Photochemical Phase Transition Behavior of Polymer Azobenzene Liquid Crystals with Electron-Donating and -Accepting Substituents at the 4,4′-Positions

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ABSTRACT: Photochemical phase transition behavior of polymer liquid crystals (LCs) with donor−acceptor azobenzene moieties which contain both electron-donating and -accepting substituents at the 4,4′-positions has been explored. Polymer azobenzene LCs were prepared which show nematic (N) LC behavior in the *trans* form but no LC phase in the *cis* isomer. Photoirradiation of a thin film of the azobenzene LCs (∼200 nm) in the *trans* form resulted in disappearance of the N phase due to *trans*−*cis* photoisomerization of each mesogen, and the initial N phase was recovered when the irradiated sample was kept in the dark because of *cis*−*trans* thermal isomerization and reorientation of *trans*-azobenzenes. Time-resolved measurements with a laser pulse (355 nm; 10 ns, fwhm) revealed that the N-to-isotropic (I) phase transition took place in 200 μs. The thermal I−N phase transition of a donor−acceptor azobenzene LC with an acrylate main chain occurred in 800 ms at 135 °C. This response is faster by one order of magnitude than the response of non-donor−acceptor azobenzene LCs. In the sample with a methacrylate main chain, however, the thermal recovery of the N phase took place slowly. These phenomena are interpreted in terms of the mobility of segments of the polymer.

Introduction

Photochemical phase transition of nematic (N) liquid crystals (LCs) has attracted great interest from both fundamental and practical viewpoints.[2−9] The photochemical phase transition is an isothermal phase transition triggered by a photochemical reaction of photochromic molecules, such as azobenzene and spiropyran derivatives. For example, the *trans* form of the azobenzene derivatives stabilizes the LC phase when dispersed in the LC phase because of the rodlike shape of the molecule. 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 induces disorganization of the phase structure. We reported previously that the photochemical N-to-isotropic (I) phase transition took place in 200 μs in low-molecular-weight and polymer NLCs with azobenzene moieties as both mesogens and photosensitive chromophores.[10−14] The birefringence of the LCs vanishes on photochemical phase transition; thus, we can switch the light transmitted through a pair of crossed polarizers, with the LC sample between them.[10,11] Furthermore, we can control the intensity of the light reflected from the interface between the LC and the glass substrate,[13,14] because the photochemical phase transition accompanies a large change in the refractive index of the sample.[12] The photoresponsive LCs, therefore, may be applicable to all-optical switching materials.

When photoirradiation was ceased, the initial N phase was restored thermally after some time. Above 100 °C, the N phase recovered in several seconds in both low-molecular-weight and polymer azobenzene LCs.[10,11] This response is about 10^4 times slower than the response of the photochemical N−I phase transition. We, therefore, have to accelerate the thermal I−N phase transition to utilize the photoresponsive LCs for all-optical switching materials. At temperatures below the glass transition temperature (T_g), no recovery of the N phase was observed in the polymer LC, since reorientation of the mesogens was hardly attained in the absence of segmental motion of the main chain of the polymer.[10,11] Thus, the polymer azobenzene LCs can be expected for optical image storage materials below T_g.[10]

The thermal I−N phase transition is composed of two processes: *cis*−*trans* thermal back-isomerization of the azobenzene moieties and reorientation of mesogenic *trans*-azobenzenes. The rate-determining step of the thermal I−N phase transition is the *cis*−*trans* back-isomerization.[11] The thermal *cis*−*trans* isomerization of donor−acceptor azobenzenes, which contain both an electron donor and an acceptor in a single molecule, is generally faster than that of the non-donor−acceptor azobenzene derivatives.[15] The thermal I−N phase transition in the donor−acceptor azobenzene LCs, therefore, may be induced quickly. In this paper, we reported the photochemical N−I phase transition and the thermal I−N phase transition behavior of polymer azobenzene LCs with donor−acceptor substituents at the 4,4′-positions. In addition, we explored the effect of the structure of the main chain of the polymer on the phase-transition behavior of the azobenzene LCs.

