Photochemically Induced Isothermal Phase Transition in Polymer Liquid Crystals with Mesogenic Cyanobiphenyl Side Chains

Tomiki Ikeda,* Seiji Kurihara, Durga B. Karanjit, and Shigeo Tazuke†

Photochemical Process Division, Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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ABSTRACT: Photochemically induced isothermal phase transition in polymer liquid crystals (PLC) with side-chain mesogenic cyanobiphenyl has been explored. The PLC samples studied are poly[4-[(acryloyloxy)alkoxy]-4′-cyanobiphenyl] (PACBn), in which the alkyl spacer length $(CH_2)_n$ was varied as $n = 3, 5, 6$, and 11, and the copolymers of PACB3 with 4′-methoxy-4-[(acryloyloxy)alkoxy]azobenzene (AAZOm) where $m = 3, 6$, and 11 (copolymer $n-m$). In the homopolymers, a photoresponsive molecule, 4-butyl-4′-methoxyazobenzene (BMAB), was doped to induce the photochemical phase transition. Photoirradiation of the PACB5/BMAB (5 mol %) film at 460 nm caused trans → cis isomerization of BMAB, which induced simultaneously nematic (N) → isotropic (I) phase transition of the host PLC. This process was reversible, and photoirradiation at 525 nm, which induced cis → trans isomerization of BMAB, restored the system to the initial state (N). The photochemical phase transition was strongly dependent on the spacer length (n and m) and the molecular weight of the host PLC's. Among the PLC samples examined, the photochemical phase transition was observed in PACB3, PACB5, copolymer 3–3, and copolymer 3–6. On the basis of the calorimetric studies and the order parameters, the efficiency was found to be closely correlated to the orientational ordering of the initial state of the host PLC's. The photochemical N → I phase transition took place more effectively in a system with a less ordered N state. The photochemical phase-transition behaviors of the present PLC systems are discussed in relation with those of PLC's with mesogenic phenyl benzoate side chains previously reported.

Introduction

Low molecular weight liquid crystals have been widely used as active media in display devices. The working principle of these display devices is essentially an electrooptic effect, thus requiring matrix arrangement of transparent electrodes.[1] For improved resolution, laser beam addressed display systems have recently been developed.[1] These systems are based on thermooptic effects of the liquid crystals. Although high resolution has been achieved by the use of the focused laser beam (<10 μm ϕ), stability of the stored image is not satisfactory.[1]

Use of polymer liquid crystals (PLC) as optical image storage materials has become a current topic.[2] Advantages of PLC over the low molecular weight liquid crystals as image storage materials are as follows. (1) Because of glass transition phenomenon (T_g), segmental motion of the polymer chains can be frozen-in; thus it is expected that the stored image can be kept stable below T_g for a long period. (2) Good film-forming properties of the polymers expectedly enable cell-free performance of the image storage materials, which is evidently favored from the applicational viewpoint. (3) Low fluidity of the polymers is favorable for the long-term stability of the stored image.

Shibaev et al.[3] and Coles and Simon[4] reported the laser-addressed PLC storage displays in which heat-mode writing was employed. Photon-mode image storage in the PLC was first reported by Eich and Wendorff as "holographic" optical storage.[5,6] In their system, photoisomerization of photochromic groups (azobenzene derivatives) incorporated into the PLC's induced "grating" in the PLC, which was a consequence of the change in the refractive index resulting from the isomerization.

We have demonstrated photochemically induced isothermal phase transition in liquid crystals aiming at optical image storage systems.[7-12] The working principle of our systems is *isothermal phase transition of the liquid crystals* at the irradiation site; thus we can expect a high contrast and a high signal-to-noise ratio for the stored information. In early papers,[11,12] we reported the photochemical phase-transition behavior of PLC's with side-chain phenyl benzoate mesogens. We have revealed that the rate of the photochemical phase transition is closely related to thermodynamic properties and order parameters of the host PLC's. In this paper we report the photochemically induced phase transition of the PLC's with side-chain cyanobiphenyl mesogens and discuss the photochemical phase-transition behavior with reference to the thermodynamic properties of the PLC's. Choice of cyanobiphenyl is based on the following aspects. First, cyanobiphenyls are another group of mesogens widely used for display devices.[2] Second, because of their emissive nature, fluorescence spectroscopy can be used to characterize the liquid-crystalline behavior. This method is in fact a powerful tool to investigate particularly microscopic interaction between mesogens and is now in progress in our laboratory.

