



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl18>

Time-Resolved Observation of Isothermal Phase Transition of Liquid Crystals Induced by Photoisomerization of Azobenzene Dopant

S. Kurihara^a, T. Ikeda^a, T. Sasaki^a, H.-B. Kim^a & S. Tazukes^a

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

Version of record first published: 24 Sep 2006.

To cite this article: S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim & S. Tazukes (1991):
Time-Resolved Observation of Isothermal Phase Transition of Liquid Crystals Induced by
Photoisomerization of Azobenzene Dopant, *Molecular Crystals and Liquid Crystals*, 195:1, 251-263

To link to this article: <http://dx.doi.org/10.1080/00268949108030905>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any
substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,
systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any
representation that the contents will be complete or accurate or up to date. The
accuracy of any instructions, formulae, and drug doses should be independently
verified with primary sources. The publisher shall not be liable for any loss, actions,
claims, proceedings, demand, or costs or damages whatsoever or howsoever caused
arising directly or indirectly in connection with or arising out of the use of this material.

Time-Resolved Observation of Isothermal Phase Transition of Liquid Crystals Induced by Photoisomerization of Azobenzene Dopant

S. KURIHARA, T. IKEDA,[†] T. SASAKI, H.-B. KIM and S. TAZUKE[‡]

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

(Received August 6, 1990; in final form September 4, 1990)

Keywords: Photochemical phase transition; response time; azobenzene; pulsed laser; time-resolved measurements; birefringence

The isothermal phase transition behavior of azobenzene guest/liquid crystal host mixtures induced by nanosecond laser pulse was investigated. Two kinds of azobenzene derivatives were employed as dopant, 4-butyl-4'-methoxyazobenzene (BMAB) and 4-hydroxyazobenzene (HOAB), in order to examine the heat effect on the phase transition. BMAB showed a trans to cis photoisomerization while HOAB showed little isomerization even by prolonged photoirradiation. In the BMAB/5CB mixture, the photochemical nematic (N) → isotropic (I) phase transition was found to be completed within ~100 ms at the reduced temperature of 0.998 on irradiation of a single laser pulse of 10 ns FWHM which gave the cis isomer of BMAB. Contrary to the BMAB/5CB mixture, no phase transition of the HOAB/5CB mixture was observed by the laser flash, indicating that the N-I phase transition observed for the BMAB/5CB mixture is ascribed to the photochemical reaction of the dopant, not to the heat-mode process. The photochemical phase transition was found to depend on such factors as the concentration of the dopant, the power of the laser pulse and irradiation temperature. The large amount of the cis isomer simultaneously produced with a single pulse induced the phase transition rapidly.

INTRODUCTION

Liquid crystals (LCs) have been extensively used as active media in display devices. The function of these display cells is principally based on the electro-optic effect of the LCs; thus the electric-field-induced reorientation process of the mesogens is responsible for the change in the optical properties of the systems. In the application of the LC systems as display devices, a quick response to the applied electric field is essential and a variety of mesogens have been examined for their ability to respond quickly. In particular, ferroelectric LCs have been reported to be powerful candidates for a fast response in the time region of μs due to spontaneous polarization.^{1,2}

[†] To whom correspondence should be addressed.

[‡] Deceased on July 11, 1989.

Optical image recording is a current topic of interest owing to high resolution; thus high density of stored information.³ The most straightforward approach in the link of the optical source to the storage materials is the use of lasers as the heat source. Since the laser-beam can be focused to $<10\ \mu\text{m}\phi$, irradiation of LC cells with the laser beam results in a rapid increase in temperature along the beam trace, inducing thermal phase transition of the irradiated sites.³ Heat-mode image recording can be done in this way with high resolution. Although the heat-mode recording has a number of merits, photon-mode recording is expected to be superior in view of much higher resolution and the possibility of multiplex recording.⁴ Unfortunately, however, very few successful examples have been reported so far on LC systems of the photon-mode recording, although studies on the photon-mode response of LCs have been extensively conducted.

