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# Photochemical Image Storage in Polymer Liquid Crystals[1)]

Tomiki IKEDA, Shin HORIUCHI, Durga B. KARANJIT, Seiji KURIHARA,
and Shigeo TAZUKE*
Photochemical Process Division,
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

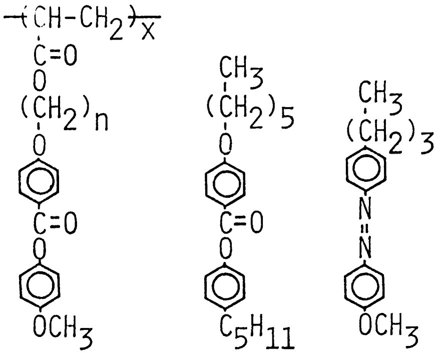
Amplified optical image storage has been demonstrated in polymer liquid crystals (PLC). A small amount (< 5 mol%) of a low molecular weight mesogen with a photoresponsive moiety, 4-butyl-4'-methoxyazobenzene (BMAB), was doped in the films of polyacrylates with mesogenic side chain, poly(4'-methoxyphenyl-4-acryloyloxyalkoxybenzoate)(PAn), in which the alkyl spacer length $(CH_2)_n$ was varied as n = 2, 3, 5, and 6. Photoirradiation of the PA3/BMAB film with a 366 nm light caused trans →cis isomerization of BMAB, which induced simultaneously the nematic (N)→isotropic phase transition of the PLC films. This photochemically induced phase transition was reversible and photoirradiation with a 525 nm light which induced cis→trans isomerization restored the system to the initial phase (N). The photo-induced phase transition was found to be strongly dependent on molecular weight of the host PLC and temperature.

High density and high speed image recording systems have become a matter of general interest. We have presented a novel concept for the improved image recording system, which has been expressed as photochemically triggered phase transition.[2-4)] Photoreaction (eg. photoisomerization) of chromophores in the molecular aggregate systems can act as a perturbation to the whole systems. If the molecular aggregate system possesses more than two thermodynamically stable phases, such a perturbation can induce an isothermal phase transition, which is usually accompanied with a large change in physical properties of the system. Information provided in the form of photoreaction is amplified and stored as physical change in the whole system. Merits of this way of image storage is evident. Since the photosignals are converted to physical change of the system, a variety of methods can be used for a nondestructive read-out of the stored information. Furthermore, only a small degree of photoreaction may be enough to bring about the phase transition, so that amplification of the signals as well as prevention of fatigue of photoresponsive molecules can be achieved simultaneously. We have demonstrated several examples for the photochemically triggered phase transition in low molecular weight systems.[2-4]

Polymeric materials may be the best choice for supporting materials from the practical point of view. In fact, the polymeric materials with "intrinsic" image storage ability would be desirable since thin films of the polymers can be used as image storage materials. Another advantage accompanied by the polymeric materials is that the polymers exhibit the glass transition, below which the segmental motion of the polymeric materials is frozen-in, so that the stored information may be kept stable for a long period.

In this paper, we report the optical image storage in the polymer liquid crystals (PLC) by means of photochemically triggered phase transition. Use of PLC for the image storage materials has commenced recently.[5-7] However, as exemplified by the laser-addressed PLC storage display,[5] heat-mode writing was exclusively employed in these systems. Furthermore, in some cases, dye chromophores were incorporated into the PLC to enhance "heat" absorption.[5,6] Contrary to the heat-mode writing, our system is entirely "photon-mode" as in the case of vision.[8]

Structure of the PLC's used in this study is shown in Fig. 1. They were prepared by the method reported by Ringsdorf et al.[9] and fractionated by a preparative gel permeation chromatography (GPC). The polymer films were prepared by casting the polymer solution in chloroform containing 5 mol% of BMAB onto a glass plate. The films were then dried under reduced pressure. The polymer film was placed in a thermostatted block and irradiated with a monochromatic light to cause trans→cis (366 nm) or cis→trans (525 nm) photoisomerization of the doped BMAB. The phase transition behavior was followed by monitoring the intensity of the linearly polarized light transmitted through a pair of crossed polarizers.[3] One example is shown in Fig. 2 where the trans-



PAn PPHB BMAB

Fig. 1. Structure of LC's used in this study.

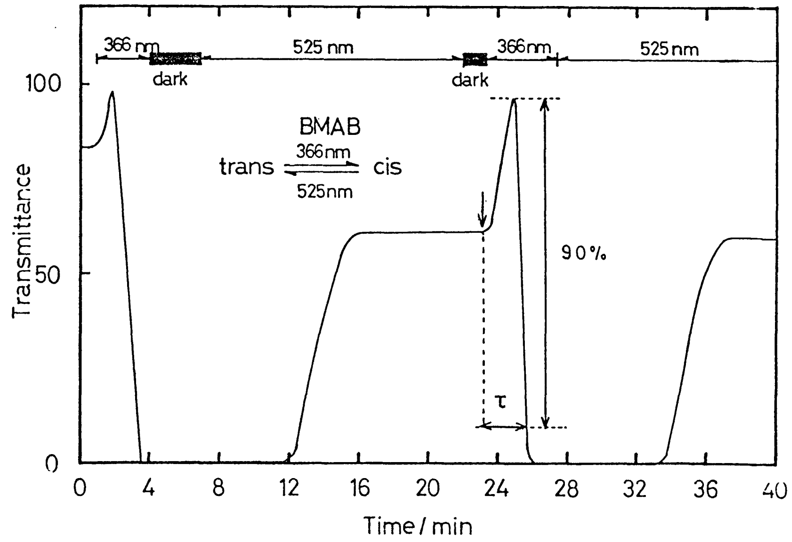


Fig. 2. Photochemically induced phase transition in PA3/BMAB system.

mittance $(I_t)$ is measured as a function of irradiation time. It is clear that trans → cis photoisomerization of the doped BMAB (366 nm) brought about N → I phase transition as demonstrated by complete loss of birefringence $(I_t = 0)$ and cis → trans isomerization (525 nm) restored the whole system to the initial state (N). Reversible phase transition of PLC could, thus, be induced by photochemical reaction of a small amount of the incorporated photoresponsive molecules.

