Time-Resolved Observation of Photochemical Phase Transition in Polymer Liquid Crystals

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ABSTRACT: Time-resolved measurements were performed on photochemically induced isothermal phase transitions of polymer liquid crystals (PLCs). Two types of PLCs were employed. One type consists of PLCs with mesogenic side chains of phenyl benzoate and cyanobiphenyl, which were doped with azobenzene derivatives. The other consists of copolymers in which azobenzene units were covalently attached to the same chain as the mesogenic side chains. Using a nanosecond pulsed laser, we found that the relaxation time required for the nematic (N) to isotropic (I) phase transition was in a time range of 10 (copolymer LC)–100 ms (homopolymer LC doped with azobenzene derivative) at $T/T_{NI} = 0.999$, which was comparable to that of low molecular weight liquid crystals. Effects of temperature, laser power, and the structure of photoresponsive guest molecules were discussed.

Introduction

Photochemical phase transition has been extensively studied in relation to optical image storage systems.[1-8] Photochemical isothermal phase transitions are triggered by a photochemical reaction of photoresponsive molecules doped in the matrix liquid crystals (LCs). In previous studies, azobenzene[7] and spiropyran[8] derivatives were used as the photoresponsive guest molecules. In the azobenzene/LC mixtures, the trans forms of azobenzenes are favorable for the stabilization of the LC phase because of their rodlike shape, while the cis forms act as an "impurity" to the system; thus, photoisomerization from the trans to the cis form causes a lowering of the LC to isotropic (I) phase transition temperature (T_c) of the mixture, and when the T_c of the mixture is reduced below the irradiation temperature, the phase transition is induced isothermally. This process is different from the "heat-mode" process, where lasers are usually employed as a heat source and irradiated sites undergo the phase transition due to a rise in temperature above T_c.[9-11] Studies on the photochemical phase transition have been successfully extended to polymer liquid crystalline (PLC) systems.[7a,b,e] Homopolymer LCs with photoresponsive dopants and copolymer LCs containing the photoresponsive units were studied under steady-state irradiation. These studies led to the conclusion that the photochemical phase transition in PLCs can be a working principle for an optical image recording system which shows a high resolution and a high stability of the stored information.

The photochemical phase transition is composed of two processes. The first process is the photochemical reaction of the doped molecules, which is followed by the phase transition of the matrix LCs. Under steady-state irradiation, the two processes occur simultaneously: a gradual decrease of T_c by accumulation of, for example, the cis form of azobenzene guests. It is, therefore, very difficult to explore the time course of the second process alone. We have studied the relaxation time of the photochemical phase transition in low molecular weight LCs by time-resolved observation of birefringence.[6] The relaxation time for the low molecular weight LCs was found to be in the range of ~100 ms at a temperature of $T/T_{NI} = 0.998$.

In this study, we have explored the relaxation time of the photochemical phase transition of PLCs by means of a pulsed laser so as to produce a sufficient amount of the cis form of doped azobenzene derivatives within ~10 ns, a time scale that is infinitesimal in comparison with that of the phase transition; thus, T_c of the system was lowered instantaneously below the irradiation temperature, and the relaxation of the nematic to isotropic phase was followed by time-resolved measurements of birefringence.

Experimental Section

Preparation of Samples. The structures of host PLCs and azobenzene derivatives used in this study are shown in Figure 1. Poly[4′-methoxyphenyl 4-((acryloyloxy)propoxy)benzoate] (PAPB3) and poly[4-((acryloyloxy)propoxy)-4′-cyanobiphenyl] (PACB3) were used as the matrix PLCs, and azobenzene derivatives [BMAB, 1AB*n*CB, AB(*n*CB)$_2$] were used as the photoresponsive guest molecules; 4-hydroxyazobenzene (HOAB) was used as a reference dopant. Preparation of these compounds was described in previous papers.[7a,c,e] The number-average molecular weight (M_n) of the PLCs was determined by gel permeation chromatography (GPC; Toyo Soda HLC-802, column, GMH6 × 2 + G4000H8 + G2500H8; eluent, chloroform), and the glass transition temperature (T_g) and the phase transition temperature of the PLCs were determined by a differential scanning calorimeter (DSC; Seiko I&E SSC-5000) and by microscopic observation (Mettler FP-80, FP-82, and Olympus BH2), respectively. All of the PLC samples used in the present study exhibited the nematic phase alone as the LC phase. The nematic to isotropic phase transition temperature (T_{NI}) was defined as a temperature where the birefringent phase was completely lost. Furthermore, the biphasic temperature range was also determined for each PLC by the polarizing microscopy. The biphasic range (ΔT_{NI}) was defined as $\Delta T_{NI} = T_{NI} - T'$, where T' is the temperature at which the isotropic phase started to appear. The concentration of azobenzene derivatives doped in PLCs was 3 mol %, and the content of azo unit in the copolymers was 3.8 mol %. Thermodynamic properties of PLCs are given in Table I.