In the late 1960s, Haas *et al.* reported a change in the selective reflectivity of a cholesteric LC mixture composed of cholesteryl bromide and other cholesteryl derivatives on photoirradiation.⁵ This change in the reflectivity arose from a change in the helical pitch of the cholesteric LC resulting from the photochemical reaction of cholesteryl bromide in the LC mixture. They also found that irradiation with a UV light of LC cells containing mesogens with stilbene units in the molecules brought about trans \rightarrow cis isomerization of the stilbene units, causing simultaneously nematic (N) \rightarrow isotropic (I) phase transition of the host LC. This was interpreted as a result of a lowering of the N-I phase transition temperature (T_{NI}) of the mixture.⁶ The change in the selective reflectivity reported by Haas *et al.* was an irreversible process and reversible change of the selective reflectivity was reported by Sackmann who studied the effect of photoisomerization of azobenzene doped in cholesteric LCs on the helical pitch.⁷ Ogura *et al.* reported the photochemical phase transition of smectic LC doped with photochromic azobenzene derivatives.⁸ Photoirradiation of the mixture with a UV light caused the trans \rightarrow cis isomerization of the dopant, lowering the T_{SN} of the mixture, and induced the phase transition to the N state at the exposed area. In this way, the image was stored in the mixture, which was then kept very stable by transforming the N phase to the S phase by photoirradiation with a visible light. The studies on the optical image storage systems have been successfully extended to polymer liquid crystalline (PLC) systems.^{9–15} We also have demonstrated the photochemical isothermal phase transition of low molecular weight LCs¹⁶ and of PLCs¹⁷ aiming at the optical image storage systems. The working principle of these systems is *the isothermal phase transition of the LCs* at the irradiation site, thus we can expect high contrast and a high signal-to-noise ratio for the stored image.

The photochemical phase transition of LCs consists of two processes. The first process is the photochemical reaction of the photochromic dopant, which is followed by the second process, phase transition of the host LC. The studies on the photochemical phase transition of the photoresponsive guest/host LC mixtures so far reported were entirely under steady-state photoirradiation. Under steady-state irradiation, the two processes occur simultaneously and it is therefore very difficult to explore the two processes independently. For an improved response of the guest/host mixture in the photochemical phase transition, the second process, relaxation of the host LC to one of the bistable states, is to be investigated in full detail since

the time range required for the second process is expected to be longer than that of the photochemical reaction of the dopant. Furthermore, it is essential to explore the “intrinsic” response of LCs in the photon-mode phase transition in order to realize the limit of the photon-mode recording systems. One approach to study the “intrinsic” relaxation process of the host LC is to generate the photochemical reaction sufficient enough to bring about the isothermal phase transition of the host LC within a very short period. This can be done by the use of a pulsed laser with a short pulse width.

In this paper, we explore the relaxation process of the host LC in the photochemical $N \rightarrow I$ phase transition of the azobenzene guest/host LC mixtures on irradiation of a nanosecond-pulsed laser. We produced a sufficient amount of the *cis* form of the azobenzene dopant within ~ 10 ns with a single pulse of the laser and followed the relaxation process of the host LC from *N* to *I* by means of time-resolved measurements of birefringence.

Special precaution was taken to distinguish between the photon-mode process and the heat-mode process. In order to estimate the contribution of the heat-mode process to the photochemical phase transition, we used 4-hydroxyazobenzene (HOAB) as a reference dopant, which has similar electronic properties to 4-butyl-4'-methoxyazobenzene (BMAB), but is not isomerized on photoirradiation.

EXPERIMENTAL

Preparation of Samples

Host liquid crystals (LCs) and azobenzene derivatives used in this study are shown in Figure 1. The host LCs were purchased from Merck Co. and used without further purification. Azobenzene derivatives, 4-butyl-4'-methoxyazobenzene (BMAB) and 4-hydroxyazobenzene (HOAB), were used as the photoresponsive dopant and their preparation was described in the previous paper.¹⁶ BMAB and HOAB were doped in 5CB at various concentrations.

