(26) Neff, V. D. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; Ellis Horwood: Chichester, 1974; Vol. 2, pp 231-253.
(27) Noel, C.; Laupretre, F.; Friedrich, C.; Fayolle, B.; Bosio, L. *Polymer* **1984**, *25*, 808.
(28) Landreth, B. M.; Stupp, S. I. *Macromolecules* **1987**, 2083.
(29) Watanabe, J.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 2288.
(30) Iimura, K.; Koide, N.; Ujiie, S. *11th Liq. Cryst., Int. Conference, 11th* **1986**, θ-112-M5.
(31) Toriumi, H.; Furuya, H.; Abe, A. *Polym. J. (Tokyo)* **1985**, *17*, 895.
(32) Konstantinov, I. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, C3-475.

Photochemically Induced Isothermal Phase Transition in Polymer Liquid Crystals with Mesogenic Phenyl Benzoate Side Chains. 2. Photochemically Induced Isothermal Phase Transition Behaviors

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ABSTRACT: Photochemically induced isothermal phase transition in polymer liquid crystals (PLC) with mesogenic phenyl benzoate side chains has been demonstrated. PLC's examined are poly(4′-methoxyphenyl 4-((acryloyloxy)alkoxy)benzoate) (PAPB*n*), in which the alkyl spacer length $(CH_2)_n$ was varied as n = 2, 3, 5, or 6 and their copolymers with 4′-methoxy-4-((acryloyloxy)alkoxy)azobenzene (AAZO*m*) where m = 2, 3, 5, 6, or 11 (poly(APB*n*-*co*-AAZO*m*) or copolymer *n*-*m*). Two types of systems have been explored: one is composed of PAPB*n* doped with a small amount of a low molecular weight (MW) mesogen with a photoresponsive moiety, 4-butyl-4′-methoxyazobenzene (BMAB), and the other is copolymer *n*-*m*. Photoirradiation of the PAPB3/BMAB (5 mol %) film at 366-nm light caused the trans → cis isomerization of BMAB, which induced simultaneously the nematic (N) → isotropic (I) phase transition of the PLC film. This process was reversible, and photoirradiation at 525 nm which induced the cis → trans isomerization of BMAB restored the system to the initial phase (N). The phase transition behavior was found to be strongly dependent on the spacer length (*n*) and MW of the PLC. Similar isothermal phase transition behaviors were observed in copolymer 3-*m*; however, in other copolymers like copolymer 6-*m* the isothermal phase transition could not be induced photochemically. Among the PLC samples examined, copolymer 3-3 showed the highest rate of isothermal phase transition. On the basis of the calorimetric studies and order parameter determinations reported in the preceding paper, the efficiency of the photochemically induced isothermal phase transition was found to be closely related to orientational ordering of the initial state of the PLC. Thus, the N → I isothermal phase transition took place more effectively in a system with a less ordered N state. Resolution of the stored image was estimated as 2∼4 μm on the basis of experiments where copolymer 3-3 was covered with a photomask and irradiated with the third harmonic of a YAG laser.

Introduction

Liquid crystals (LC) have been most extensively used as display materials. Successful application of the LC display cells covers the numerical data displays for wrist watches and calculators, sentence displays for word processors, and full-color TV displays. The function of these display cells are essentially based on the electrooptic effect of the LC, requiring a matrix arrangement of the transparent electrodes.[1,2] Thus, a high resolution over a large area is a tough problem for these LC cells to overcome.[2]

A laser beam addressed display has been recently developed.[1,2] This is principally based on the thermooptic effects of the LC's, and frequently electrothermooptic effects are also employed. Since the laser beam can be focused to <10-μm diameter, high resolution can be expected for the laser beam addressed displays.[2] The write-in process includes irradiation of the LC cells with a laser beam, a rapid increase in temperature along the laser beam trace results in a phase transition from the liquid crystalline state (nematic (N) or smectic (S)) to the isotropic (I) state, and removal of the laser beam leads to rapid cooling of the isotropic trace, producing light scattering centers such as honeycomb and focal conic textures.[2] These light scattering centers remain in the LC cells; thus they can display static figures. However, stability of the stored information is not satisfactory, and the high contrast will be lost after some period.[1,2]

The use of polymer liquid crystals (PLC) as optical storage materials has become a current topic in view of the glass transition (T_g) phenomenon and processability of polymers. Cell-free polymer films with the ability of long-term information storage are evidently favored from an industrial viewpoint. The laser beam addressed recording has been achieved in side-chain PLC's[3-5] and in main-chain PLC.[6] They are mainly based on the thermooptic effects, but photochemical reactions play an important roll in the write-once storage materials.[5]

Photon-mode optical image storage in PLC's has been demonstrated by Eich and Wendorff.[7,8] Their system is composed of PLC's with side-chain photochromic azoben-

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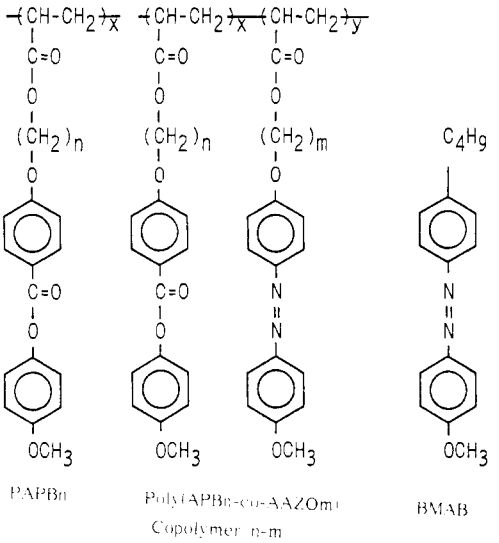

Figure 1. Structure of liquid crystals used in this study and their abbreviations.

zene moieties, and photoirradiation caused isomerization of the photochromic molecules, inducing "grating" in the PLC. The grating is produced by the change in the refractive index of the medium resulting from isomerization.