PLCs were dissolved in chloroform solutions of azobenzene derivatives, and the resulting solutions were cast onto glass plates (film thickness ~20 μm). After drying at room temperature, samples were heated under vacuum at 60 °C for several hours and annealed at a temperature of $T/T_{NI} = 0.99$ so as to exhibit the liquid crystalline phase.

Time-Resolved Observation. Figure 2 shows the experimental setup used for the time-resolved observation of the photochemical phase transition behaviors of PLCs induced by photoirradiation with the nanosecond pulsed laser. A Spectron HL-21 Nd:YAG laser (the third harmonic, 355 nm; pulse width, 12 ns fwhm) was used as an excitation light source, and a He–Ne laser (633 nm, 5 mW) was used as an analyzing light source. The sample film was thermostated and placed between two crossed

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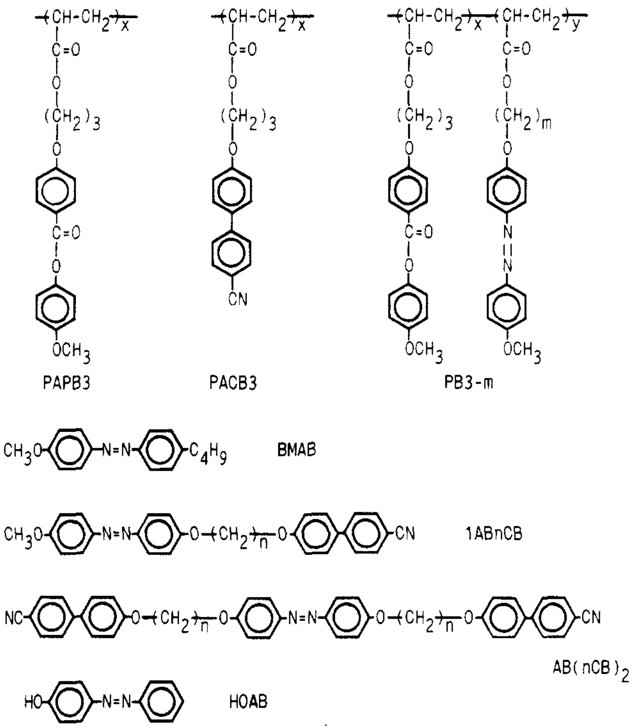

Figure 1. Structures of PLCs and azobenzene derivatives used in this study.

polarizers. The He–Ne laser passed through the sample film and was focused onto the entrance slit of a Jabin-Ybon HR-320 monochromator. The change in transmittance of the He–Ne laser was measured with a Hamamatsu R-928 photomultiplier and recorded with an Iwatsu TS-8123 storage scope. The power of the laser pulse was measured with a Scientech 365 power meter.

The experimental setup used to measure the photoisomerization was the same as given in Figure 2 except that a xenon arc lamp was used as the analyzing light source. The analyzing light was collimated, passed through a color filter (Toshiba UV-D36C) to pass only the light near the absorption maxima of the trans isomer of the azobenzene derivatives, and focused onto the sample. The transmitted light was collected after the sample, refocused onto the entrance slit of the monochromator, and recorded with the storage scope.