Samples were prepared by placing the mixtures in cells which consisted of two

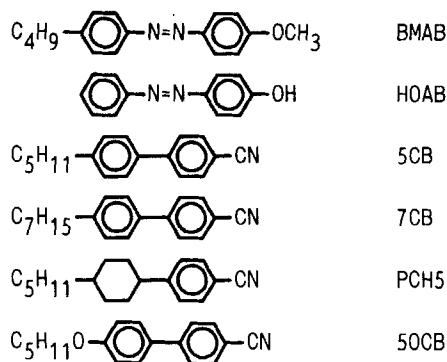


FIGURE 1 Host liquid crystals and azobenzene derivatives used in this study.

parallel glass plates coated with polyimide and rubbed to obtain homogeneous alignment. The cell gap was 6 and 9 μm .

The transition temperatures of the mixtures were observed by a microscopic observation (Mettler FP-80, FP-82 and Olympus BH2). The absorption spectra were measured with a Hitachi 320 spectrophotometer.

Time-Resolved Observation

Figure 2 shows the experimental set-up used to study the time-resolved observation of the photochemical phase transition behaviors induced by photoirradiation with the nanosecond-pulsed laser. A Spectron HL-21 Nd:YAG laser (the third harmonic, 355 nm; 5 mJ/pulse; pulse width, 10 ns) was used as an excitation source and the light was focused so that the excitation and analyzing beams overlapped at the cell. The analyzing light source used in the present work was a He-Ne laser (633 nm, 5 mW). The sample cell was thermostated and placed between two crossed polarizers, the polarizing directions of which were set at an angle of 45° with respect to the orientation axis of the cell. The He-Ne laser light passed through the sample mixture 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 set-up 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 an interference filter (a Toshiba UV-D36B) 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.

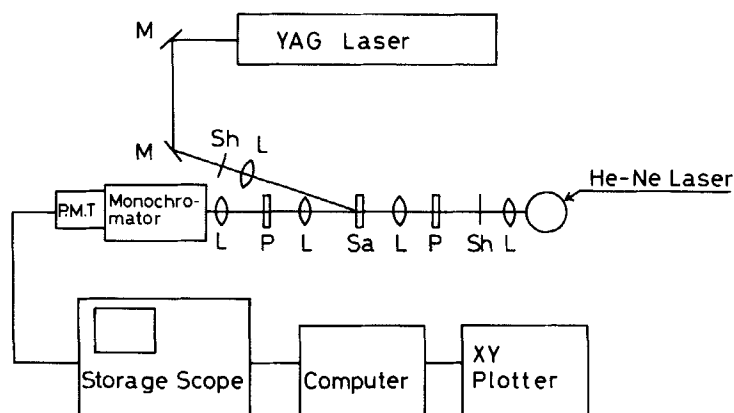


FIGURE 2 Schematic diagram used for the time-resolved measurements of the photochemical phase transition behaviors. P, polarizer; Sh, shutter; Sa, sample.

RESULTS AND DISCUSSION

Photoisomerization of Dopants by Irradiation of Nanosecond Laser Pulse

The absorption spectra of the azobenzene derivatives in ethanol and 5CB are shown in Figure 3. The absorption maxima of both BMAB and HOAB in ethanol were at 348 nm: the extinction coefficients ϵ were ~ 28000 (BMAB) and ~ 26000 (HOAB), respectively. BMAB in ethanol exhibited the trans-cis isomerization by photoirradiation at 355 nm as shown in Figure 3(A). The UV irradiation of HOAB in ethanol, however, did not result in the photoisomerization to give the cis isomer. The photoisomerization behaviors of the azobenzene derivatives in 5CB are shown