Experimental Section

Materials. Figure 1 shows the structures of the polymer azobenzene LCs as well as their abbreviations used in this study. **PA6AB2** and **PM6AB2** have a 4-ethoxyazobenzene moiety, and **PA6ABCN** and **PM6ABCN** have a donor−acceptor azobenzene moiety as mesogen and a photoresponsive moiety in the side chain. In the abbreviations, PA and PM

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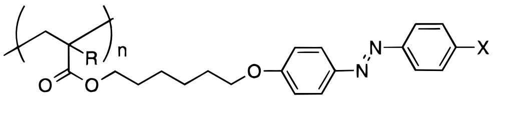

PA6AB2: R = H, X = OC_2H_5
PM6AB2: R = Me, X = OC_2H_5
PA6ABCN: R = H, X = CN
PM6ABCN: R = Me, X = CN

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

Table 1. Phase Transition Temperature and Molecular Weight of Polymer LCs Used in This Study[a]

polymer	main chain	X	M_n	M_w/M_n	phase transition temperature (°C)
PA6AB2	acrylate	OEt	9 100	1.3	G 45 N 155 I
PM6AB2	methacrylate	OEt	58 000	2.3	G 68 N 150 I
PA6ABCN	acrylate	CN	5 300	1.2	G 29 N 135 I
PM6ABCN	methacrylate	CN	17 000	1.4	G 49 N 163 I

[a] Abbreviations: G, glass; N, nematic; I, isotropic; M_n, number-average molecular weight; M_w, weight-average molecular weight.

indicate the structure of the main chain of the polymer: the former means polyacrylate, and the latter means polymethacrylate. These polymers were prepared and purified as reported previously.[16,17] 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 of the polymers was determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 X 2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. LC 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. The thermotropic properties of the LCs were determined with a differential scanning calorimeter (DSC, 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 and molecular weight of the polymer LCs are given in Table 1.

Photoinduced Phase Transition. The photochemical phase transition behavior of the polymer LCs was investigated by means of an apparatus already reported.[7] Samples were prepared by casting the chloroform solution ($\sim 10^{-3}$ M) of the polymers onto a glass substrate which had been coated with poly(vinyl alcohol) and rubbed to align mesogen. The solvent was removed under reduced pressure at room temperature. After the solvent was removed completely, the LC film was annealed at a temperature just below the N–I phase-transition temperature (T_{NI}). The thickness of the LC films was estimated as ~200 nm by absorption spectroscopy on the basis of the molar extinction coefficients of the azobenzene moieties. The LC films were placed in a thermostated block and irradiated at 366 nm with a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35 + IRA-25). The intensity of the linearly polarized light at 633 nm from a He–Ne laser (NEC, GLC5370, 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 N–I phase transition were performed with a laser pulse from a Nd:YAG laser (Spectron, SL805 laser system; the third harmonic, 355 nm; 30 mJ/cm^2; 10 ns, fwhm). The transmittance of the probe light through crossed polarizers was measured with a photomultiplier (Hamamatsu, R-928) as a function of time and recorded with a storage scope (Iwatsu, DS-8631).

Thermal *cis–trans* Isomerization Behavior of Azobenzenes. We observed a change in absorbance at the absorption maximum of the *trans*-azobenzenes in the LC phase to examine the thermal *cis–trans* isomerization behavior of the azobenzene moieties. The azobenzene LC film was placed in an absorption spectrometer (Shimadzu UV-200S). The film was irradiated at 366 nm (5 mW/cm^2) for 10 min in the LC phase, and then we measured the change in absorbance with time at the absorption maximum (at 360 nm).

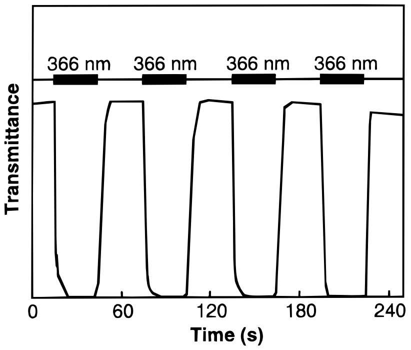

Figure 2. Photochemical N–I and thermal I–N phase transitions of **PA6ABCN**. Photoirradiation at 366 nm was performed at 130 °C.