Experimental Section

Materials. Structures of the PLC's used in this study are shown in Figure 1. Acrylates with mesogenic cyanobiphenyls in the side chain (ACBn) were prepared by the method reported by Shibaev et al.,[13] and the acrylates with side-chain azobenzene moieties (AAZOm) were synthesized by a method similar to that employed by Ringsdorf et al.[11,14]

4-Butyl-4′-methoxyazobenzene (BMAB) were prepared and purified as reported previously.[7] 4-(n-Pentyloxy)-4′-cyanobiphenyl (5OCB), 4-(n-hexyloxy)-4′-cyanobiphenyl (6OCB), and 4-n-undecyl-4′-cyanobiphenyl (11OCB) were purchased from Merck Co. and were used without further purification. Their phase-transition temperatures as well as thermodynamic data are listed in Table I.

Polymerization was conducted in tetrahydrofuran (THF) by the use of azobis(isobutyronitrile) (AIBN) as an initiator. Benzene was also used in place of THF when high molecular weight polymers were prepared. In copolymerization, conversion was

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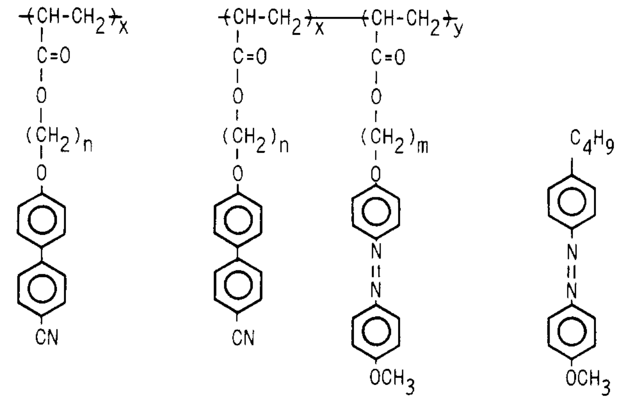
* Author to whom correspondence should be addressed.

† Deceased July 11, 1989.



PACBn Copolymer n-m BMAB

Figure 1. Structures of liquid crystals used in this study.

Table I
Thermodynamic Properties of nOCB[a]

n	T_{NI}	ΔH_{NI}, kJ/mol	ΔS_{NI}, J/mol·K
5	69.9	0.21	0.62
6	76.8	0.56	1.60
11[b]	87.3	2.83	7.86

[a] Determined by DSC. [b] Data for smectic to isotropic phase transition.

always kept low (<15%). All polymers were purified by repeated precipitation from chloroform solution into methanol.

Characterization of Polymers. Molecular weights (MW) of the polymers were determined by gel permeation chromatography (GPC; Toyo Soda HLC-802, column, GMH6 × 2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. GPC was also employed for fractionation of the polymers. Liquid-crystalline behavior and phase-transition behavior were examined on an Olympus Model BHSP polarizing microscope equipped with Mettler hot-stage Models FP-80 and FP-82. Thermotropic properties of the polymers were determined with a differential scanning calorimeter (SEIKO I&E SSC-5000) at a heating rate of 10 °C/min. At least four scans were performed for each sample to check reproducibility.

Composition of the copolymers was determined by absorption spectroscopy on the basis of molar extinction coefficients of the azo monomers separately determined. The azobenzene content of the copolymers was 4.7 mol % (copolymer 3–3), 5.1 mol % (copolymer 3–6) and 4.0 mol % (copolymer 3–11).

Polarized IR spectra were recorded with a JEOL JIR-3505 FT-IR spectrometer with the aid of a gold-wire glid polarizer. Oriented samples of the PLC films for the FT-IR measurements were prepared by casting the polymer solution in chloroform onto CaF_2 plates, followed by placing the cast film in the magnetic field of 2.1 T as described previously.[11] The film was heated in the magnetic field above the nematic to isotropic phase-transition temperature of the sample and cooled gradually just below the phase-transition temperature, and the sample was kept at this temperature for at least 10 h.

Photoinduced Phase Transition. Photochemical phase-transition behavior of PLC's was followed by means of an apparatus already reported with some modifications.[12] In the modified apparatus, the absorbance of the azobenzene derivatives incorporated could be measured in situ at the photoirradiation wavelength. Thus, the photoisomerization behavior of the photochromic molecules was followed simultaneously with photoirradiation. Polymer films were prepared by casting the polymer solution in chloroform on to glass plates. After they were completely dried under reduced pressure, the films were annealed in a thermostat at temperatures where the PLC films showed liquid-crystalline phase. The polymer films were then examined for their liquid-crystalline behavior with the polarizing microscope. The polymer films thus prepared were placed in a thermostated block and irradiated with a monochromatic light from a Jasco CRM-FA irradiator. The photochemically induced phase-transition behavior was followed by monitoring of the intensity of the linearly polarized light at 633 nm from a He–Ne laser transmitted through a pair of crossed polarizers with a photodiode.[12]

