase (Figure 2, inset). The absorbance at 360 nm decreased abruptly on pulse irradiation and then increased slightly. This increase in absorbance at a later stage may be interpreted in terms of a rise in temperature due to the laser pulse irradiation. The rise in temperature caused a change in density of BMAB with concomitant variation of refractive index. The change in the refractive index altered the transmittance of the analyzing light and could be observed as the change in absorbance. Consequently, absorbance at 360 nm increased slightly.

Phase Transition Behavior of Low Molecular Weight LCs. It was observed with a polarizing microscope that the *trans* form of all the azobenzene derivatives used in this study showed the NLC phase, while the *cis* form showed no LC phase. Linearly polarized light at 830 nm from a diode laser could be transmitted through a pair of crossed polarizers, between them the azobenzene film was placed, because of the birefringence of the liquid-crystalline azobenzene. Transmittance of the probe light decayed immediately upon irradiation at 366 nm in the N phase as shown in Figure 3 for 8AB8. This was caused by the

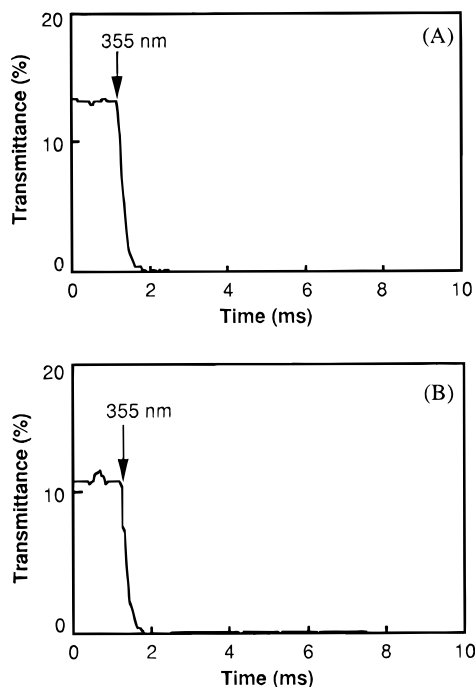


Figure 4. Time-resolved measurements of the photochemical N-I phase transition induced by pulse irradiation (355 nm; 10 ns, fwhm): (A) BMAB at 35 °C; (B) 8AB8 at 110 °C.

disappearance of the LC phase due to the photoisomerization of the azobenzene with concomitant loss of birefringence. The transmittance of the probe light recovered approximately in 30 s when photoirradiation was ceased. At a temperature greater than 100 °C, thermal *cis-trans* back-isomerization took place effectively, followed by reorientation of mesogens, so that the N phase was recovered rapidly when the LC film was kept in the dark. The photochemical N-I phase transition and thermal I-N phase transition occurred repeatedly in 8AB8. The N-I phase transition was also induced in BMAB at 35 °C on the same time scale as 8AB8. Thermal recovery of the N phase, however, required several hours. BMAB shows an N phase at a temperature lower than that of 8AB8. At 35 °C, thermal *cis-trans* back-isomerization occurs very slowly so that thermal recovery of the N phase needed a much longer time.

Figure 4 shows time-resolved measurements of the photochemical N-I phase transition in BMAB and 8AB8. To discuss the phase transition behavior quantitatively, the response time of the N-I phase transition (τ_{N-I}) was defined as the time necessary to reduce the transmittance of the probe light to 10% of the maximum value. Similarly, we defined the response time of the I-N phase transition (τ_{I-N}) as the time required to restore the transmittance to 90% of the maximum value. It became apparent that $\tau_{N-I} = 200 \mu\text{s}$ in both BMAB (Figure 4A) and 8AB8 (Figure 4B). This response was faster by 1–2 orders of magnitude than the response of NLCs reported so far.^{1,2} To examine if a heat-mode process was involved in the phase transition, the LC films were irradiated with a high-power infrared laser pulse at 1064 nm using a Nd:YAG laser (fundamental; 1 J/cm²; 10 ns, fwhm), but no phase transition was induced in any sample.