Results and Discussion

Time-Resolved Observation of Photochemical Phase Transition of Homopolymer LCs Doped with Azobenzene Derivatives. A typical example of the time-resolved measurements is shown in Figure 3, where the change in transmittance of the He–Ne laser through BMAB/PAPB3 (M_n = 3600) film between crossed polarizers is indicated as a function of time after pulse irradiation (curve 1). The irradiation was performed at T/T_{NI} = 0.999 with a pulse of 0.28 J/cm^2. After a single shot of the laser pulse, the transmittance of the He–Ne laser decreased and became 0 within ~200 ms, indicating that the photochemical phase transition in this mixture was completed within this time. The phase transition was further confirmed by microscopic observation by the use of a polarizing microscope. As demonstrated in Figure 4, a clear schlieren texture was observed on the whole area of the BMAB/PAPB3 film at T/T_{NI} = 0.999 before pulse excitation, while after irradiation of a single pulse, the irradiated area of the film became dark, indicating that the I phase was induced at the irradiated site.

To verify that the phase transition was induced by the trans–cis photoisomerization of BMAB, but not by the heat-mode process, the same measurement was performed on the HOAB/PAPB3 mixture (Figure 3, curve 2). As shown in Figure 5, HOAB had electronic properties very similar to those of BMAB (absorption maximum and extinction coefficients), while it exhibited no photoisomerization behavior even in solution on prolonged exposure to a light which caused the trans–cis photoisomerization of BMAB. No phase transition was observed in the HOAB/PAPB3 mixture after irradiation even though the transmittance changed to some extent. The absence of a phase transition was also confirmed by microscopic observation. It is, therefore, safely concluded that the phase transition shown in Figure 3 was induced by the photoisomerization of BMAB. Similar results were obtained on PACB3 in which the cyanobiphenyl groups were used as mesogens.

It is worth referring here to the photoisomerization behavior of BMAB in PLCs. We tried to follow the time course of the trans–cis isomerization by transient absorption spectroscopy; however, this was unsuccessful. Our laser possesses a pulse width of 12 ns fwhm, and within this time the isomerization was found to be completed. After a single pulse irradiation, the absorption due to the trans form decreased abruptly like a step function, but no decay of the absorption could be detected even in the shortest time range available for our apparatus (resolution ~12 ns) and in the longer time range (500 ms) in which the relaxation of mesogens was observed.

We should also mention the narrow biphasic range observed for the present PLC samples. This is partly because M_n of the samples was very low in general. ΔT_{NI} as small as 0.1 °C indicates that the phase at T/T_{NI} = 0.999 is no longer biphasic but evidently nematic for the present PLC samples.

Effect of Temperature. The photochemical phase transition is induced by the lowering of the N–I phase transition temperature as described above, so that the temperature of PLCs under irradiation is important. To discuss the influence of temperature on the photochemical phase transition, we define the relaxation time, τ, as the time required to reduce the transmittance of the He–Ne laser to 1/e of the initial value. In Figure 6, τ is plotted against the irradiation temperature. As seen in this figure, τ is remarkably influenced by the irradiation temperature; the closer is the irradiation temperature to the phase transition temperature, the shorter becomes the relaxation time τ. This temperature dependence can be explained in terms of stability of the liquid crystalline phase in the initial state. As the temperature before irradiation approaches T_{NI}, the stability of the LC phase is reduced; thus, the transition from an ordered N phase to a disordered I phase can be induced more easily when a perturbation in the form of the trans–cis photoisomerization of the guest molecule is applied.

Effect of Laser Power. The power of the pulsed laser affected the photochemical phase transition as shown in Figure 7 for the BMAB/PAPB3 mixture. The photochemical phase transition was only observed with the laser power higher than 0.22 J/cm^2, and the relaxation time τ was shortened with increasing laser power. As shown in Figure 8, the amount of cis isomer produced with a single pulse of the laser increased with the laser power, so that this laser power dependence can be ascribed to the amount of cis isomer produced by the laser pulse. The photochemical phase transition can be interpreted as the relaxation process from a thermodynamically unstable to a stable state. Thus, the larger is the amount of the cis form (destabilizer) in LC phase, the smaller is the thermodynamic stability of the LC.