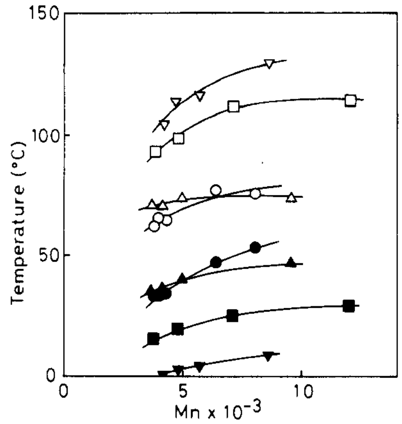


Figure 2. Phase-transition behaviors of PACBn as a function of molecular weight. PACB3: (●), T_g; (○), T_{NI}. PACB5: (▲), T_g; (△), T_{NI}. PAPB6: (■), T_g; (□), T_{NI}. PACB11: (▼), T_g; (▽), T_{SI}.

Results and Discussion

Thermotropic Properties of PLC's. In DSC thermograms (heating), we observed two endothermic events: one occurring at lower temperature as a shift of the base line toward the endothermic direction was due to the glass transition of the polymers (T_g), and the other corresponded to nematic (N) to isotropic (I) phase transition of the polymer liquid crystals (T_{NI}). In PACB11, a peak at higher temperature was due to smectic (S) to isotropic phase transition (T_{SI}). We assigned each phase on the basis of textures observed with the polarizing microscope. In order to examine the MW effect of the polymers on the thermotropic properties, nearly monodispersed polymer samples with varying MW's were subjected to DSC measurements. Here, the polydispersity index (M_w/M_n) of the samples was in the range of 1.0–1.3. Figure 2 shows the phase-transition behaviors of the homopolymers as a function of MW. None of the monomers (ACBn) exhibited a liquid-crystalline phase. T_g and T_{NI} (T_{SI}) values of the polymers increased with MW except that for PACB5, which showed little temperature dependence.

Phase-transition behaviors were also investigated for copolymer *n–m* in which *n* was fixed to 3 and *m* was varied as 3, 6, and 11. All the samples of copolymer 3–*m* exhibited the liquid-crystalline phase (N). In order to compare the photochemical phase-transition behaviors of copolymer *n–m* and PACBn doped with BMAB, the composition of the copolymers was designed so as to be similar to those of the doped systems. Namely, in the doped systems, the concentration of the doped BMAB was usually 5 mol %; thus the content of the azo monomer (AAZOm) in the copolymers was intended to be as close as possible to 5 mol %. Figure 3 indicates the MW dependence of the phase-transition temperature of copolymer 3–*m*. As in the case of the homopolymers, T_g and T_{NI} increased with increasing MW.

In Figure 4, thermodynamic data on the phase transition of PACBn (ΔH_C and ΔS_C) are shown as a function of MW. Contrary to T_g and T_{NI}, both ΔH_C and ΔS_C showed little temperature dependence. These trends were in contrast to the thermodynamic behaviors observed for PLC's with side-chain phenyl benzoate mesogens.[11,15] The thermodynamic data on copolymer 3–*m* are also shown in Figure 5 as a function of MW.

Order Parameters Determined by IR Dichroism. For a uniaxially symmetrical system, the dichroic ratio,

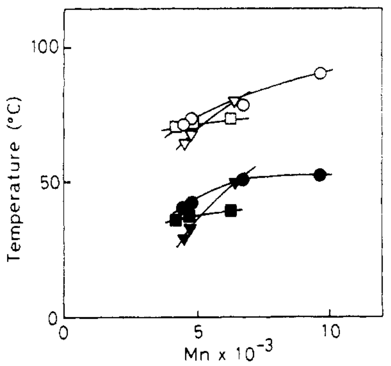


Figure 3. Phase-transition behaviors of copolymer 3-*m* as a function of molecular weight. copolymer 3-3: (●), T_g; (○), T_{NI}. copolymer 3-6: (■), T_g; (□), T_{NI}. copolymer 3-11: (▼), T_g; (▽), T_{NI}.

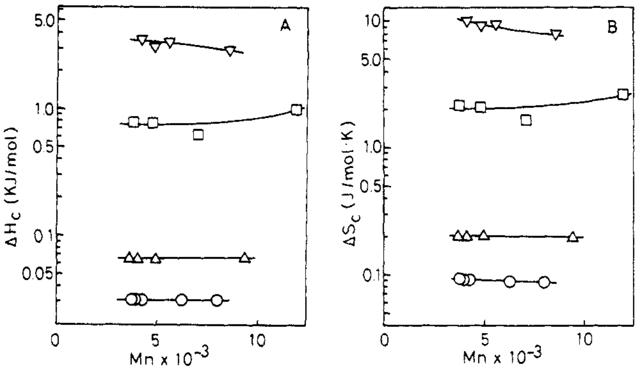


Figure 4. Thermodynamic data on the phase transition of PACBn as a function of molecular weight. A, ΔH_C; B, ΔS_C. (○), PACB3; (△), PACB5; (□), PACB6; (▽), PACB11.