Under the present experimental setup, the photochemical N-I phase transition was observed only in the thin films (~200 nm) in all samples. In thick films, the pumping light was absorbed entirely at the surface of the films, since molar extinction coefficients of azobenzenes are very large ($\sim 2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) at 366 and 355 nm, and the photochemical reaction was induced only in the surface area. Consequently, the N-I phase transition occurred only in the surface of the films, leaving the

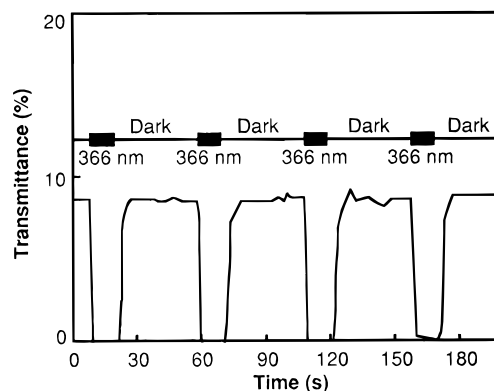


Figure 5. Photochemical N-I phase transition and thermal I-N transition of PA6AB2. Photoirradiation was performed at 140 °C.

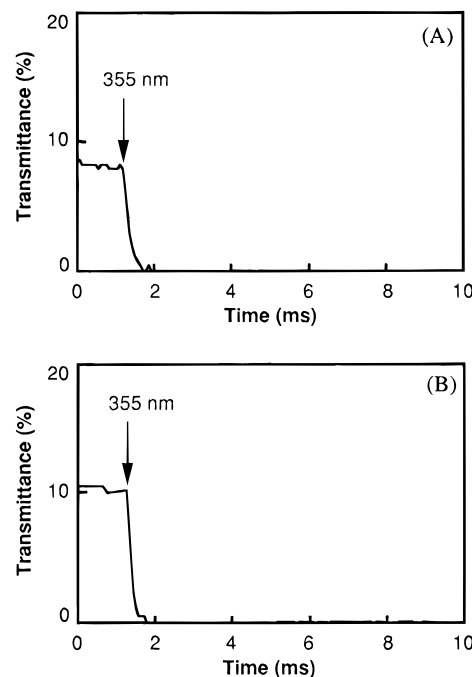


Figure 6. Time-resolved measurements of the photochemical N-I phase transition induced by pulse irradiation (355 nm; 10 ns, fwhm) in PA6AB2: (A) at 140 °C; (B) at room temperature (below T_g).

remaining part of the films intact as an N phase. The present optical setup allows us to detect the N-I phase transition only when it takes place completely across the films.

Photochemical Phase Transition Behavior of Polymeric LC. The photochemical N-I phase transition and thermal I-N phase transition also occurred repeatedly in PA6AB2 at 140 °C as shown in Figure 5. At this temperature, the thermal *cis-trans* back-isomerization of the azobenzene moiety took place more effectively than that at 110 °C (Figure 3), and it took only 7–8 s for the recovery of the N phase. In the temperature range between T_g and 140 °C, the thermal I-N phase transition was also observed because *cis-trans* back-isomerization of the azobenzene occurred thermally.

Time-resolved measurements revealed that $\tau_{N-I} = 200 \mu\text{s}$ even in the polymeric sample as shown in Figure 6. In general, the response time of the polymeric LCs is longer than that of the low molecular weight LCs, since in the polymeric LCs the mobility of mesogens is highly restricted by the main chain of the polymer.

In a system where the center of gravity of each molecule is aligned regularly as in crystals, optical anisotropy is observed even after the anisotropy in the shape of each molecule is

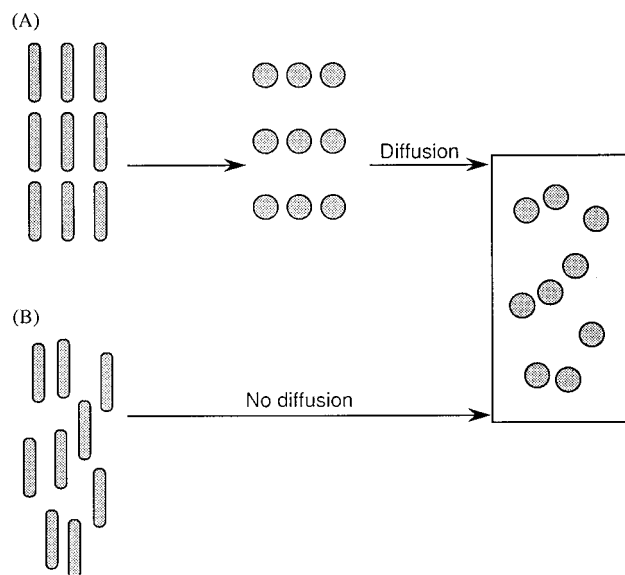


Figure 7. Schematic illustration for loss of optical anisotropy. In the crystal, diffusion is required for the loss of optical anisotropy (A). In the N phase, however, the phase transition does not require lateral movement of LC molecules (B).