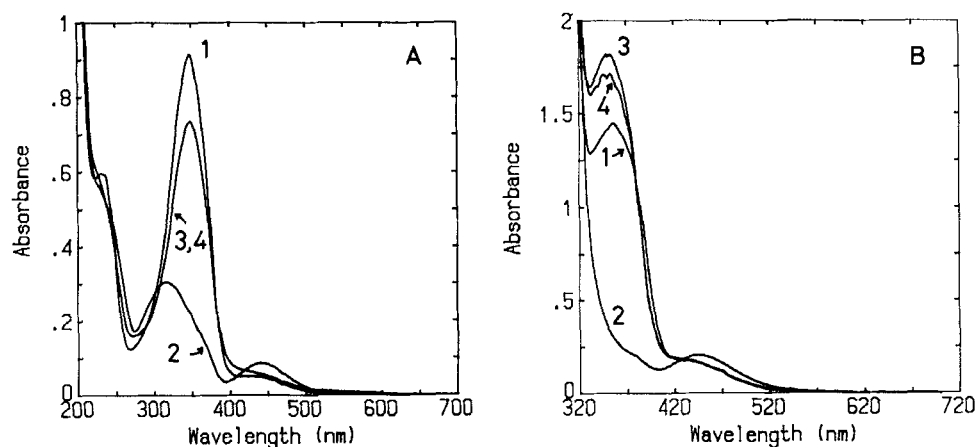


FIGURE 3 Absorption spectra of BMAB and HOAB in ethanol (A) and 5CB (B). 1. BMAB before irradiation; 2. BMAB after irradiation at 355 nm with Nd:YAG pulsed laser; 3. HOAB before irradiation; 4. HOAB after irradiation at 355 nm with Nd:YAG pulsed laser. Laser power, 5 mJ/pulse.

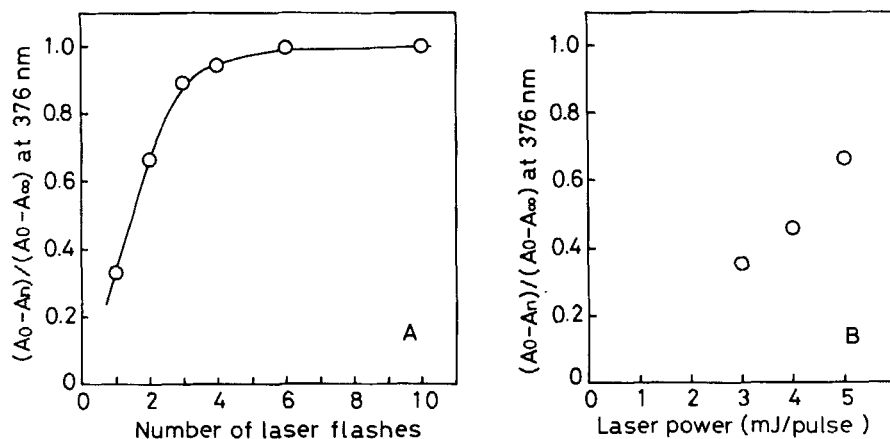


FIGURE 4 Course of trans-cis photoisomerization of BMAB in 5CB as evaluated by the change in $(A_0 - A_n)/(A_0 - A_\infty)$ as a function of the number of the laser flashes (A) and the power of the pulsed laser (B). A_0 , A_n and A_∞ are the absorbances at 376 nm before irradiation, $T_{red} = 0.998$; 2, $T_{red} = 0.997$; 3, $T_{red} = 0.996$; 4, $T_{red} = 0.994$. Laser power, 5 mJ/pulse; BMAB, 3 mol%.

in Figure 3(B). In 5CB, BMAB isomerized by photoirradiation at 355 nm, while little photoisomerization of HOAB was observed even by prolonged irradiation. The absorption maxima in 5CB were at 356 nm for BMAB and at 354 nm for HOAB, respectively.

In Figure 4(A) is shown the degree of the trans-cis isomerization of BMAB in 5CB, evaluated by a parameter $(A_0 - A_n)/(A_0 - A_\infty)$, as a function of the number of the laser flashes, n . Here, A_0 , A_n and A_∞ denote the absorbances of BMAB at 376 nm before irradiation, after n flashes and after prolonged irradiation where no change in the absorbance was further observed. Typically, A_0 was 1.2 and A_n decreased with n , and finally reached a value of 0.3. After about 4 laser flashes, the mixture reached apparent photostationary composition. It is noted that the amount of the cis form was about 30% of the whole content of the dopant when irradiated with a single pulse of the laser. In addition, the amount of the cis form produced was found to depend on the laser power. The amount of the cis form after two laser flashes is given as a function of the laser power in Figure 4(B). It is clearly seen that the amount of isomerization increases with the laser power.