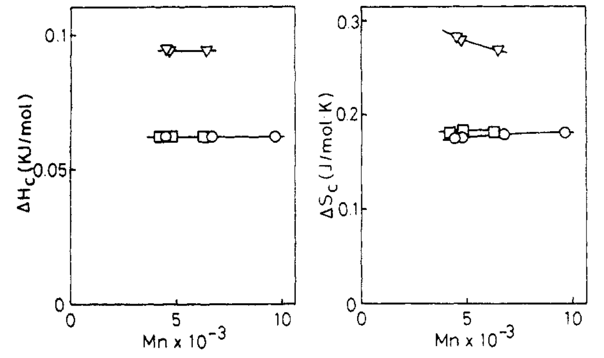


Figure 5. Thermodynamic data on the N → I phase transition of copolymer 3-*m* as a function of molecular weight. A, ΔH_C; B, ΔS_C. (○), copolymer 3-3; (□), copolymer 3-6; (▽), copolymer 3-11.

R, can be given by eq 1,[16] where $\epsilon_\parallel$ and $\epsilon_\perp$ are the

$$R = \frac{\epsilon_\parallel}{\epsilon_\perp} = \frac{4\cos^2\alpha\langle\cos^2\theta\rangle + 2\sin^2\alpha\langle\sin^2\theta\rangle}{2\cos^2\alpha\langle\sin^2\theta\rangle + \sin^2\alpha\langle 1+\cos^2\theta\rangle} \tag{1}$$

absorption coefficients measured with the IR beam polarized parallel and perpendicular to the optical axis of the molecule, respectively. θ is the angle between the direction of the long axis of the molecule and the optical axis of the uniformly oriented liquid crystal, and α is the angle between the long axis of the molecule and the direction of the vibrational transitional moment. In the case where the vibrational transitional moment is oriented parallel to the long axis of the molecule, the order parameter, *S*, can be written in the form of eq 2.[16]

$$S = \frac{R-1}{R+2} \tag{2}$$

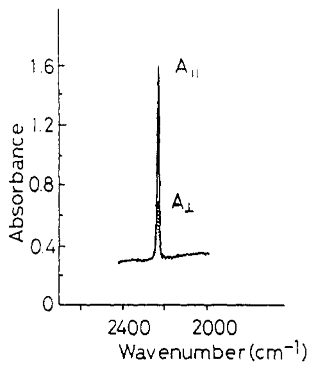


Figure 6. FT-IR polarized absorption spectra of PACB5 at 36 °C. M_n = 3900. (—) Polarized parallel to the optical axis; (···) polarized perpendicular to the optical axis.

Figure 6 shows the FT-IR polarized absorption spectra of PACB5 measured at 36 °C. A peak at 2220 cm^{-1} is due to the C≡N stretching vibration. In this peak, $\epsilon_\parallel$ is much larger than $\epsilon_\perp$, which is apparently a consequence of the parallel orientation of the corresponding vibrational transition moment to the molecular long axis. We used this peak for the determination of the order parameters of the PLC's.

Figure 7 shows the order parameters of PACBn with M_n = ~4000 as a function of the reduced temperature (T_{red} = T/T_{NI}). It is seen that the order parameters for PACB3 and PACB5 are nearly constant at T_{red} < ~0.93 and then decrease rather steeply with temperature. They are lowest at a temperature close to the phase transition temperature. This is a common tendency observed for the order parameters.[11,16] However, the temperature profile of *S* for PACB6 is somewhat strange. The value of *S* starts to decrease at T_{red} as low as ~0.8 and thereafter decreases rather monotonically with temperature. In order to explore this strange behavior of PACB6, we studied the time course of the change in the order parameters. The value of *S* of PACB6 was found to depend on the time elapsed after the oriented sample was transferred from the magnetic field. The *S* value decreased with time, indicating that relaxation may take place from a uniaxially oriented state to presumably a polydomain in PACB6. This time-dependent behavior was not observed for PACB3 and PACB5. Thus, the values of *S* presented for PACB6 are not reliable.

Photochemically Induced Phase Transition. Photochemically induced phase-transition behavior is shown in Figure 8 where a PACB5 film doped with 5 mol % of BMAB was irradiated at 460 nm to bring about trans → cis photoisomerization of BMAB and at 525 nm to cause cis → trans reverse isomerization of the dopant. Transmittance of the linearly polarized light at 633 nm through the crossed polarizers between which the sample was placed, I_t, was measured simultaneously as a function of time. It is clear that the trans → cis photoisomerization of the doped BMAB (460 nm) brought about nematic (N) → isotropic (I) phase transition of the host PLC as demonstrated by complete loss of birefringence (I_t = 0), and the cis → trans isomerization (525 nm) restored the whole system to the initial state (N). Reversible isothermal phase transition of the PLC can be induced in this way by photochemical reaction of the incorporated photoresponsive molecules.