Results and Discussion

Characterization of the Polymers. All the polymers used in this study showed the N phase. The phase transition temperature and T_g were summarized in Table 1. The annealing of the azobenzene LC films at a temperature just below their T_{NI} gave a well-aligned monodomain of the LC phase. It was observed with a polarizing microscope that the films became dark when viewed with the rubbing direction parallel to one of the crossed polarizers and that the transmitted light intensity was highest when the rubbing direction was 45° with respect to the polarizers. This result indicates that all mesogens of the polymer LCs are aligned into one direction to form a monodomain of the LC phase.

The absorption spectra of *trans*-azobenzenes exhibit their absorption maxima at around 350 nm due to a $\pi-\pi^*$ transition and at around 450 nm due to an $n-\pi^*$ transition. The absorbance at around 350 nm was reduced by photoirradiation at 366 nm due to the *trans–cis* photoisomerization of the azobenzene moieties. After irradiation with visible light (>420 nm), the absorbance was restored, owing to *cis–trans* photochemical back-isomerization. This indicates that the photoisomerization of the azobenzene moieties took place reversibly by photoirradiation. In addition, when the polymers irradiated at 366 nm were kept in the dark, the *cis–trans* back-isomerization also occurred thermally.

Photochemical Phase Transition and Thermal Phase Transition Behavior of Polymer Azobenzene LCs. Effect of Substituents of Azobenzene Moieties. Linearly polarized light at 633 nm could transmit through a pair of crossed polarizers, with the azobenzene film between them, because of the birefringence of the azobenzene LCs. As shown in Figure 2 for **PA6ABCN**, transmittance of the probe light decayed immediately upon irradiation at 366 nm in the N phase. This was caused by the photochemical N–I phase transition of the azobenzene LCs due to the *trans–cis* photoisomerization of the azobenzene.[11] When photoirradiation was ceased, the transmittance of the probe light recovered. Since the mesogenic *trans*-azobenzene restored thermally, the initial N phase recovered when the irradiated film was kept in the dark. In all samples, the photochemical phase transition was induced repeatedly.

Figure 3 shows the time-resolved measurements of the photochemical N–I and the thermal I–N phase

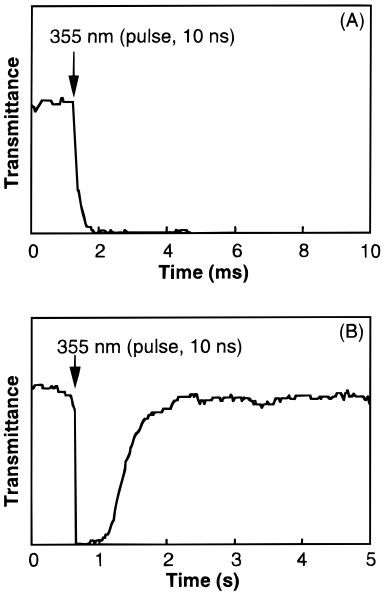

Figure 3. Time-resolved measurements of the photochemical N−I and thermal I−N phase transitions of **PA6ABCN**: (A) photochemical N−I phase transition at 127 °C; (B) thermal I−N phase transition at 135 °C.

transitions in **PA6ABCN**. 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 response time of the I−N phase transition as the time required to restore the transmittance to 90% of the maximum value.[11] The photochemical N−I phase transition in **PA6ABCN** was induced in 200−300 μs (Figure 3A). This response is similar to that observed in **PA6AB2**.[10,11] On the other hand, the thermal recovery of the N phase in **PA6ABCN** occurred faster than that in **PA6AB2**: it took 800 ms in **PA6ABCN** at 135 °C while it took 7−8 s in **PA6AB2** at 140 °C.[11]

It is worth noting here that the photochemical phase transition was induced in 200−300 μs at room temperature (25 °C) in all polymer LCs. These polymers show the T_g at 29−68 °C, so that the N−I phase transition could be induced even below T_g.[10] Furthermore, when the polymer films were irradiated with a laser pulse at 355 nm at room temperature and kept at the same temperature in the dark, the I phase induced at the irradiated site was very stable.[10]