The advantage of the photon-mode recording over the heat-mode recording lies in the superior resolution and possibility of multiplex recording in the photon-mode recording.[9] Heat diffusion evidently worsens the resolution. A variety of information associated with the photon-mode recording (energy, polarization, and coherency) are also advantages of the photon-mode recording.[9] For high sensitivity and high signal to noise ratio (S/N) of the recording, other methods than direct reading of the photochemical reaction are to be developed. Vision is a good model. In visual cells, photons are absorbed by retinal photoreceptors and photoisomerization of the photoreceptors takes place.[10] A photochemical reaction occurring at a local site of the visual cells causes a conformational change in whole protein molecules, and subsequently the photosignals are amplified.[10] This principle has been applied to several systems for the demonstration of the photochemically induced phase transition of the systems.[11-15] In this paper, the photochemically induced phase transition behaviors of the PLC's whose thermodynamic properties and order parameters were fully investigated in the preceding paper[16] are studied with special reference to the orientational ordering of the PLC's. Factors affecting the photochemically induced isothermal phase transition of the PLC's are explored to construct effective optical image storage systems, and finally resolution of the stored image is examined.

Experimental Section

Materials. Structure of the PLC's used in this study is shown in Figure 1. Syntheses of acrylates with mesogenic phenyl benzoates in the side chain (APB*n*) and acrylates with side-chain azobenzene moieties (AAZO*m*) are described in the preceding paper.[16] Abbreviations used for the homopolymers and copolymers are also indicated in Figure 1.

Photoinduced Phase Transition. Photoinduced phase transition behavior of PLC's was followed by means of an apparatus schematically illustrated in Figure 2. Polymer films were prepared by casting the polymer solution in chloroform onto glass plates. The films were then dried under reduced pressure, and their LC behavior was examined with a polarizing microscope. Unlike low molecular weight LC's, annealing of

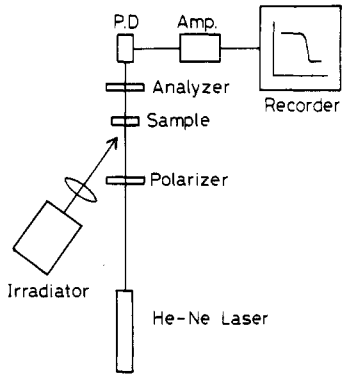

Figure 2. Schematic diagram for the measurement of photochemically induced phase transition.

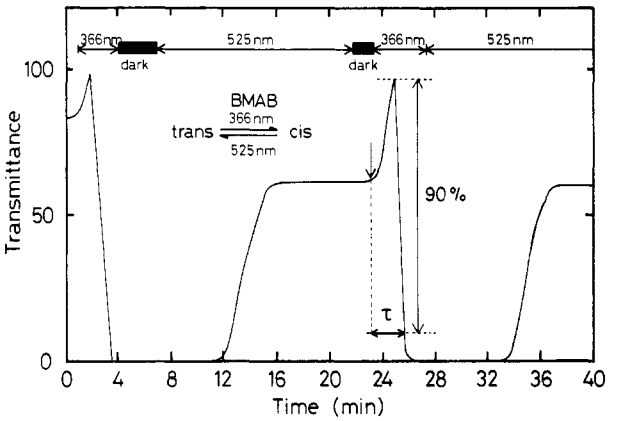

Figure 3. Photochemically induced phase transition behavior of PAPB3 doped with 5 mol % of BMAB. Transmittance between a pair of the crossed polarizers is plotted as a function of irradiation time (λ_{ex} = 366 nm or 525 nm). Photoirradiation was performed at the reduced temperature, $T_{red.}$ (T/T_{NI}), of 0.99.

the polymer films was crucial in the case of thermotropic main-chain PLC's;[17] thus in the present study the polymer films were subjected to annealing in a thermostat at temperatures where the PLC films showed LC phases. The polymer films thus prepared were placed in a thermostated block and irradiated with monochromatic light from a JASCO CRM-FA irradiator. Phase transition behavior was followed by monitoring the intensity of the linearly polarized light at 633 nm from a He–Ne laser transmitted through a pair of crossed polarizers with a PIN photodiode.[13]

Results and Discussion

I. Photochemically Induced Phase Transition in Homopolymers. A typical example of the photochemically induced phase transition behavior is shown in Figure 3 where a PAPB3 film doped with 5 mol % of BMAB was irradiated at 366 or 525 nm. Transmittance of the linearly polarized light through the crossed polarizers between which the sample was placed, I_t, was measured simultaneously as a function of time. It is clear that trans → cis photoisomerization of the doped BMAB (366 nm) brought about the nematic (N) → isotropic (I) phase transition of the host PLC as demonstrated by the complete loss of birefringence (I_t = 0) and the cis → trans isomerization (525 nm) restored the whole system to the initial state (N). Reversible phase transition of the PLC can be induced in this way by photochemical reaction of a small amount of the incorporated photoresponsive molecules.