It is worth mentioning here that the photochemical N → I phase transition was apparently dependent on the wavelength of the irradiation light. Usually, we employ the light of ~360-nm wavelength to cause the trans → cis photoisomerization of azobenzene derivatives because

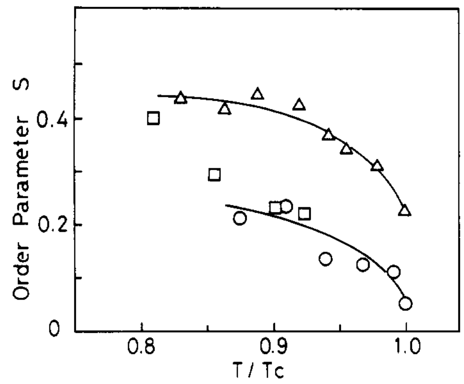


Figure 7. Order parameters of PACBn determined by FT-IR dichroism as a function of T_{red}. (○), PACB3; (△), PACB5; (□), PACB6.

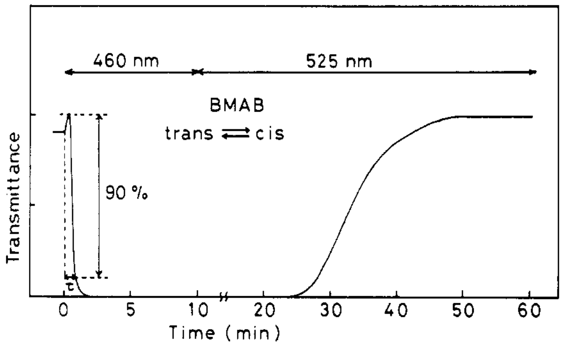


Figure 8. Photochemical phase-transition behavior of PAPB5 doped with 5 mol % of BMAB. Transmittance between a pair of the crossed polarizers is plotted as a function of irradiation time (λ_{ex} = 460 or 525 nm). Photoirradiation was performed at the reduced temperature, T_{red} (T/T_{NI}), of 0.99.

absorption maxima exist around 360 nm (Figure 10). At first, we used the 365-nm light to cause the N → I phase transition in the present study and found that the photochemical N → I phase transition was induced only in PACB3 and its copolymer (copolymer 3–6). We then tried the light with longer wavelengths than 365 nm and found that the photochemical N → I phase transition could be induced in PACB5 and copolymer 3–6 at 460 nm. Because of a high scattering nature and a severe interference associated with the present PLC samples (see below), the absorption spectra of BMAB doped in the PLC samples could not be measured reliably. Although the absorbance of BMAB in the PLC's at 365 nm could not be determined, it was presumed on the basis of the film thickness, the molar extinction coefficient, and the concentration of BMBA that photons of 365 nm were absorbed entirely at the surface layer of the PLC samples containing BMAB and the photochemical N → I phase transition took place only at the surface layer. Under this situation, the deeper layer of the PLC samples presumably remained in the liquid-crystalline phase, thus showing the birefringence. In the present experimental setup, the photochemical phase transition was only detectable for samples in which the phase was changed to the I state throughout in the direction of depth. At 460 nm, the incident light may penetrate much more deeply because of the lower absorbance at this wavelength than at 365 nm. Thus, trans → cis photoisomerization, followed by the N → I phase transition of the matrix PLC's, took place along the locus of the irradiation light through the total layer of the PLC films. Thus, the light of 460 nm was employed thereafter in the study of the photochemical N → I phase-transition behaviors.

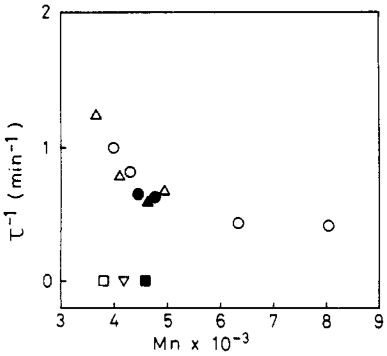


Figure 9. Molecular weight dependence of the photochemical phase-transition behaviors of PLC's. The rate of the phase transition, τ^{-1}, is plotted as a function of molecular weight. (○), PACB3; (△), PACB5; (□), PACB6; (▽), PACB11; (●), copolymer 3–3; (▲), copolymer 3–6; (■), copolymer 3–11. In the case of the homopolymers, BMAB was doped at 5 mol %.