Fatigue Resistance of Polymer Azobenzene LC. We evaluated the fatigue resistance of the polymer azobenzene LC with **PA6ABCN** in detail. Figure 4 shows the time-resolved measurements of the photochemical phase transition in **PA6ABCN** before (A) and after irradiation with some laser pulses (B and C). As shown in Figure 4, the initial transmittance of the probe light was decreased by repeating the photochemical phase transition. After we irradiated with 600 pulses of laser, the transmittance of the probe light in the N phase decreased to about 30% of the level in the virgin sample. This decrease of the transmittance may be due to byproducts produced by the photochemical side reaction of the azobenzenes. Because the byproducts destabilized the LC phase, the order parameter of the LC was lowered and the transmittance of the probe light decreased. Although the photochemical phase transition took place after 800 irradiation pulses, the transmittance in the N phase decreased to 15% of the level in the virgin sample. After pulse irradiation was repeated more than 1000 times, the transmitted light in the N phase could not be detected under the present experimental setup. In conclusion, the photochemical phase transition in **PA6ABCN** can be repeated about 1000 times by irradiation with laser pulses.

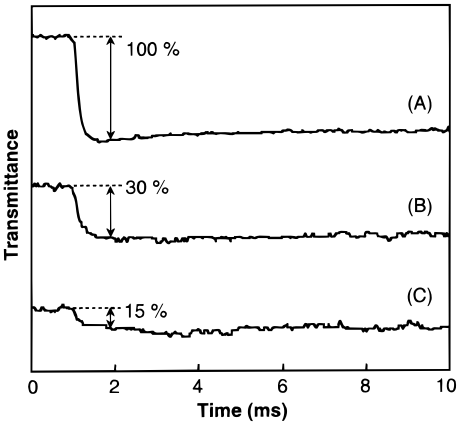

Figure 4. Time-resolved measurements of the photochemical phase transition of **PA6ABCN**: (A) in virgin sample; (B) after 600 irradiation pulses; (C) after 800 irradiation pulses. Laser pulse irradiation at 355 nm (30 mJ/cm^2) was performed at 102 °C. The repetition rate of the pulse irradiation was 0.1 Hz.

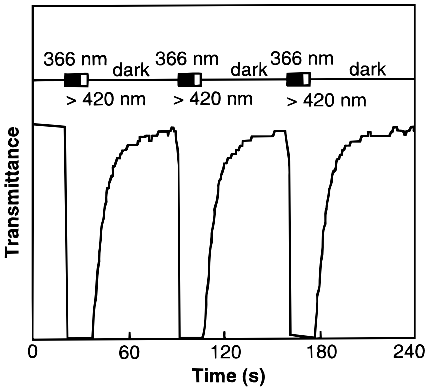

Figure 5. Effect of visible-light irradiation on the photochemical phase transition of **PA6ABCN**. Photoirradiation at 366 nm and >420 nm was carried out at 78 °C.

Effect of Visible-Light Irradiation on the I−N Phase Transition. The *cis−trans* back-isomerization of the azobenzene moiety was also induced photochemically by visible-light irradiation. The *cis−trans* photoisomerization is faster than the thermal isomerization. When we induce the *cis−trans* photoisomerization of the azobenzene with visible light, therefore, we can expect that the N phase recovers more quickly. Thus, the effect of the *cis−trans* photoisomerization of the azobenzene moieties on the I−N phase transition was investigated for **PA6ABCN**. The LC film was irradiated at 366 nm for 10 s at 76 °C, and then the photochemical N−I phase transition took place. At this temperature, the N phase recovered thermally in 43 s when the irradiated film was kept in the dark. However, when the film was irradiated with visible light at >420 nm for 5 s after the N−I phase transition to bring about the *cis−trans* photoisomerization, the I−N phase transition was caused in 26 s (Figure 5). Since the *cis−trans* isomerization of the azobenzene proceeded effectively by visible-light irradiation, the I−N phase transition occurred quickly. These results suggested that one can further accelerate the I−N phase transition by visible-light irradiation.