Observation of the PLC samples with the polarizing microscope revealed that the PLC changed its appearance gradually upon photoirradiation. Before irradia-

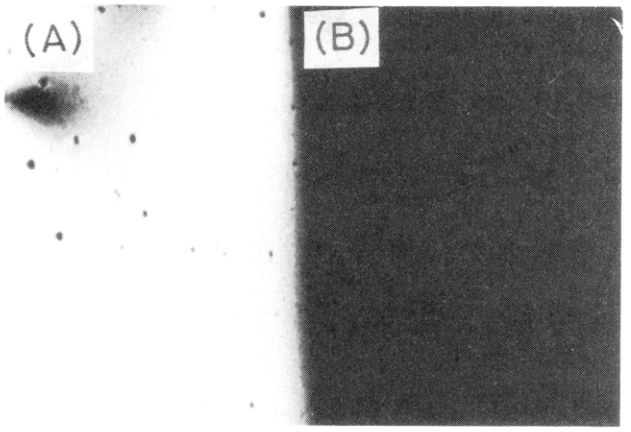

Figure 4. Texture of PAPB3 doped with 5 mol % of BMAB observed in the polarizing microscope. Left half (A) is the nematic phase (before irradiation) and right half (B) is the isotropic phase induced by photoirradiation at 366 nm. Half of the PLC film (A) was covered to prevent exposure to light.

tion, the PLC samples showed LC domains (Figure 4A). On irradiation, the PLC sample was planted with a number of small black spots (droplets) which grew with irradiation time, and finally the anisotropic area disappeared. This observation indicates that the isotropic domains are seeded on photoirradiation probably at the site where *cis*-BMAB is formed. The isotropic domains increased with an increase in the extent of the trans → cis isomerization of the dopant. However, growth of the isotropic domains seems not to be gradual but abrupt when the system reaches a certain critical stage. Eventually, all of the birefringent phase is lost, leaving a completely isotropic melt at $I_t = 0$ (Figure 4B).

In Figure 3, I_t changed in a peculiar way in the course of the N → I phase transition. Namely, it goes up on photoirradiation at 366 nm and then drops down to $I_t = 0$. This apparently strange behavior of I_t can be explained in the following way. In nematic LC's, the optical axis lies along the long axis of the mesogens and birefringence associated with the nematic LC phase can be expressed in the form of eq 1, where n_e and n_o indicate

$$\Delta n = n_e - n_o \tag{1}$$

the refractive index of the medium against extraordinary and ordinary light, respectively. When light passes through a nematic LC layer with a thickness of d, a difference in the phase is produced between the two types of lights, $(2\pi/\lambda)\Delta nd$, where λ is the wavelength of the light. Thus, the light intensity observed after the pair of crossed polarizers between which the LC sample is placed can be expressed as shown in eq 2.[18] Equation 2

$$I_t \propto \sin^2\left(\frac{\pi d\Delta n}{\lambda}\right) \tag{2}$$

indicates that if $\Delta n = 0$ as in the case of isotropic liquids, $I_t = 0$. The following expression holds for interference order m.[18]

$$\frac{d|\Delta n|}{\lambda} = \left(m + \frac{1}{2}\right) + \epsilon \tag{3}$$

Here, m is an integer and ϵ is a real number satisfying the condition of $-(1/2) < \epsilon < (1/2)$. Equation 3 indicates that m is a function of d, Δn, and λ. In the present study, $\lambda = 633$ nm and Δn is unequivocally determined by the PLC employed. Thus, m is practically dependent on the thickness of the PLC film. The photoinduced N → I phase transition is a process equivalent to $|\Delta n| \rightarrow 0$. Thus, I_t is considered to change periodically according to eq 2. In fact, the periodic behavior of I_t was found to change depending on d of the sample film. A similar behavior of I_t was observed in the thermal N → I phase transition.[18]

In Figure 3, one can readily realize that the time required for the I → N phase transition induced by the 525 nm light is much longer than that for the N → I phase transition induced by the 366 nm light. This was true for all cases explored in the present study regardless of the homopolymers doped with BMAB or the copolymers containing azobenzene moieties. Two reasons are considered. One is due to the low extinction coefficient of the cis form of azobenzene moieties. Under the present experimental setup, the light intensity at 525 nm is higher than that of 366 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 the cis → trans isomerization, leading consequently to a lower rate of phase transition. The other reason is related to orderness of the system. The rate of "order" to "disorder" change is considered to be higher than that of "disorder" to "order" change. If a part of the whole system has a disordered structure, then this system can be regarded as "disorder". On the other hand, the system is recognized as "order" only after the disordered part is removed completely from the system.

It must be mentioned here that long-term storage of information can be achieved by cooling the PLC film below the T_g of the polymer. The PAPB3/BMAB film was irradiated at 366 nm, and the N–I phase transition was confirmed by transmittance of polarized light. This film was then quickly cooled to −20 °C and kept below the T_g of the PAPB3 employed (20 °C). Observation of the film with the polarizing microscope revealed that the I phase formed at the site of photoirradiation still remained unchanged after 5 weeks.