Time-Resolved Photochemical Phase Transition Behaviors

Typical examples of the change in transmittance of the He-Ne laser light passed through a pair of the crossed polarizers between which the sample was placed, I_t , are given as a function of time after one laser flash in Figure 5. Here, 5CB was used as the host LC, and two kinds of dopants were used: BMAB and HOAB. The concentration of the dopant was 3 mol%, and the cell gap was 6 μm . The irradiation was performed at a reduced temperature $T_{\text{red}} (= T/T_{\text{NI}})$ of 0.998, where T_{NI} is the thermal $N \rightarrow I$ phase transition temperature.

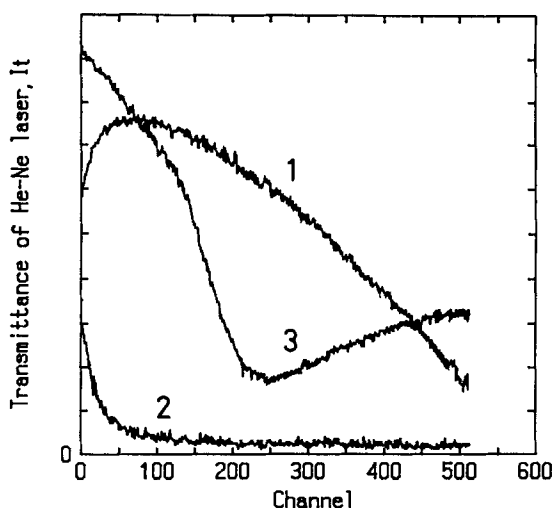


FIGURE 5 Time-resolved photochemical phase transition behaviors of BMAB/5CB and HOAB/5CB. 1, BMAB/5CB (100 ms/512 channel); 2, BMAB/5CB (1 s/512 channel); 3, HOAB/5CB (1 s/512 channel). Laser power, 5 mJ/pulse; $T_{\text{red}} = 0.998$; BMAB, 3 mol %.

It is clearly seen that I_t for the BMAB/5CB mixture decreased with time and finally became 0, which is ascribed to the complete loss of birefringence (curve 2). This means that the $N \rightarrow I$ phase transition of the BMAB/5CB mixture was induced photochemically after a sufficient amount of the cis form was produced with a single pulse of the laser. It must be mentioned here that the time required for the photoisomerization of BMAB in 5CB was quite short and comparable to those observed for azobenzene compounds in solution.¹⁸ In an attempt to analyze the time-course of the trans-cis photoisomerization in the LC medium, we tried to detect the decay of the absorbance due to the trans form of BMAB, however, it was unsuccessful. The maximum time resolution obtained in our apparatus was 10 ns, and within this time the photoisomerization was completed. No matter what the time was, it was short enough to assume that the trans-cis isomerization took place simultaneously with the laser pulse. The time required for the phase transition of the BMAB/5CB mixture was ~ 100 ms as demonstrated by curve 2, so that the formation of the cis form can safely be expressed by a delta function with infinitesimal time width.

Contrary to the behavior of the BMAB/5CB mixture, HOAB/5CB did not exhibit the phase transition, although the change in I_t was observed as shown in Figure 5 (curve 3). The change in I_t is most probably due to a rise in temperature caused by heat associated with non-radiative deactivation of the excited HOAB. These results clearly indicate that the N-I phase transition observed for the BMAB/5CB mixture resulted from the photochemical reaction of the dopant, thus termed "photon-mode," and not from the heat generated by the laser irradiation (heat-mode). The phase transition of the BMAB/5CB mixture may be best interpreted in terms of the T_{NI} depression caused by the accumulation of the cis form of BMAB. Curves 1 and 2 show the change in I_t obtained for the BMAB/5CB mixture at different time scales (curve 1; 100 ms/512 channel). At the initial stage, I_t was found to increase. This change in I_t is explicable in terms of the interference, as thoroughly discussed in previous papers under steady-state irradiation.^{16,17}