Effect of Molecular Weight of PLC. It is generally recognized that as the molecular weight of a PLC and its

Table I
Thermodynamic Properties of PLCs Used in This Study

	M_n	M_w/M_n	phase transition temp,[a] °C	ΔT_{NI}[b]	H_{ni}, kJ/mol	S_{ni}, J/(mol K)	[Azo], mol %
PAPB3	3600	1.22	g 24 n 62.3 i	<0.1	0.35	1.04	
	5500	1.22	g 26 n 69.1 i	0.1	0.35	1.01	
	6200	1.30	g 30 n 74.0 i	0.1	0.33	0.96	
	12000	1.63	g 37 n 78.0 i	0.9	0.39	1.11	
PACB3	5000	1.31	g 29 n 72.1 i	<0.1	0.34	0.98	
PB3-3	3500	1.23	g 30 n 63.7 i	<0.1	0.18	0.53	3.8
PB3-5	5400	1.29	g 29 n 70.2 i	<0.1	0.29	0.83	3.8

[a] Phase transition temperature (T_{NI}) was determined as the temperature where the LC phase completely disappeared. [b] Biphasic temperature range in which the isotropic phase started to appear and all of the birefringent phase disappered.

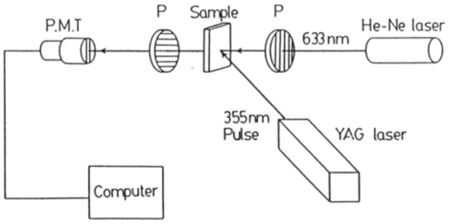

Figure 2. Schematic diagram for the time-resolved measurements of photochemical phase transition behaviors.

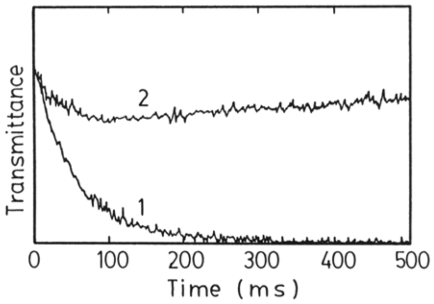

Figure 3. Time-resolved observation of the photochemical phase transition behaviors of PAPB3 doped with 3 mol % azobenzene derivatives. 1, BMAB; 2, HOAB. Laser power, 0.28 J/cm^2; T/T_{NI} = 0.999.

bulk viscosity increase, the response to an external perturbation is delayed. The dependence of the relaxation time on the molecular weight of PLC in the photochemical phase transition of the BMAB/PAPB3 mixture is shown in Figure 9. We can see that the relaxation time τ did not depend on the molecular weight (M_n) of PLC, at least in the molecular weight range employed in this study ($M_n <$ 12 000). The irradiation temperature was T/T_{NI} = 0.999 so that the liquid crystalline phase was less stable, and the difference in the mobility of mesogens between N and I states was thought to be small regardless of the molecular weight. Furthermore, since side-chain PLCs were used in this study, the degree of freedom in the mobility of mesogens was to some extent independent of the main chain. These factors will explain the observed independence of τ on M_n of the host PLCs. It should be mentioned here that for the sample with M_n = 12 000 the measurements were performed in the biphasic state, since ΔT_{NI} = 0.9 °C for this sample.

In the previous work,[6] the values of τ for low molecular weight LCs were found to be ~100 ms at T/T_{NI} = 0.999, which is comparable to those of PLCs. Note that there is little difference in the relaxation time in the photochemical phase transition between low molecular weight LCs and PLCs.

Effect of Structure of Photoresponsive Molecules. It has been reported that the structure of photoresponsive molecules such as 1AB*n*CB and AB(*n*CB)$_2$ (see Figure 1) affects the response time of photochemical phase transition in low molecular weight LCs and in PLCs under steady-state irradiation.[7c,d] 1AB*n*CB and AB(*n*CB)$_2$ (*n* = 3–6; the number of methylene units in the spacer chains) are the photoresponsive molecules specially designed for specific orientation of the azobenzene moieties in host LCs. When *n* was an even number, the azobenzene moiety was found to be aligned parallel to the direction of matrix mesogens due to interaction between the end mesogen in the azobenzene guest and host mesogens. A clear odd–even effect was observed for the response time under steady-state irradiation: the response time of the photochemical phase transition was much shorter for even than for odd *n*. The results have demonstrated that the amount of photoisomerization required to induce the N–I phase transition is different, depending on the structure of the photoresponsive guest molecules. However, it has not been clarified yet if the relaxation time for the N–I phase transition would be affected by the structure of the azobenzene guests when a sufficient amount of the cis isomer is instantaneously produced in the system. The values of τ for 1AB*n*CB/PLC and AB(*n*CB)$_2$/PLC are given