In order to discuss the phase transition behavior quantitatively, we defined the response time, τ, as the time required to reduce the transmittance across the crossed polarizers, I_t, to 10% of the maximum value (Figure 3).

Effect of the Cis → Trans Thermal Isomerization. Cis to trans thermal isomerization of azobenzene takes place. For the effective fixation of the stored information, the thermal stabilities of the cis form of the azobenzene chromophore and the induced I phase should be explored. The PAPB3/BMAB (5 mol %) film was irradiated at 366 nm to induce the N → I phase transition at the reduced temperature $T_{red.}$ (= T/T_{NI}) of 0.99. After the phase transition was confirmed, the PLC film was left at the same temperature in the dark. Two kinds of PLC films were examined, and the results are shown in Figure 5. For the PLC film with $M_n = 3000$, the temperature at which $T_{red.} = 0.99$ was 41 °C; thus the thermal cis → trans isomerization took place rather slowly. At this temperature, therefore, the I → N phase transition was slow as seen in curve 3 of Figure 5. Photoirradiation of this PLC film with the 525 nm light was effective, and the I → N phase transition took place much faster under photoirradiation (curve 4). On the other hand, for the PAPB3/BMAB film with $M_n = 3700$, the temperature at which $T_{red.} = 0.99$ was 58 °C; thus the thermal cis → trans isomerization occurred so fast at this temperature that photoirradiation to cause the cis → trans isomerization hardly affected the I → N phase transition behavior of the PLC film (curves 1 and 2). The thermal cis → trans isomerization of BMAB doped in PAPB3 with $M_n = 3700$ was also followed by absorption spec-

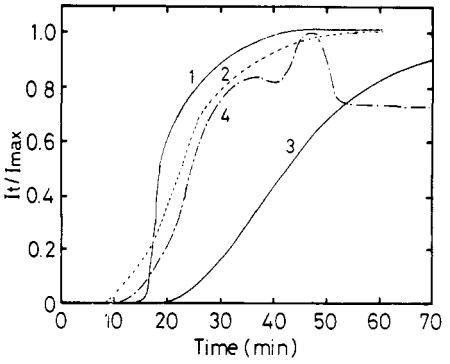

Figure 5. Phase transition of BMAB doped (5 mol %) PAPB3 induced by cis → trans isomerization: 1, no irradiation, M_n = 3700; 2, irradiated at 525 nm, M_n = 3700; 3, no irradiation, M_n = 3000; 4, irradiated at 525 nm, M_n = 3000.

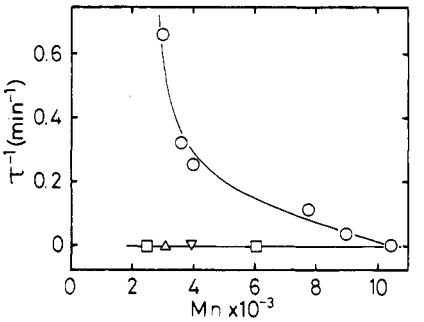

Figure 6. Molecular weight dependence of the photochemically induced phase transition behaviors of the homopolymers (PAPBn) doped with 5 mol % of BMAB: (△), PAPB2/BMAB; (○), PAPB3/BMAB; (▽), PAPB5/BMAB; (□), PAPB6/BMAB.

troscopy. After the PLC film was irradiated at 366 nm for a sufficiently long period, the film was left at 58 °C in the dark and the absorption spectra of the PLC film were taken successively. At this temperature, ~30 min was necessary for complete recovery of the trans form. One can see in Figure 5 that the onset of the I → N phase transition in the dark is ~15 min after photoirradiation ceased. At this stage, ~50% of the cis form was transformed to the trans form. In any event, the stored information in the PLC in the form of the I phase could safely be frozen-in by quenching the PLC film below T_g before the I → N phase transition started.

Effect of Molecular Weight and Spacer Length. In Figure 6 is shown the molecular weight (MW) dependence of the phase transition behavior of the homopolymers (PAPBn) doped with 5 mol % of BMAB. T_{NI} of the homopolymers was dependent on both MW and the spacer length (n) as shown in the preceding paper;[16] thus the photochemically induced phase transition behavior was examined at $T_{red.}$ of 0.99 for all cases. The rate of the phase transition evaluated by the reciprocal of the response time, τ^{-1}, was strongly dependent on M_n of the host PLC. In the case of PAPB3, τ^{-1} decreased with increasing M_n, and at $M_n > 10^4$ no phase transition was induced even after prolonged irradiation. Contrary to the behavior of PAPB3, no phase transition was induced in PAPB2, PAPB5, and PAPB6 on prolonged irradiation even though the trans → cis photoisomerization of the doped BMAB was confirmed by absorption spectroscopy.