In Figure 8, the change in I_t is peculiar in the course of the N → I phase transition. Namely, it goes up on photoirradiation at 460 nm and then drops down to I_t = 0. This apparently strange behavior of I_t can be explained in terms of interference, which was thoroughly discussed in the previous paper.[12] One also realizes that the time required for the I → N phase transition (525 nm) is much longer than that for the N → I phase transition (460 nm). Two reasons are considered. One is due to low extinction coefficient of the cis form of the azobenzene moieties. Under the present experimental setup, the light intensity at 525 nm is higher than that of 460 nm; however, the number of photons absorbed by the cis form is much smaller than that absorbed by the trans form. This results in a lower rate of cis → trans isomerization, leading consequently to a lower rate of the phase transition. The second reason is related to order of the system. The rate of the "order" to "disorder" change is considered to be higher than that of the "disorder" to "order" change, since the former is more favored entropically than the latter.

The photochemical phase-transition behavior was examined for the other PLC samples, and the results are summarized in Figure 9 where the rates of the photochemical phase transition evaluated by the reciprocal of the response time (τ, Figure 8), the time required for I_t to be reduced to 10% of the maximum value, are plotted as a function of the molecular weight of the host PLC's. The phase transition could not be induced photochemically in PACB6 (MW = 3800), PACB11 (MW = 4200), and copolymer 3–11 (MW = 4550) even on prolonged irradiation at any wavelengths. It is clearly seen that the photochemical phase transition was induced more effectively in the samples with smaller molecular weight. Furthermore, in copolymer 3–3 the photochemical phase transition was not so effectively induced in comparison with that of PACB3, which is in sharp contrast to the photochemical phase-transition behavior of the copolymer composed of phenyl benzoate monomer and AAZO with the same alkyl spacer length (n = m = 3).[12]

We tried to follow the rate and the degree of photoisomerization of the doped BMAB during the course of photoirradiation. Unfortunately, however, the high scattering nature of the present PLC samples as well as the severe interference as described above prevented measurement of the absorbance in situ or the absorption spectra of BMAB in the PLC's by the use of a conventional absorption spectrometer. We used the low molecular weight analogues (nOCB, n = 5, 6, and 11) in place of the PLC's to explore the photochromic behavior of BMAB incorporated in the liquid-crystalline phase. Although

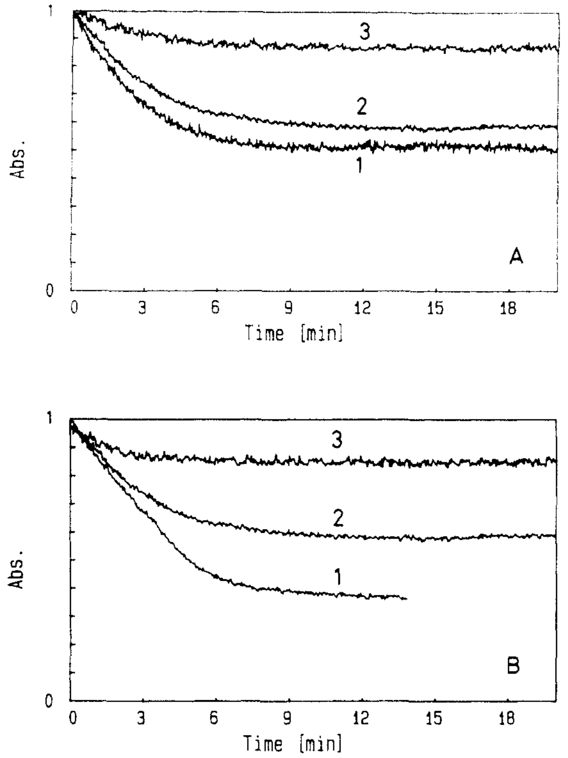


Figure 10. Change in absorbance of BMAB doped in nOCB at 365 nm on photoirradiation. 1, 5OCB; 2, 6OCB; 3, 11OCB. A, at 75 °C; B, at the reduced temperature of 0.99. Photoirradiation was performed at 365 nm.

nOCB showed different phase-transition behavior (T_{NI}) and thermodynamic data (ΔH_C and ΔS_C) from those of PACBn, a general trend is preserved. Namely, the phase-transition temperature as well as ΔH_C and ΔS_C increases with an increase in the value of n. The change in absorbance of BMAB doped in nOCB on photoirradiation at 365 nm is shown in Figure 10 as a function of the irradiation time, where the absorbance was measured at 365 nm, which is due mainly to the absorption of the trans form of BMAB. In this case, the concentration of BMAB was kept low (1 mol %) in order to prevent the photochemical phase transition of the host liquid crystals. At 75 °C and at $T_{red} = 0.99$, the rate of the trans → cis photoisomerization evaluated by the initial slope of the curve increased in the order of 11OCB < 6OCB < 5OCB. Furthermore, the degree of isomerization, which can be estimated by the absorbance at a stationary state (A_∞), also increased in the same order. For the degree of the photoisomerization, a higher value of A_∞ means a lower degree of the isomerization. The low rate as well as the low degree of the photoisomerization observed for 11OCB is not due to a high rate of thermal reverse isomerization (cis → trans) but most probably to the rigid nature of the matrix liquid crystal.