eliminated (Figure 7A). On the other hand, in NLCs optical anisotropy originates only from the anisotropy in molecular shape (rod-like shape) and the center of gravity of each molecule is distributed randomly. Although the molecular shape is anisotropic even in the *cis* form, the optic axis of the molecule is distributed randomly. Therefore, in the NLCs the optical anisotropy disappears if the anisotropy in the shape of each molecule vanishes through *trans*–*cis* isomerization as shown in Figure 7B. Note that a phase transition of this type does not require lateral movement of LC molecules; the center of gravity of each molecule remains almost unchanged. Then it is possible that the phase transition takes place similarly in low molecular weight LCs as well as in polymeric LCs. The polymeric azobenzene LCs show a much wider temperature range in general for the N phase, so they are advantageous in view of a wide temperature range available for the optical switching.

It is worth noting that $\tau_{N-I} = 200 \mu\text{s}$ even below T_g as demonstrated in Figure 6B. There has been a significant number of studies on the mechanism of photoisomerization of azobenzene derivatives concerned with an inversion mechanism or a rotation mechanism. It is now accepted that photoisomerization of azobenzenes occurs mainly through an inversion mechanism.^{15,16} This mechanism requires a much smaller sweep volume for isomerization than the rotation mechanism. In addition, although the segmental movement of the main chain of the polymers is frozen below T_g , movement of side chains is allowed to some extent. Thus, the azobenzene derivatives can isomerize in relatively rigid matrices such as polymer matrices below T_g , depending on the spatial and temporal distribution in size of the free volume in the polymer.^{17–19}

In PA6AB2, it was observed that the thermal *cis*-to-*trans* back-isomerization took place in 24 h at room temperature (25 °C). Although the *trans* form was recovered nearly completely, the isotropic glass (glassy state in which the mesogenic *trans*-azobenzenes are randomly aligned) induced at the irradiated site below T_g still remained unchanged at room temperature even after 1 year. To explore this strange behavior of PA6AB2, we studied the change in orientation of the mesogenic *trans*-azobenzene moieties before and after photoirradiation at room temperature.

For a symmetrical system, the dichroic ratio R can be given by eq 1:²⁰

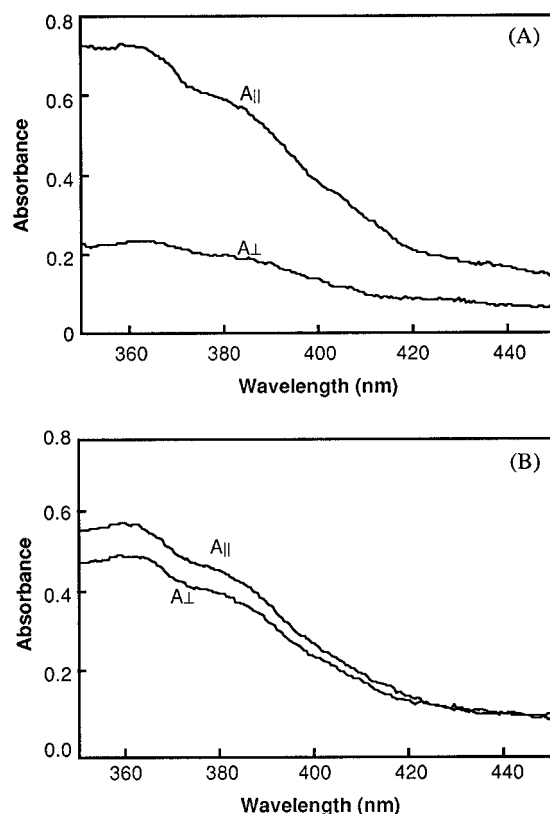


Figure 8. Polarized absorption spectra of PA6AB2: (A) before irradiation; (B) after irradiation.