Effect of BMAB Concentration. Figure 7 shows the effect of BMAB concentration doped in PAPB3 (M_n = 3000) on the rate of the N → I phase transition. The rate increased with the concentration of BMAB up to 5 mol % and then decreased, and eventually it was satu-

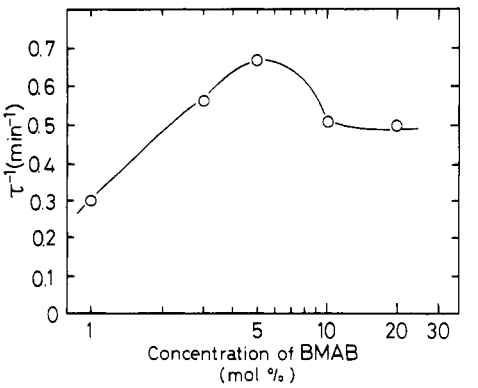

Figure 7. Concentration dependence of BMAB doped in PAPB3 on the rate of the photochemically induced phase transition. M_n of PAPB3 was 3000.

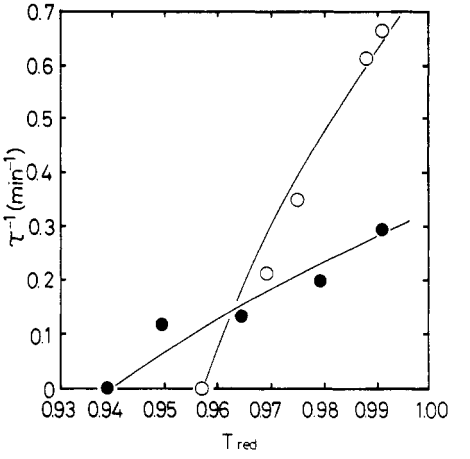

Figure 8. Temperature dependence of the photochemically induced phase transition behaviors of PAPB3 doped with 5 mol % of BMAB: (○), M_n = 3000; (●), M_n = 3700.

rated. A calorimetric study and the polarizing microscopy revealed that the PAPB3/BMAB film showed a homogeneous mixture macroscopically below the BMAB concentration of 20 mol %. However, unlike the copolymers containing the azobenzene moieties, complete mixing of the host PAPB3 and the guest BMAB may be very difficult at the molecular level. Thus, microdomain of the guest molecules may exist, although the area of the microdomain itself is too small to be detected by DSC measurements and the polarizing microscopy. However, if such microdomains exist, structural perturbation conducted by the trans → cis photoisomerization may not act effectively on the host mesogens to induce the phase transition of the host PLC. Furthermore, when the concentration of BMAB is high, the majority of the incident photons are absorbed at the surface layer of the PAPB3/BMAB mixture. The phase transition may take place at the surface layer of the PLC film. However, the rest of the PLC layer remains nearly unchanged. Because of the low extinction coefficient of the cis form of BMAB at 366 nm, the incident photons tend to penetrate deeply as the trans form at the surface layer is consumed. These two factors may explain the phenomenon that the rate decreases with the concentration above 5 mol %.

Effect of Temperature. Figure 8 shows the temperature dependence of the photochemically induced phase transition behavior of the PAPB3/BMAB (5 mol %) mixture. Two host PAPB3's were employed: one with M_n = 3000 and the other with M_n = 3700. In Figure 8, the rate of the phase transition, τ^{-1}, is plotted as a function of the reduced temperature. One can see that the rate

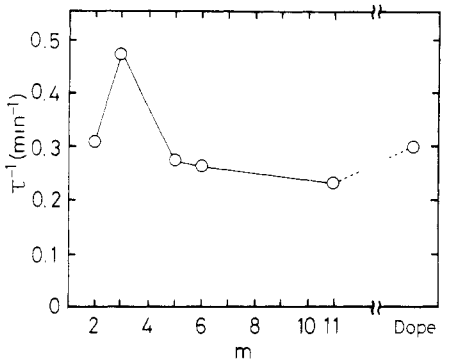

Figure 9. Photochemically induced phase transition behaviors of copolymer 3-*m* as a function of the number of the methylene units in the spacer chain attached to the azobenzene moieties (*m*). PAPB3/BMAB system is also included for comparison.

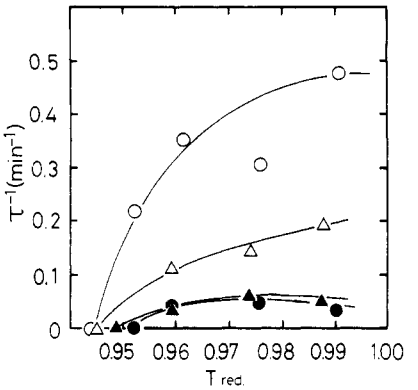

Figure 10. Photochemically induced phase transition behavior of copolymer 3-3 with different M_n: M_n = 3500 (○, ●); M_n = 6200 (△, ▲); (○, △), N → I transition; (●, ▲), I → N transition.

of the phase transition increases with $T_{red.}$, and it is highest at $T_{red.}$ = 0.99 among the temperatures examined. The rate of the isothermal N → I phase transition is closely related to lowering the phase transition temperature induced by the accumulation of the cis form of BMAB.[13] 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 temperature is low, a large amount of the cis form is necessary to lower T_{NI} of the system below the temperature; thus the rate of the phase transition is expected to be low. The phase transition takes place at a lower $T_{red.}$ in PAPB3 with M_n = 3700 than that in PAPB3 with M_n = 3000; however, the reason is not clear at this stage.