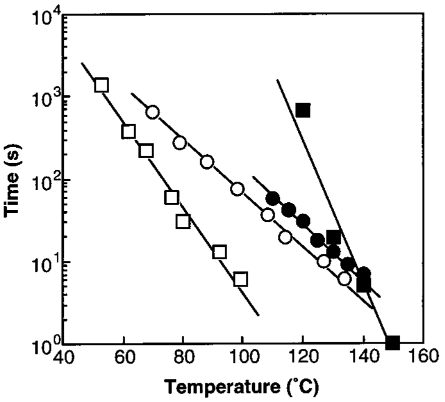

Figure 6. Response time for the thermal I–N phase transition of polymer azobenzene LCs as a function of temperature: (○), **PA6AB2**; (●), **PM6AB2**; (□), **PA6ABCN**; (■), **PM6ABCN**.

Effect of the Main Chain of the Polymer. A similar photochemical N–I phase transition behavior was also observed in the methacrylate polymers (**PM6AB2** and **PM6ABCN**). However, the methacrylate polymers were different from the acrylate polymers in the thermal I–N phase transition behavior. Figure 6 shows the response time for the I–N phase transition of the polymer LCs as a function of temperature. In all polymers, the response time decreased with increasing temperature. At all temperatures, the thermal I–N phase transition of the methacrylate polymers was slower than that of the corresponding acrylate polymers. From these results, it can be assumed that the structure of the main chain of the polymers affects the *cis*–*trans* thermal isomerization process of the azobenzene moiety or the reorientation process of the mesogenic *trans*-azobenzene.

Thermal *cis*–*trans* Isomerization Behavior of Azobenzene. The thermal I–N phase transition consists of two processes: the *cis*–*trans* thermal isomerization and the reorientation of the mesogenic *trans*-azobenzenes. To explore the difference in the thermal I–N phase transition behavior between these polymers, we studied the thermal *cis*–*trans* isomerization process in detail. The thermal isomerization behavior was observed by absorption spectroscopy. For the *cis*–*trans* isomerization, the first-order rate constant (k_{c-t}) was determined by fitting the experimental data to the equation[18]

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -k_{c-t}t \qquad (1)$$

where A_t, A_0, and A_∞ are the absorbance at 360 nm at time t, time zero, and infinite time, respectively. Typical examples of the first-order plots according to eq 1 for the *cis*–*trans* isomerization of the azobenzene films at various temperatures were shown in Figure 7. As shown in Figure 7, eq 1 gives a good fit to the thermal *cis*–*trans* isomerization. From the slope of the first-order plots, we obtained the k_{c-t} values at each temperature.

The values of k_{c-t} of the donor–acceptor azobenzenes were larger than those of the corresponding non-donor–acceptor azobenzenes at any temperatures. In other words, the thermal *cis*–*trans* isomerization of the donor–acceptor azobenzenes proceeds more effectively than that of the non-donor–acceptor azobenzenes.[19–27] Note that the rate-determining step of the thermal recovery of the N phase is the *cis*–*trans* isomerization process.[11] Since the rate-determining step was accelerated with the donor–acceptor pair, the thermal I–N phase transition of **PA6ABCN** occurred more quickly than that of **PA6AB2**.

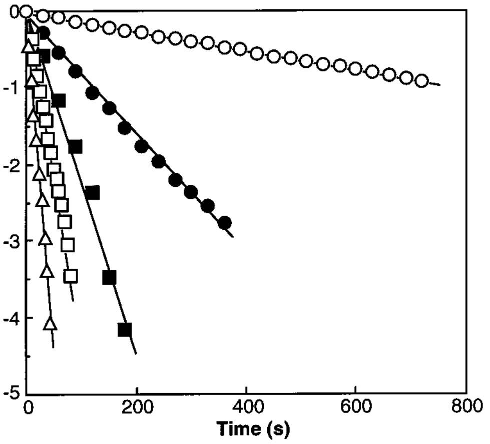

Figure 7. First-order plots for *cis*–*trans* thermal isomerization in **PM6AB2**: (○) at 50 °C; (●) at 70 °C; (■) at 80 °C; (□) at 90 °C; (△) at 100 °C.