Temperature Dependence

It is worth mentioning here the effect of temperature on the photochemical phase transition behaviors of the guest/host mixtures. Figure 6 shows the change in I_t for the BMAB/5CB mixture at various temperatures on irradiation with the nano-second-pulsed laser. It is clear that the time required for the $N \rightarrow I$ photochemical phase transition at $T_{red} = 0.998$ was obviously shorter than those at lower temperatures, and those at $T_{red} = 0.997$ and $T_{red} = 0.96$ were approximately equal. Although the phase transition was no longer observed at $T_{red} = 0.994$ with a single pulse of the laser, a few laser pulses could cause the phase transition photochemically. As discussed above, the isothermal phase transition in the present system can be interpreted as a lowering of the phase transition temperature brought about by accumulation of the cis form of the dopant. Thus, if a sufficient amount of the cis form is produced within infinitesimal time, the relaxation rate seems to be independent of the irradiation temperature. The faster rate of the phase transition at $T_{red} = 0.998$ might indicate some contribution of the heat-mode process.

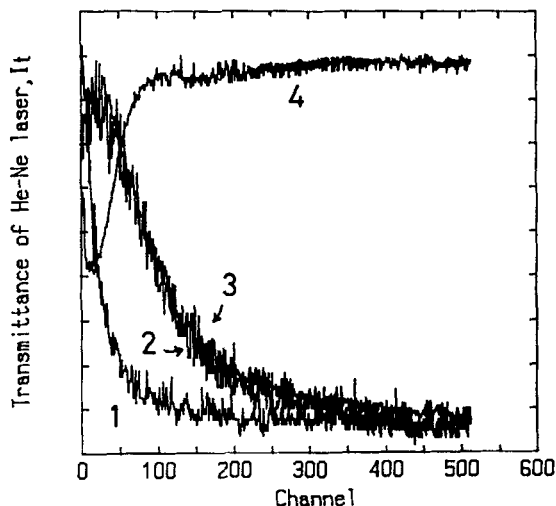


FIGURE 6 Temperature dependence of the photochemical phase transition of the BMAB/5CB mixture. 1 s/512 channel. 1, $T_{red} = 0.998$; 2, $T_{red} = 0.997$; 3, $T_{red} = 0.996$; 4, $T_{red} = 0.994$. Laser power, 5 mJ/pulse; BMAB, 3 mol%.

Concentration Dependence and Cell Gap Dependence

The concentration dependence on the photochemical phase transition behaviors is indicated in Figure 7. Irradiation was performed at $T_{red} = 0.998$, and three kinds of the BMAB/5CB mixtures were employed, where the concentration of BMAB was 1, 3 and 5 mol%. The mixture with 3 mol% of BMAB exhibited a faster rate of phase transition than that of the mixture with 1 mol% of BMAB. The depression

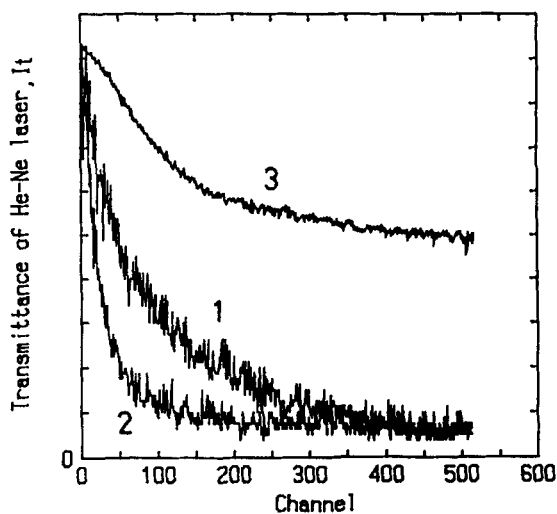


FIGURE 7 Dependence of the photochemical phase transition on the concentration of BMAB doped in 5CB. 1 s/512 channel. 1, 1 mol%; 2, 3 mol%; 3, 5 mol%. Laser power, 5 mJ/pulse; $T_{red} = 0.998$.

of T_{NI} brought about by the photoisomerization of the dopant may reasonably be regarded as a function of the concentration of the cis form produced. As in the case of the melting point depression, T_{NI} is expected to decrease with increasing the concentration of "impurity" (cis form) in the system. It seems, therefore, reasonable that the photochemical phase transition of the BMAB/5CB mixture with 3 mol% dopant took place faster than that with 1 mol% dopant, since the concentration of the cis form produced with a single pulse of the laser is higher in the former than in the latter. No phase transition was observed in the BMAB/5CB mixture with 5 mol% of BMAB, which may be a result of the simple inner filter effect of BMAB, since the absorbance of the mixture at 355 nm was high enough (>3). The photochemical phase transition was probably induced at the surface layers, but under the present experimental set-up the phase transition is recognized only when it occurs throughout the layers normal to the cell surface.