II. Photochemically Induced Phase Transition in Copolymers. Effect of Spacer Length *n* at APB*n*. The photochemically induced phase transition behavior was examined in the copolymers with different spacer lengths between the main chain and the mesogenic phenyl benzoate group, *n*. In copolymers 6-3 and 6-6, the phase transition could not be induced photochemically. Thus, the phase transition behavior of copolymer 3-*m* was investigated in full detail. Figure 9 shows the rate of the isothermal transition as a function of the number of the methylene units in the spacer chain attached to the azobenzene moiety in copolymer 3-*m* with M_n = ~3500. One can see that copolymer 3-3 exhibited the highest rate of phase transition and the other copolymers showed nearly identical rates. Furthermore, PAPB3/BMAB also showed a similar rate to the other copolymers.

Effects of Molecular Weight and Temperature. Similar MW dependence of the phase transition behavior to that of the doped system PAPB3/BMAB was observed in copolymer 3-3. Figure 10 shows the rate of the phase transition of copolymer 3-3 with M_n of 3500 and 6200 at various temperatures. Since the values of T_{NI} are different depending on M_n, the rate was plotted as a function of the reduced temperature. It is clear that the rate of the N → I phase transition is higher in the low MW PLC than the high MW sample. The rate increased somewhat monotonically with temperature in both samples with different MW's.

III. Comparison of the Photochemically Induced Phase Transition Behavior with Thermodynamic Data and Order Parameters. The photochemically induced phase transition behavior was found to be strongly dependent on MW and the spacer length (*n*) of the host PLC. In fact, the photochemically induced phase transition was only observed in the homopolymer and the copolymers of APB3 with M_n less than 10^4. In the preceding paper, thermodynamic data as well as order parameters of the PLC's were fully investigated.[16] It was revealed that the entropy change associated with the N-I phase transition, ΔS_{NI}, is well correlated to the order parameters (*S*) determined by FT-IR dichroism. Namely, in the PLC with a small value of ΔS_{NI}, the value of *S* was small, indicating the less ordered structure in the N state. Such parallel relation between ΔS_{NI} and *S* has been commonly observed in LC's.[19] Thus, ΔS_{NI} can be used as a measure for the orientational ordering of the PLC of interest, although it is just an indirect one.[19] Support for this is given by the Flory-Ronca theory which predicts that ΔS_{NI} is proportional to the second power of *S*:[20]

$$\Delta S_{NI} = (1/2)n_x k S^2/T_{red.} \quad (4)$$

where n_x is a number of the components, *k* is the Boltzmann constant, and $T_{red.}$ is the reduced temperature (T/T_{NI}). The fact that the polymers containing APB3 units exhibited the lowest values of ΔS_{NI} and *S* among the homopolymers and the copolymers examined indicates that the orientational ordering in the APB3-containing PLC's is lowest among the polymers. Before irradiation, in the initial state, the structure of the APB3-containing PLC's in the N state is less ordered; thus structural perturbation impulsed in the form of the trans → cis isomerization of the azobenzene moiety acts most effectively to induce a disordered (isotropic) structure of the PLC.

Molecular weight dependence of the rate of the N → I phase transition observed in PAPB3/BMAB (Figure 6) can be similarly interpreted in terms of the orientational ordering of the host PLC in the N state. As described in the preceding paper,[16] ΔS_{NI} of PAPB3 decreases with decreasing M_n below M_n = ~10^4 and the rate of the phase transition increases with decreasing M_n. These results suggest that in PAPB3 with low M_n the orientational ordering is low; thus the isothermal N → I phase transition can be effectively induced by the photochemical reaction.

Different behavior in the photochemically induced phase transition observed for copolymer 3-*m* and PAPB3/BMAB can again be interpreted on the basis of the orientational ordering in the initial N state of the PLC's. The phase transition occurred most effectively in copol-

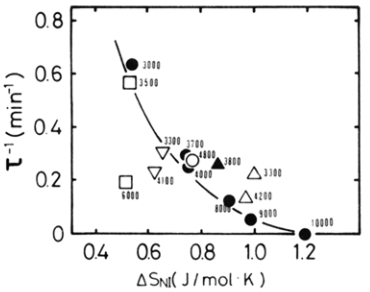

Figure 11. Photochemically induced phase transition behavior of the PLC's as a function of the change in entropy at the N → I transition (ΔS_{NI}): (▽), copolymer 3–2; (□), copolymer 3–3; (○), copolymer 3–5; (▲), copolymer 3–6; (△), copolymer 3–11; (●), PAPB3/BMAB (5 mol %). Numbers in the figure indicate M_n of the samples.

ymer 3–3 which possessed the lowest values of ΔS_{NI} and S among the PLC samples. In copolymer 3–3, another factor may contribute to the effective phase transition behavior: azobenzene moieties in this PLC are located adjacent to the phenyl benzoate groups because both groups are attached to the polymer main chain with the same alkyl spacers; thus the structural perturbation caused by the photoisomerization may be most effective.

In Figure 11 is shown the rate of the isothermal N → I phase transition (τ^{-1}) of the homopolymer and the copolymers as a function of their ΔS_{NI} values. Data were taken from the measurements at $T_{red.} = 0.99$. All the PLC films that exhibited the photoinduced phase transition are included in the figure. It is evident that τ^{-1} is well correlated to ΔS_{NI}; thus the photochemically induced phase transition takes place effectively in the less ordered system.