In the preceding section, thermodynamic data as well as order parameters of the PLC's were investigated. Results showed that PACB3 possesses low values of S in the whole temperature range. Coupled with the extraordinarily low values of the thermodynamic parameters (ΔH_C and ΔS_C) of PACB3, this result indicates that PACB3 has a less ordered structure in the N state. The parallel tendency between ΔS_C and S can be rationalized if we assume that PLC's have the same values of entropy in the isotropic state. Namely, a large value of ΔS_C means a small value of entropy in the N state, thus higher orientational ordering in the N state. Such a parallel relationship has been already reported for side-chain PLC's[11] and main-chain PLC's.[17,18] Thus, ΔS_C can be used as a measure for the orientational ordering of liquid crystals of interest, although it is just an indirect one.[17] Support for this view is given by the Flory–Ronca theory, which predicts that ΔS_C is proportional to the second power of S.[19]

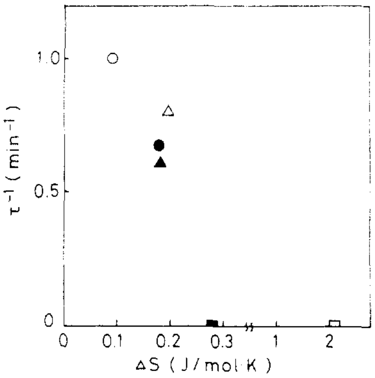


Figure 11. Photochemical phase-transition behaviors of PLC's as a function of ΔS_C. (○), PACB3; (△), PACB5; (□), PACB6; (●), copolymer 3–3; (▲), copolymer 3–6; (■), copolymer 3–11. In the case of the homopolymers, BMAB was doped at 5 mol %.

In 11OCB, the value of ΔS_C is higher than those of 5OCB and 6OCB, suggesting a higher orientational ordering of 11OCB in the N phase based on the above consideration. In a highly ordered structure, mesogens as well as dopants are expected to have low mobility. Support for this has been obtained by the time-resolved fluorescence spectroscopy. Fluorescence analysis of main-chain PLC's with mesogenic p-phenylenediacrylic acid (PDA) revealed that the mobility of the emissive mesogens (PDA) was lower in the systems with higher values of ΔS_C.[20] Thus, it is reasonably assumed that the photoisomerization of BMAB is suppressed in a matrix with a highly ordered structure. This explains the photochromic behavior of BMAB in the nOCB matrices. Furthermore, the photochemical phase-transition behavior observed for the PLC's is explicable on the same basis. In Figure 11, the rate of the photochemical phase transition, τ^{-1}, is plotted as a function of ΔS_C of the PLC samples, where the molecular weight of the samples is ~4000. It is clearly seen that the photochemical phase transition was only induced for the PLC's with ΔS_C less than 0.2, and it was most effective in the PLC with the smallest value of ΔS_C. The effect of MW on the photochemical phase transition may also be explained in terms of suppressed isomerization of BMAB in the PLC's with a higher MW. In these PLC samples, viscosity becomes higher with increasing MW, leading to suppression of the photoisomerization.

The effect of temperature on the photochemical phase-transition behavior was examined as a function of the reduced temperature. The rate of the phase transition, τ^{-1}, was strongly dependent on the temperature. In the case of PACB3, the rate decreased with decreasing temperature and the maximum rate was observed at $T_{red} = 0.995$. The rate of the isothermal phase transition is closely related to lowering of the phase-transition temperature brought about by accumulation of the cis form of BMAB.[7] Namely, T_{NI} decreases as the concentration of the cis form increases, and when T_{NI} of the system is lowered below the irradiation temperature, the isothermal phase transition is induced. Thus, when the irradiation temperature is close to T_{NI} of the initial state, the amount of the cis form required to lower T_{NI} below the irradiation temperature is rather small and the phase transition is induced rapidly. On the other hand, when the irradiation