The cell gap dependence was also examined. The mixture injected in a cell with a 9- μm gap did not show the photochemical phase transition with a single laser pulse.

Laser Power Dependence

The power of the pulsed laser affected the photochemical phase transition behaviors as shown in Figure 8 for the BMAB/5CB mixture when the power was varied from 3 to 5 mJ/pulse. The rate of the pulse transition increased with increasing the power. The photochemical phase transition was not observed with a laser power less than 3.5 mJ/pulse. As shown in Figure 4(B), the cis isomer produced by the laser flash increased with increasing the laser power, thereby this laser power dependence as well as the concentration dependence can be ascribed to the amount

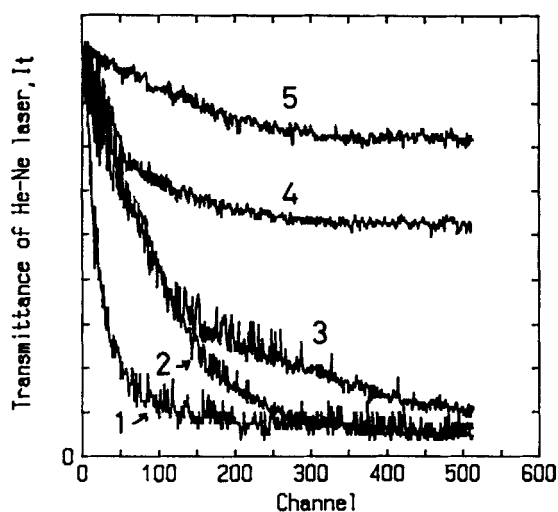


FIGURE 8 Dependence of the photochemical phase transition of the BMAB/5CB mixture on the laser power. 1 s/512 channel. 1, 5 mJ/pulse; 2, 4.5 mJ/pulse; 3, 4 mJ/pulse; 4, 3.5 mJ/pulse; 5, 3 mJ/pulse. $T_{red} = 0.998$; BMAB, 3 mol%.

of the cis isomer produced by the laser flash. As mentioned above, the large amount of the cis isomer can induce the photochemical phase transition rapidly. In addition, it is likely that a threshold of the amount of the cis isomer for the photochemical phase transition exists.

Photochemical Phase Transition in Various LCs

The photochemical phase transition behaviors of various LCs other than 5CB as the host were examined at the same reduced temperatures ($T_{\text{red}} = 0.998$) and the results are shown in Figure 9. I_t for a BMAB/7CB mixture was found to become 0 due to the $N \rightarrow I$ phase transition as in the case of the BMAB/5CB mixture. Although the others exhibited the change in I_t in a similar way to the BMAB/7CB mixture after a single laser flash, the photochemical phase transition was not induced completely. It has been revealed that the higher the T_{NI} of the LC matrix, the lower the rate of the phase transition becomes under steady-state photoirradiation.¹⁶ According to the Maier-Saupe theory,¹⁹

$$T_c = A \cdot n^2 / 4.54 \cdot k$$

where A is a constant representing the strength of dispersion force, $n = N/V$ is the concentration of molecules and k is Boltzmann's constant. The LC-forming force of an LC matrix with higher T_{NI} is considered to be stronger so that a larger perturbation is required for the phase transition to take place. The T_{NI} of the BMAB/host LC determined by microscopic observation were 36.5 °C (5CB), 43.1 °C (7CB), 54.2 °C (PCH5) and 68.6 °C (5OCB), respectively. These values of T_{NI} of the mixtures seem to be well correlated to the photochemical phase transition behaviors of the mixtures. Namely, the photochemical phase transition was observed in 5CB and 7CB which possessed rather lower values of T_{NI} , while no