IV. Use as Image Storage Materials. The present study clearly demonstrated that the reversible phase transition of the side-chain PLC's could be induced by a photochemical reaction of a small amount of the incorporated photoresponsive molecules. From the application point of view, this means that the photosignals were transformed into a structural change of the photoreceptor molecules (trans–cis isomerization), which subsequently acts as structural perturbation to the whole system, inducing the phase change of the whole system as in the case of vision. The photosignals transformed into the phase change of the whole system can be read out by the loss of birefringence. Note that the system is transparent to the monitor light (633 nm), and consequently, the readout is completely nondestructive. Merits of this way of image storage are obvious.[9] Since the photosignals are converted to the physical change of the whole system, a variety of methods other than the transmittance of the linearly polarized light described here can be used for the nondestructive readout of the stored information.[11,15]

Image storage experiments by the use of a standard photomask were conducted on copolymer 3–3 with M_n = 3500. The PLC films were prepared by casting as described in Experimental Section. After annealing, the photomask was directly placed on the PLC film and the resulting sample was irradiated with the third harmonic (355 nm) of a Q-switched pulsed Nd:YAG laser (Spectron SL803). Irradiation was performed at 54 °C ($T_{red.} = 0.98$) for 30 s at a repetition rate of 10 Hz. After exposure, the PLC film was cooled to room temperature (below T_g) and resolution of the stored image was examined in the polarizing microscope. Photographs of the photomask and the stored image are shown in Figure 12. Close

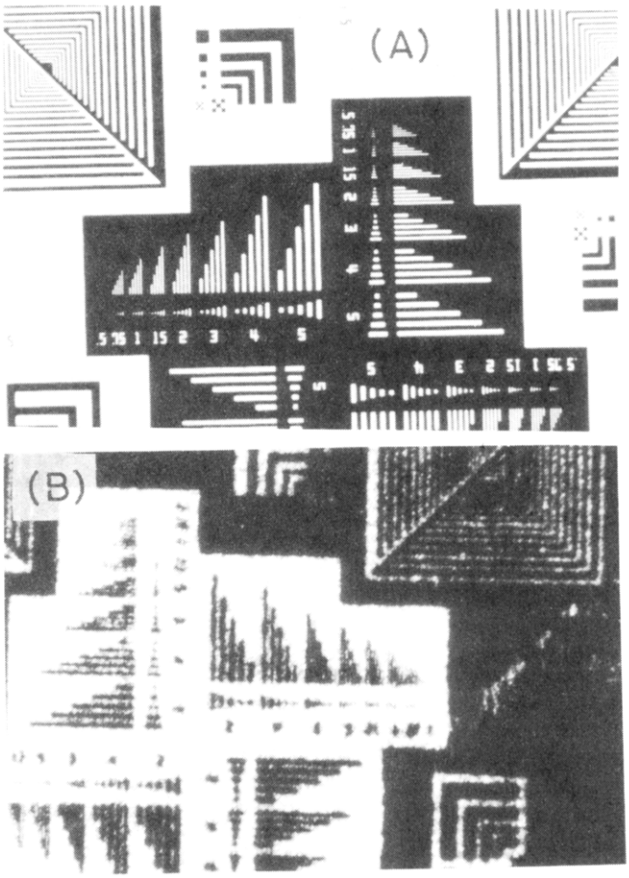

Figure 12. Binary test pattern stored in copolymer 3–3 by a laser beam at 355 nm. (A) Test pattern used as photomask. Numbers in the figure indicate the width of the lines. (B) Stored test pattern observed in the polarizing microscope. M_n = 3500.

inspection of the stored test pattern indicates that resolution up to 2∼4 μm has been achieved.

Registry No. APB_2 (homopolymer), 79462-29-6; APB_3 (homopolymer), 118086-64-9; APB_5 (homopolymer), 118086-66-1; APB_6 (homopolymer), 82200-54-2; $(APB_3)(AAZO_2)$ (copolymer), 123642-70-6; $(APB_3)(AAZO_3)$ (copolymer), 123642-72-8; $(APB_3)(AAZO_5)$ (copolymer), 123642-74-0; $(APB_3)(AAZO_6)$ (copolymer), 123642-76-2; $(APB_3)(AAZO_{11})$ (copolymer), 123642-78-4; BMAB, 31401-33-9.

References and Notes

(1) Dewey, A. G. *Opt. Eng.* **1984**, *23*, 230.
(2) Sasaki, A. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 103.
(3) Shibaev, V. P.; Kostromin, S. G.; Plate, N. A.; Ivanov, S. A.; Vetrov, V. Y.; Yakovlev, I. A. *Polym. Commun.* **1983**, *24*, 364.
(4) Coles, H. J.; Simon, R. *Polymer* **1985**, *26*, 1801.
(5) Pinsl, J.; Brauchle, C.; Kreuzer, F. H. *J. Mol. Electron.* **1987**, *3*, 9.
(6) Griffin, A. C.; Hoyle, C. E.; Gross, J. R. D.; Venkataram, K.; Creed, D.; McArdle, C. B. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 463.
(7) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59.
(8) Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 467.
(9) Tazuke, S.; Ikeda, T. In *The Effects of Radiation on High-Technology Polymers*; Reichmains, E., O'Donnell, J. H.; Eds.; ACS Symposium Series 381; American Chemical Society: Washington, DC, 1989; pp 209–223.
(10) Yoshizawa, T. *Adv. Biophys.* **1984**, *17*, 5.
(11) Tazuke, S.; Kurihara, S.; Yamaguchi, H.; Ikeda, T. *J. Phys. Chem.* **1987**, *91*, 249.
(12) Yamaguchi, H.; Ikeda, T.; Tazuke, S. *Chem. Lett.* **1988**, 539.
(13) Tazuke, S.; Kurihara, S.; Ikeda, T. *Chem. Lett* **1987**, 911.
(14) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Chem. Lett.* **1988**, 1679.