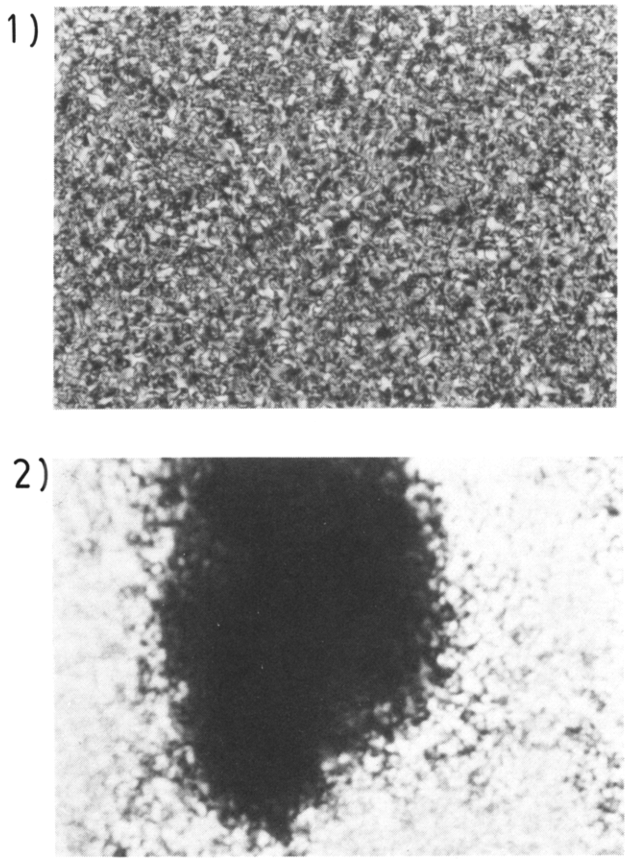

Figure 4. Textures of PAPB3 observed in the polarizing microscope. 1, Before irradiation; 2, after irradiation of pulsed laser (0.28 J/cm^2; T/T_{NI} = 0.999).

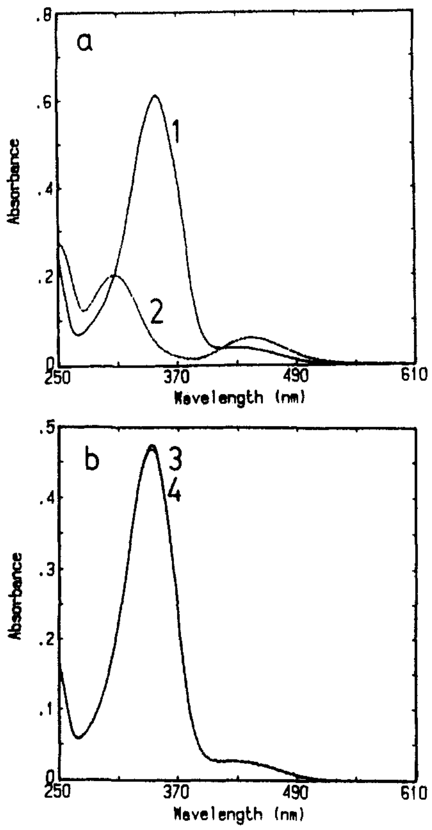

Figure 5. Absorption spectra of BMAB (a) and HOAB (b) in ethanol. 1, BMAB before irradiation; 2, BMAB after irradiation at 355 nm; 3, HOAB before irradiation; 4, HOAB after irradiation at 355 nm.

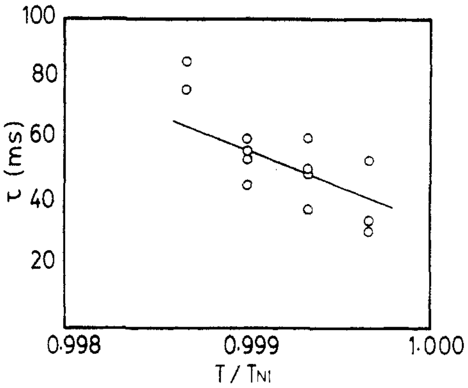

Figure 6. Effect of irradiation temperature on the relaxation time of the photochemical phase transition of BMAB/PAPB3. Laser power, 0.28 J/cm^2.