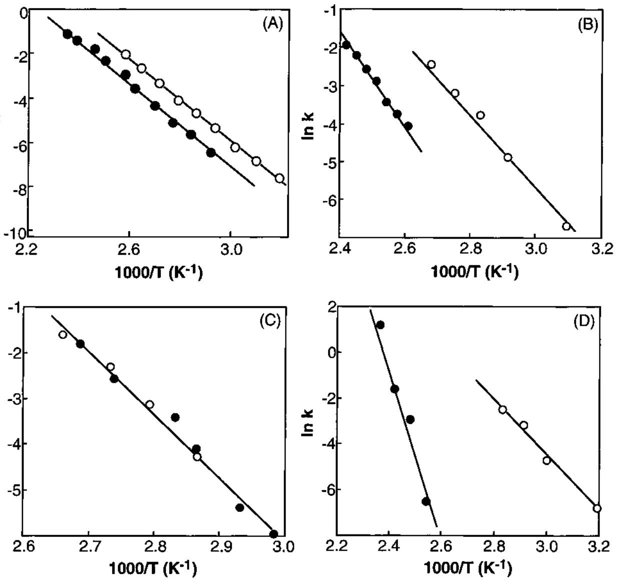

Figure 8. Arrhenius plots for the thermal *cis*–*trans* isomerization of the azobenzene moiety and the thermal I–N phase transition in polymer LCs: (A) **PA6AB2**; (B) **PM6AB2**; (C) **PA6ABCN**; (D) **PM6ABCN**: (○) for *cis*–*trans* isomerization; (●) for the I–N phase transition.

Figure 8 shows the Arrhenius plots for the *cis*–*trans* isomerization. We obtained values of an activation energy (E_a) from the slope of these plots. Figure 8 also shows the Arrhenius plots for the thermal I–N phase transition of the polymer LC films. The rate constant of the I–N phase transition was defined as a reciprocal of the response time. In the acrylate polymers, the slope of the Arrhenius plots for the phase transition was the same as that for the *cis*–*trans* isomerization.[11] This means that the E_a value of the I–N phase transition was identical with that of the *cis*–*trans* isomerization in the acrylate polymers. For example, in **PA6ABCN**, the values of E_a were 26 kcal/mol for the *cis*–*trans* isomerization and 28 kcal/mol for the I–N phase transition (Figure 8C). Namely, the rate-determining step of the I–N phase transition is the *cis*–*trans* isomerization process in the acrylate polymers.[11] In the methacrylate polymers, however, the value of E_a for the I−N phase transition was different from that for the isomerization process: $E_a = 24$ kcal/mol for the *cis*−*trans* isomerization and $E_a = 81$ kcal/mol for the I−N phase transition in **PM6ABCN** (Figure 8D). The same tendency was observed in **PA6AB2** and **PM6AB2** (Figure 8A and B).[11] The E_a for the thermal isomerization showed almost the same values between acrylate and methacrylate polymers. This result suggests that the *cis*−*trans* isomerization process was not affected by the structure of the main chain of the polymer. Therefore, the difference in the thermal I−N phase transition between these polymers may be interpreted as the reorientation process of the mesogenic *trans*-azobenzene playing an important role in the phenomena. It is known that the flexibility of the polymer main chain influences the temperature range of the LC phase and the LC−I phase-transition temperature of polymer LCs, because the mobility of the segments of the polymers affects the LC behavior.[28−30] The methacrylate main chain is more rigid than the acrylate main chain; thus, the segmental motion of the main chain of the methacrylate polymers may be restrained. For this reason, the reorientation process of the methacrylate polymers was slower than that of the acrylate polymers.

Conclusion

The photochemical N−I phase transition of the polymer azobenzene LCs was induced in 200 μs by irradiation with a laser pulse to bring about the *trans*−*cis* photoisomerization of azobenzenes. When the photoirradiation was ceased, the initial N phase was recovered thermally. In the photochemical N−I phase transition, the effect of substituents at the 4,4′-positions of the azobenzene moiety and the structure of the main chain of the polymer was not observed. On the other hand, the thermal recovery of the N phase depended strongly on the substituents and the main chain structure. The electron-donating and -accepting substituents at the 4,4′-positions of the azobenzenes accelerated the thermal I−N phase transition, because the thermal *cis*−*trans* isomerization of the azobenzene with donor−acceptor took place effectively. This suggests that the polymer azobenzene LCs with electron donors and acceptors are potential quick-responsive all-optical switching materials. Further, the I−N phase transition was also accelerated by visible-light irradiation.