In Fig. 3 is shown the molecular weight (MW) dependence of the phase transition behavior of PAn. Note that the rate of phase transition as evaluated by the reciprocal of the response time $(\tau)$ is strongly dependent on MW in the case of PA3 where the response time was defined as the time taken to reduce the transmittance acoss the crossed polarizers, I(t), to 10% of the maximum value (see Fig. 2). With increasing MW, $\tau^{-1}$ decreased and at MW > $10^4$ no phase transition could be induced even after prolonged irradiation. Another interesting point is that in a model monomeric mesogen, 4-pentylphenyl-4'-hexyloxybenzoate (PPHB), $\tau^{-1}$ was again very small. Preliminary results have implied that $\tau^{-1}$ is significantly influenced by $T_{NI}$ of the host LC in the case of low molecular weight LC's when the photoresponsive mesogen is fixed to BMAB.10) Host LC with higher $T_{NI}$ possesses a tendency to exhibit a longer response time. Choice of the model monomeric mesogen was based on the fact that PPHB showed the closest value of $T_{NI}$ to PA3 among its analogs. Unexpectedly, PA5 exhibited no liquid crystalline phase for samples with Mn = 25 000 and 7 000 as evidenced by

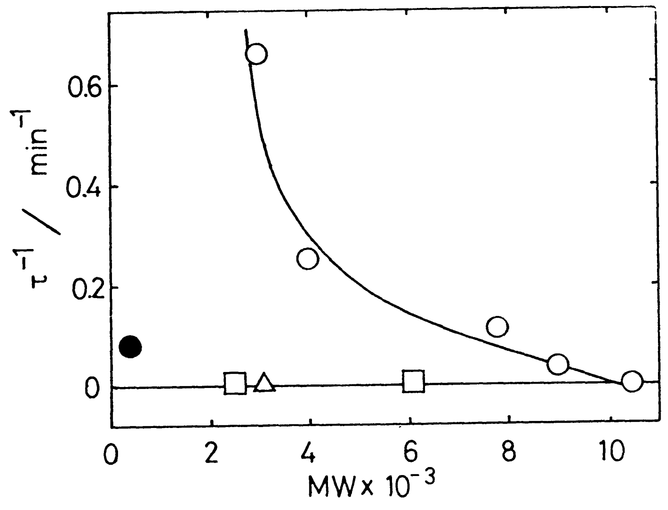


Fig. 3. Phase transition behavior of PAn/BMAB as a function of molecular weight.
(○), PA3/BMAB; (△), PA2/BMAB; (□), PA6/BMAB; (●), PPHB/BMAB.

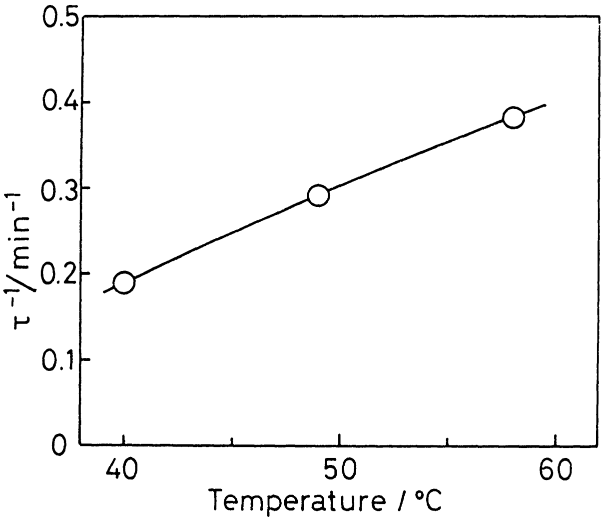


Fig. 4. Phase transition behavior of PA3/BMAB as a function of temperature.

a polarizing microscope (Olympus model BHSP) equipped with a Mettler hot stage model FP-80 and FP-82. DSC measurements performed on a SEIKO I&E SSC-5000 calorimeter showed only one endothermic event which corresponded to glass transition of the polymer ($T_g$ = 1°C). Both PA2 and PA6 exhibited the LC phase as reported previously,$^{9)}$ but no phase transition was induced on prolonged irradiation even though trans → cis photoisomerization of BMAB was confirmed by absorption spectroscopy. It must be mentioned here that $T_{NI}$ of the host PLC depends on MW and n, so that photoinduced phase transition behavior was examined at the reduced temperature ($T/T_{NI}$) of 0.99 for all cases.

Temperature dependence of the phase transition rate is shown in Fig. 4 which indicates clearly that with increasing temperature $\tau^{-1}$ increased monotonically and at temperatures close to $T_{NI}$ the phase transition took place most effectively.

It must be mentioned here that long term storage of information can be achieved by cooling the PLC film below $T_g$. The PA3/BMAB film was irradiated with a 366 nm light and the N → I phase transition was confirmed by transmittance of the polarized light. This film was then quickly cooled at -20°C and left below $T_g$ of PA3 (20°C). Observation of the film by the polarizing microscope revealed that the I phase formed at the site of photoirradiation still remained as it was after 3 weeks.

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