in Figures 10 and 11 as a function of the number of methylene units in the spacer chains. When 1ABnCB was doped in PLC, the odd–even effect was observed clearly (Figure 10); however, when AB(nCB)$_2$ was doped, no clear relation was observed between n and τ. This can be interpreted as follows: in the 1ABnCB series, when n = 4, the azobenzene moieties lie parallel to the mesogens, leading to a close packing of mesogens and azobenzene moieties in the mixtures; thus, the perturbation caused by the trans–cis photoisomerization would be effectively transferred to the host mesogens more effectively than in 1ABnCB/PLC mixtures with n = 3 and 5. On the other hand, in the AB(nCB)$_2$/PLC mixtures, AB(nCB)$_2$ was likely to be too large to be dispersed (dissolved) in PLCs even at the concentration of 3 mol %, resulting in aggregation in polymer matrices. The presence of the aggregation was also confirmed by polarizing microscopy. The aggregation of the photoresponsive guest molecules would lead to insufficient transfer of perturbation by photoisomerization to the host mesogens. This caused a reduction of efficiency in the photochemical phase transition as evidenced by longer τ compared to those for the 1ABnCB/PLC mixtures as well as the disappearance of the odd–even effect for the τ values (Figure 11).

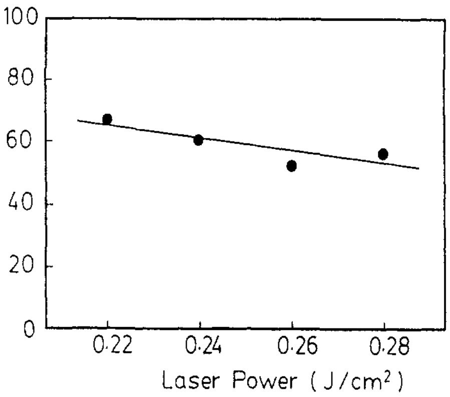

Figure 7. Effect of laser power on the relaxation time of the photochemical phase transition of BMAB/PAPB3. $T/T_{\rm NI}$ = 0.999.

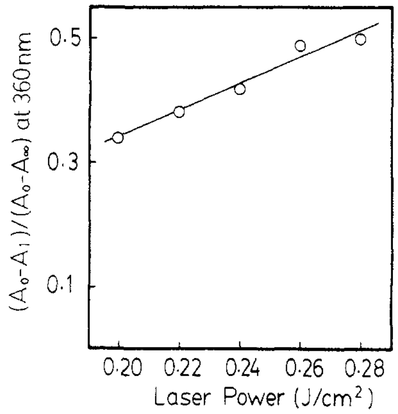

Figure 8. Course of trans → cis photoisomerization of BMAB in PAPB3 as evaluated by the change in $(A_0 - A_1)/(A_0 - A_\infty)$ as a function of the laser power. A_0, A_1, and A_∞ are the absorbances at 366 nm before irradiation, after irradiation of a single pulse, and after prolonged irradiation, respectively.

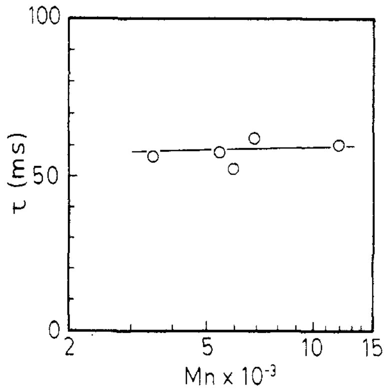

Figure 9. Effect of molecular weight (M_n) on the relaxation time of the photochemical phase transition of BMAB/PAPB3. Laser power, 0.28 J/cm^2; $T/T_{\rm NI}$ = 0.999.

Photochemical Phase Transition in Copolymer LCs. The results of the time-resolved measurements of the photochemical phase transition in the copolymer LC systems (PB3-3, PB3-5; see Figure 1) are shown in Figure 12. The relaxation process of the photochemical phase transition in the copolymer LCs was about 10 times faster than in the homopolymer LCs doped with azobenzene derivatives. In previous studies, the order parameters of

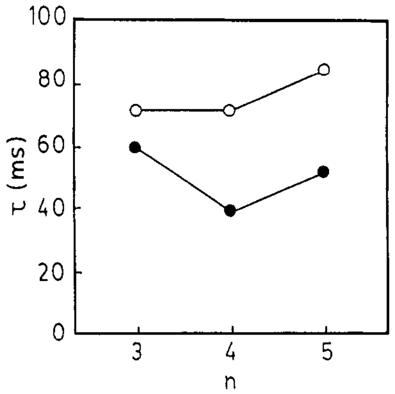

Figure 10. Relaxation time of the photochemical phase transition of 1AB*n*CB/PAPB3 and 1AB*n*CB/PACB3 mixtures as a function of the number of methylene units in the spacer chains. ●, 1AB*n*CB/PAPB3; ○, 1AB*n*CB/PACB3. Laser power, 0.28 J/cm^2; T/T_{NI} = 0.999.