The thermal I−N phase transition of the methacrylate polymers was slower than that of the acrylate polymers, since the segmental motion of the main chain of the polymer was restrained. In general, methacrylate polymers show high T_g values and low flexibility of the main chain. These features of methacrylate polymers would be disadvantageous for optical switching materials. We, however, can expect the methacrylate polymers to be optical image storage materials, because the stored image may be very stable due to their high T_g values and the low flexibility of the main chain.

References and Notes

(1) JSPS Research Fellow, 1997−1999.
(2) Leier, C.; Pelzl, G. *J. Prakt. Chem.* **1979**, *321*, 197−204.
(3) Ogura, K.; Hirabayashi, H.; Uejima, A.; Nakamura, K. *Jpn. J. Appl. Phys.* **1982**, *21*, 969−973.
(4) Odulov, S. G.; Reznikov, Yu. A.; Soskin, M. S.; Khizhnyak, A. I. *Sov. Phys. JETP* **1983**, *58*, 1154−1158.
(5) Tazuke, S.; Kurihara, S.; Ikeda, T. *Chem. Lett.* **1987**, 911−914.
(6) Kurihara, S.; Ikeda, T.; Sasaki, T.; Kim, H.-B.; Tazuke, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1751−1752.
(7) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 36−41, 42−48, 3938−3943.
(8) Kanazawa, A.; Hirano, S.; Shishido, A.; Hasegawa, M.; Tsutsumi, O.; Shiono, T.; Ikeda, T.; Nagase, Y.; Akiyama, E.; Takamura, Y. *Liq. Cryst.* **1997**, *23*, 293−298.
(9) Kanazawa, A.; Shishido, A.; Hasegawa, M.; Tsutsumi, O.; Shiono, T.; Ikeda, T.; Nagase, Y.; Akiyama, E.; Takamura, Y. *Mol. Cryst. Liq. Cryst.*, in press.
(10) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873−1875.
(11) Tsutsumi, O.; Shiono, T.; Ikeda, T.; Galli, G. *J. Phys. Chem. B* **1997**, *101*, 1332−1337.
(12) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Phys. Chem. B* **1997**, *101*, 2806−2810.
(13) Nabeshima, Y.; Shishido, A.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Hiyama, T. *Chem. Mater.* **1997**, *9*, 1480−1487.
(14) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *119*, 7791−7796.
(15) Xie, S.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1993**, *5*, 403−411.
(16) Angeloni, A. S.; Caretti, D.; Carlini, C.; Chiellini, G.; Galli, G.; Altomare, A.; Solaro, R. *Liq. Cryst.* **1989**, *4*, 513−527.
(17) Ringsdorf, H.; Schmidt, H. W. *Makromol. Chem.* **1984,** *185*, 1327−1334.
(18) Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1993**, *26*, 151−154.
(19) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004−2008.
(20) Asano, T. *J. Am. Chem. Soc.* **1980**, *102*, 1205−1206.
(21) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O.; *J. Am. Chem. Soc.* **1981**, *103*, 5161−5165.
(22) Asano, T.; Yano, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900−4904.
(23) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. *J. Am. Chem. Soc.* **1982**, *104*, 1733−1735.
(24) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. *J. Org. Chem.* **1983**, *48*, 2808−2813.
(25) Asano, T.; Okada, T. *J. Org. Chem.* **1984**, *49*, 4387−4391.
(26) Asano, T.; Okada, T. *J. Org. Chem.* **1986**, *51*, 4454−4458.
(27) Shin, D.-M.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 5206−5208.
(28) Shibaev, V. P.; Platé, N. A. *Adv. Polym. Sci.* **1984**, *60/61*, 173−252.
(29) Gemmell, P.; Gray, G.; Lacey, D. *Mol. Cryst. Liq. Cryst.* **1985**, *108*, 324−338.
(30) Shibaev, V. P. In *Liquid-Crystal Polymers*; Platé, N. A., Ed.; Plenum Press: New York, 1993; pp 193−249.

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