(15) Kurihara, S.; Ikeda, T.; Tazuke, S. *Jpn. J. Appl. Phys., Part 2* **1988**, *27*, L1791.
(16) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules*, preceding paper in this issue.
(17) Ikeda, T.; Itakura, H.; Lee, C. H.; Winnik, F. M.; Tazuke, S. *Macromolecules* **1988**, *21*, 3536.
(18) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.
(19) Watanabe, J.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 2288.
(20) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 311.

Lifetime of Living Polymers in Cationic Polymerization. 1. Methodology and Application to the HI/I_2-Initiated Living Cationic Polymerization

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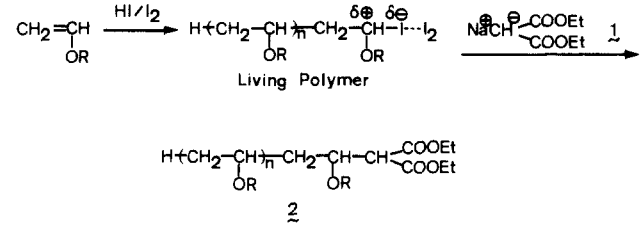
ABSTRACT: An end-capping method using sodiomalonic ester (1) as a quencher was shown to permit the determination of the concentration ([P*]) of living ends in the polymerization of isobutyl vinyl ether initiated by the hydrogen iodide/iodine (HI/I_2) system in toluene or methylene chloride at 0 to −40 °C. The terminal malonate group, thus attached to the polymer chain, could be determined by ^1H NMR spectroscopy, from the concentration of which [P*] was obtained. Throughout the polymerizations, the living-end concentration remained constant against monomer conversion and equal to the initial concentration of hydrogen iodide ($[P^*] = [HI]_0$), and the same relation held for the second-stage polymerizations that were started by adding a fresh feed of monomer to completely polymerized reaction mixtures. After the complete consumption of the monomer, however, the living end turned out to decay progressively with time, in first order with respect to [P*], and by following this decay its lifetime could be determined. The half-life of the living end, even in the absence of monomer, was relatively long, ranging from 40 to 1000 min (17 h). The decay process was slower at lower temperature but accelerated at higher iodine concentrations.

Introduction

Living polymers, by definition,[1a] have a lifetime that is long enough to permit their propagation to continue without chain transfer and termination over the time span of polymerization, as evidenced by a progressive increase in polymer molecular weight, in direct proportion to monomer conversion, as well as the formation of block polymers upon sequential addition of monomers. This definition, however, does not necessarily imply that living polymers per se should possess an infinite lifetime. They may be "killed" by purposefully added quenching agents or may undergo a spontaneous side reaction(s), particularly after the complete consumption of monomer.[1b] In cationic vinyl polymerization, for example, the quenchers include a variety of basic compounds, such as methanol, water, and amines.[2]

For some years we have been pursuing a number of living cationic polymerizations of vinyl monomers.[3] For example, a variety of vinyl ethers can be polymerized into well-defined living polymers by the hydrogen iodide/iodine (HI/I_2) initiating system.[4,5] A question that has frequently been asked but is yet unanswered is, how long is the lifetime of our living polymers (propagating species)? This is a problem of particular importance, because the lifetime is a direct measure of the stability of the growing carbocations that are no doubt the key to living cationic processes[3] and because its answer would in turn give further insight into the principles of initiator design of living cationic polymerization and into the methodology of related polymer syntheses like block copolymerization. Furthermore, the lifetime of growing carbocations in cationic polymerization has not been measured extensively, despite our attempt by stopped-flow spectroscopy.[6] This series of investigations is thus directed toward uncovering the lifetime of living propagating species in cationic polymerization of vinyl ethers and related monomers.

Scheme I
End Capping of Living Poly(IBVE) with Sodiomalonic Ester 1 (R = Isobutyl)



The simplest way to measure the lifetime of a growing species involves determination of its concentration as a function of time, thereby following its decay process, if any. As we have established quite recently (Scheme I),[7] sodiomalonic ester (1; diethyl malonate sodium salt) reacts quantitatively with the living poly(vinyl ether) growing ends that are generated by the HI/I_2 initiating system. Each polymer chain (2) thereby carries a malonate terminal group, the ^1H NMR analysis of which would in turn lead to the living-end concentration ([P*]). Specifically for vinyl ether polymerization, the carbanionic nature of the quencher 1 is beneficial and perhaps essential to an accurate determination of [P*], because the resulting carbon–carbon terminal bond of 2 is much more stable than the corresponding oxygen-, sulfer-, nitrogen-, and

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