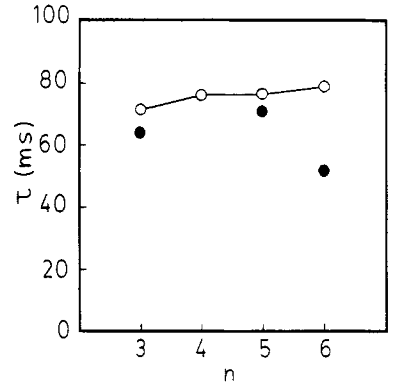

Figure 11. Relaxation time of the photochemical phase transition of AB(*n*CB)$_2$/PAPB3 and AB(*n*CB)$_2$/PACB3 mixtures as a function of the number of methylene units in the spacer chains. ●, AB(*n*CB)$_2$/PAPB3; ○, AB(*n*CB)$_2$/PACB3. Laser power, 0.28 J/cm^2; T/T_{NI} = 0.999.

mesogens in PB3-3 and PB3-5 were found to be much smaller than those of the corresponding asobenzene/homopolymer LC mixtures.[7a] This means that the change in ordering of mesogens upon the N–I phase transition is rather small in the copolymers in comparison with that in homopolymer LC systems. Furthermore, in the copolymer LCs, the azobenzene units are located in close proximity to mesogen units, which seems to be in contrast to the azobenzene/PLC mixtures where mesogens are closely packed with each other and the photoresponsive guest molecules cannot be so close to the mesogen units. Thus, in the copolymer LC systems, perturbations caused by the photoisomerization of azobenzene units can be transferred effectively to the host LCs, resulting in surprisingly efficient photochemical phase transition.

Conclusion

The relaxation time in the photochemical phase transition of PLCs has been evaluated by the use of the nanosecond laser pulse. The isothermal phase transition of the BMAB/PAPB3 mixture was induced photochemically by a single pulse of the laser with the relaxation time of ~100 ms, which is comparable to that observed for BMAB/low molecular weight LC mixtures. The relaxation time was affected by such factors as the irradiation temperature and the laser power. Furthermore, in the copolymer PLCs, the relaxation time was 10 times shorter than that in the azobenzene/PLC mixtures. These results demonstrate that the PLCs may be used for optical image storage materials with (1) excellent processability, (2) film-forming property, (3) high stability of the stored image, and (4) quick response.

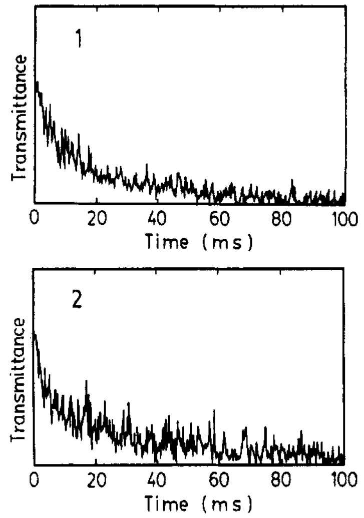

Figure 12. Time-resolved observation of photochemical phase transition behaviors of copolymer LCs. 1, PB3-3; 2, PB3-5. Laser power, 0.28 J/cm^2; T/T_{NI} = 0.999.

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Registry No. PAPB3 (homopolymer), 118086-64-9; PACB3 (homopolymer), 104357-58-6; PB3-3 (copolymer), 123642-72-8; PB3-5 (copolymer), 123642-74-0; BMAB, 31401-33-9; IAB3CB, 141484-74-4; IAB4CB, 141484-75-5; IAB5CB, 141484-76-6; AB(3CB)$_2$, 141484-77-7; AB(4CB)$_2$, 141484-78-8; AB(5CB)$_2$, 141484-79-9; AB(6CB)$_2$, 141484-80-2; HOAB, 1689-82-3.