$$R = \frac{A_{\parallel}}{A_{\perp}} = \frac{4(\cos^2 \alpha)\langle \cos^2 \theta \rangle + 2(\sin^2 \alpha)\langle \sin^2 \theta \rangle}{2(\cos^2 \alpha)\langle \sin^2 \theta \rangle + (\sin^2 \alpha)\langle 1 + \cos^2 \theta \rangle} \quad (1)$$

where A_{\parallel} and A_{\perp} are the absorbance measured with the UV beam polarized parallel and perpendicular to the optic axis of the molecule, respectively. θ is the angle between the direction of the molecular long axis and the optic axis of the uniformly oriented NLCs, and α is the angle between the molecular long axis and the direction of the transition moment. In the case where the transition moment is oriented parallel to the molecular long axis, the order parameter S can be written in the form of eq 2:²⁰

$$S = \frac{R - 1}{R + 2} \quad (2)$$

Figure 8 shows the polarized absorption spectra of PA6AB2 measured before and after irradiation at room temperature. Absorption at 360 nm is due to the π – π^* transition of the *trans*-azobenzene moiety, and we used this peak for the determination of the order parameter of PA6AB2. Before irradiation, the value of S was 0.45, indicating that the mesogens were aligned well in the N phase. After irradiation, when the *trans* forms were thermally restored, the S value decreased to 0.05, indicating that the mesogenic *trans*-azobenzenes were not aligned, forming no N phase. These results lead to the conclusion that the orientation of the mesogenic *trans*-azobenzenes became disordered through the process of thermal *cis*–*trans* back-isomerization. Even though the *trans* form was recovered thermally, orientation of the mesogens could be hardly attained in the absence of segmental motion of the main chain of the polymer below T_g (Figure 9).

Thermal I–N Phase Transition Behavior of Polymeric LC. The thermal I–N phase transition consists of two processes: thermal *cis*–*trans* isomerization and reorientation

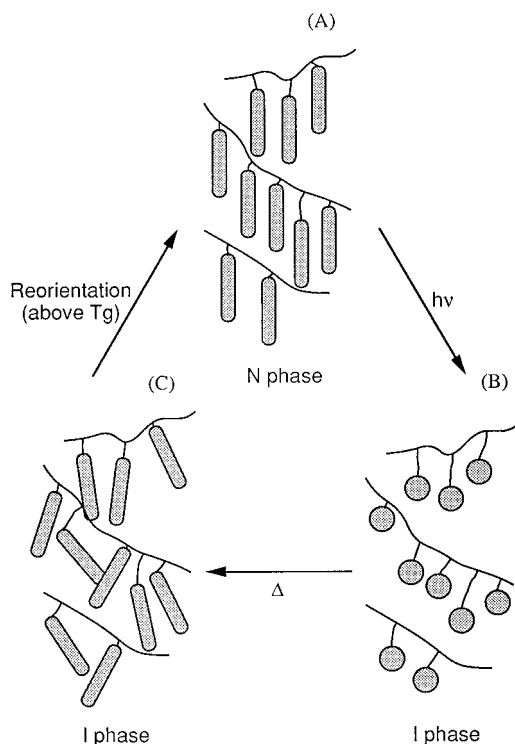


Figure 9. Schematic illustration for orientation of *trans*-azobenzene mesogens. Before irradiation, mesogens are aligned and form the N phase (A). Immediately after irradiation, the N phase disappears because of *trans*-to-*cis* photoisomerization of azobenzene (B). After thermal *cis*-to-*trans* back-isomerization of the azobenzene moieties, the mesogens (*trans* form) no longer form the N phase, since the molecular long axis of each *trans* form is random (C).