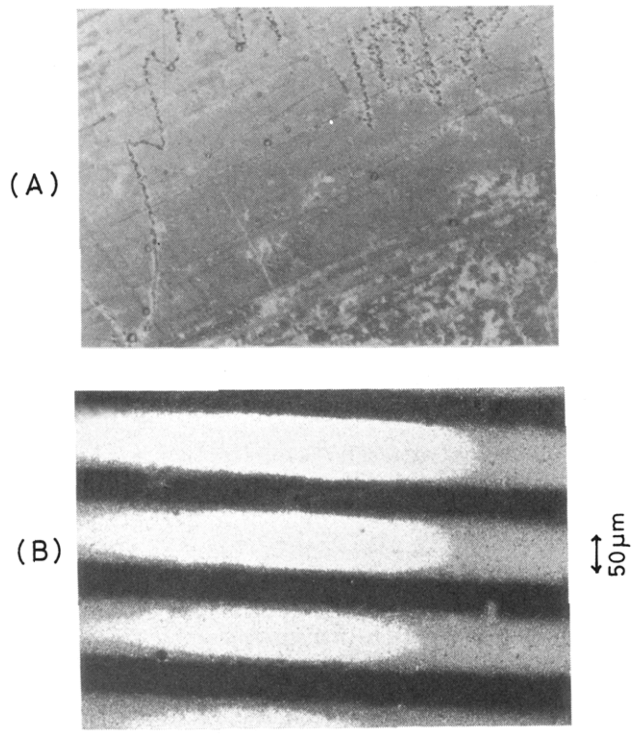


Figure 12. Photograph of test pattern stored in PACB3: (A) before irradiation; (B) after irradiation. PACB3 containing 5 mol % of BMAB was irradiated at 365 nm to induce N → I phase transition. After the irradiation, the PACB3/BMAB film was stored below T_g of the sample.

temperature is low, a large amount of the cis form is necessary to lower the T_{NI} of the system below the temperature; thus the rate of the phase transition is expected to be low.

Comparison between PLC with Side-Chain Phenyl Benzoates and PLC with Side-Chain Cyanobiphenyls. It is worth comparing the photochemical phase-transition behaviors between PLC's with side-chain phenyl benzoate (PB) mesogens[11,12] and PLC's with side-chain cyanobiphenyl (CB) mesogens here. In both systems, the photochemical phase transition is correlated to the orientational ordering of the host PLC. The phase transition is induced more effectively in the sample with less ordered structure. A significant difference has been observed for the mode of interaction of the azobenzene moiety with the PB and CB mesogens. 4,4′-Disubstituted azobenzene derivatives can form the LC phase; however, their ability to form the LC phase is rather low because of weak interaction between the azobenzene moieties.[21] Incorporation of the azobenzene derivatives into mesogenic phases composed of PB resulted in a less ordered structures of the resulting PLC's.[11] T_{NI} as well as ΔH_C and ΔS_C decreased with an increase of the azo monomer content in the copolymer.[11] Furthermore, among the copolymers composed of PB monomer and AAZOm the one with the same spacer length exhibited the lowest values of ΔS_C and S, which is another piece of evidence that the azobenzene moiety weakens interaction between PB mesogens. On the other hand, the azobenzene moiety seems to strengthen the mutual interaction between mesogens when incorporated into the PLC composed of CB mesogens. This is clearly seen in Figure 5 where ΔS_C and ΔH_C of copolymer 3–*m* are much larger than those of the pure homopolymer PACB3. It is, therefore, explicable on this basis that photochemical phase transition was not induced more effectively in copolymer 3–*m* than in PACB3 in the present study.

Image Storage Experiments. Long-term stability of the stored information was examined. The PACB3/BMAB film was covered with a standard photomask and was irradiated at 365 nm to induce the N → I phase transition. Irradiation was performed at 60 °C (T_{red} = 0.99). After exposure, the film was cooled below T_g and the stored image was examined with the polarizing microscope. A photograph of the stored optical image is shown in Figure 12. The I phase formed at the site of photoirradiation (seen as black parts due to loss of birefringence) still remained unchanged after 1 mo. Long-term storage of the stored information could be achieved in this way by cooling the irradiated PLC film below T_g of the polymer.

This result demonstrates that a photosignal is converted into the phase change of the whole system, which is in this case read out by the loss of birefringence. Merits of this way of image storage are evident. The system is transparent to the monitor light and consequently the readout is completely nondestructive. Furthermore, contrast is high enough since readout is based on the difference between the black part and bright part. This leads to high signal-to-noise ratio when the information is read out.

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Registry No. PACB*n* (*n* = 3) (homopolymer), 104357-58-6; PACB*n* (*n* = 5) (homopolymer), 78475-03-3; PACB*n* (*n* = 6) (homopolymer), 100653-74-5; PACB*n* (*n* = 11) (homopolymer), 80122-97-0; BMAB, 31401-33-9; 5OCB, 52364-71-3; 6OCB, 41424-11-7; 11OCB, 72928-29-1; copolymer 3-3, 128302-40-9; copolymer 3-6, 128302-42-1; copolymer 3-11, 128302-44-3.