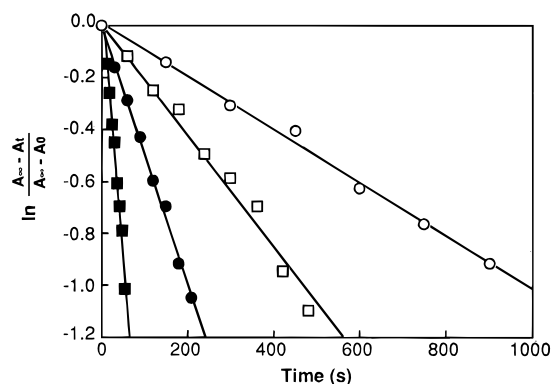


Figure 10. First-order plots for *cis*-to-*trans* thermal isomerization in PA6AB2: ○, at 49 °C; □, at 58 °C; ●, at 67 °C; ■, at 85 °C.

of mesogenic *trans*-azobenzenes. We investigated the thermal *cis*-*trans* isomerization process in detail. For the thermal *cis*-*trans* isomerization,

$$\ln \frac{[cis]}{[cis]_0} = -k_{c-t}t \quad (3)$$

where $[cis]$ and $[cis]_0$ are the concentrations of *cis*-azobenzene at time t and time zero, respectively, and k_{c-t} is the rate constant for the thermal *cis*-*trans* isomerization. The first-order rate constant was determined by fitting the experimental data to the equation

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -k_{c-t}t \quad (4)$$

where A_t , A_0 , and A_∞ are the absorbances at 360 nm at time t ,

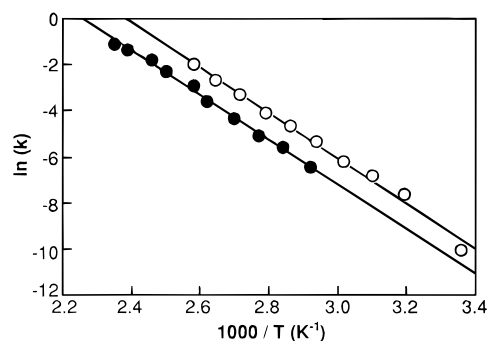


Figure 11. Arrhenius plots for *cis*-*trans* thermal isomerization of azobenzene moiety and for I-N thermal phase transition in PA6AB2: ○, for *cis*-*trans* isomerization; ●, for I-N phase transition.

time zero, and infinite time, respectively.²¹ Examples of the first-order plots according to eq 4 for the *cis*-*trans* thermal isomerization of PA6AB2 film are shown in Figure 10. We obtained a value of 19 kcal/mol as an activation energy from the slope of the Arrhenius plot (Figure 11).

Figure 11 also shows the Arrhenius plot for the thermal I-N phase transition of the PA6AB2 film. The rate constant (k_{I-N}) was defined as a reciprocal of τ_{I-N} . As can be seen in Figure 11, the slope of the Arrhenius plot for the thermal I-N phase transition is the same as that for the thermal *cis*-*trans* isomerization. Thus, the activation energy of the I-N phase transition is identical with that of the *cis*-*trans* isomerization. This result indicates that the rate-determining step of the thermal I-N phase transition is the *cis*-*trans* isomerization process.

Conclusion

Quick photoresponse has been obtained in nematic azobenzene LCs in which the azobenzene moiety plays the dual role of a mesogen and a photosensitive chromophore. In these azobenzene LCs, only the *trans* form showed an N phase while the *cis* form did not show the LC phase at any temperature. The N-I phase transition took place when the *trans*-*cis* isomerization was caused by photoirradiation. Since the *trans*-*cis* photoisomerization of the azobenzene moieties is a very fast process, the N-I phase transition was induced in 200 μs for the low molecular weight LCs and the polymer LC by the use of a short laser pulse to bring about the isomerization. The polymer LC showed quite a different behavior from those of the low molecular weight LCs because of the glass transition. At temperatures above T_g , the I phase induced at the irradiated site disappeared after some time, depending on the temperature. At high temperatures the I phase disappeared quickly because of effective thermal *cis*-*trans* back-isomerization, and at temperatures just above T_g , it disappeared very slowly. On the other hand, at temperatures below T_g , the I glass induced at the irradiated site remained very stable (more than 1 year) even though the *trans* form was restored thermally. This high stability of the I glass arises from the fact that after the *trans*-*cis*-*trans* cycles the orientation of the *trans* form became random and this random orientation was frozen in the absence of segmental motion of the main chain of the polymer below T_g . When the temperature of the irradiated sample was raised above T_g , the N phase was restored because of the reorientation process. The polymeric azobenzene LC may, therefore, be used as optical switching material above T_g and as optical image storage material below T_g .

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