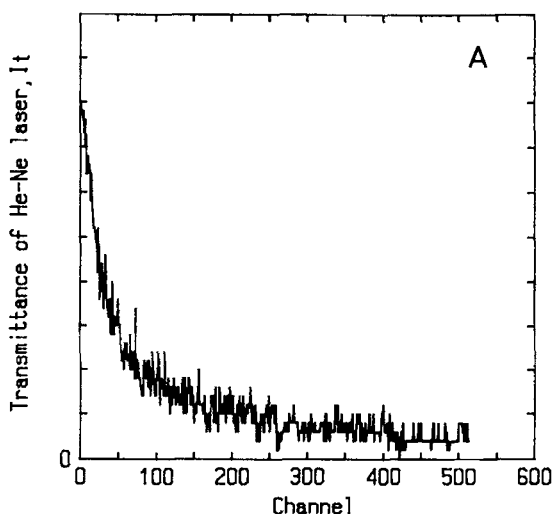


FIGURE 9 Photochemical phase transition behaviors in various host LCs. 1 s/512 channel. A, 7CB; B, 6OCB; C, PCH5. Laser power, 5 mJ/pulse; $T_{\text{red}} = 0.998$; BMAB, 3 mol%.

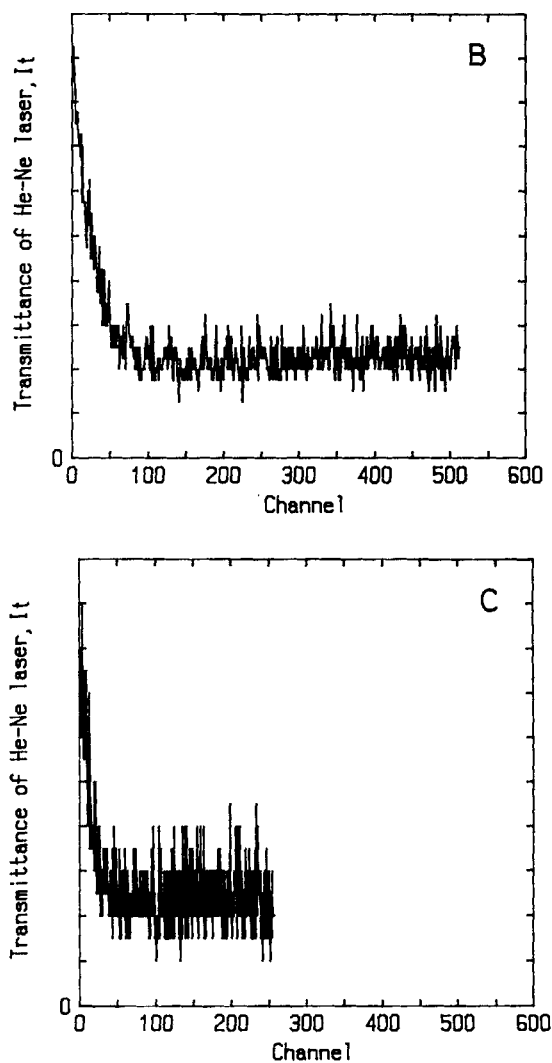


FIGURE 9 (continued)

complete phase transition occurred in PCH5 and 5OCB, which had higher T_{NI} values. Although a single laser flash could not induce the photochemical phase transition in PCH5 and 5OCB, several flashes brought about the phase transition even in these host LCs.

As a final remark, there has been no previous investigation that can be compared directly with the present results. Wyn-Jones et al. studied the dynamics of the hexagonal \rightarrow isotropic phase transition of lyotropic LCs by the temperature jump method.²⁰ The time-course of the phase transition was monitored by the time-resolved measurements of birefringence and the transition was found to occur in

~500 ms. They interpreted their results in terms of the nucleation and growth concept on micellar fission. In the case of the electric-field response of thermotropic LCs, each mesogen is affected by the applied electric field in such a way that it reorients according to the nature of its own dipole. The relaxation process of the present system is clearly different from this type of reorientation process and may be rather regarded as a thermodynamic-controlled process.

CONCLUSION

The "intrinsic" response of LCs in the photochemical phase transition has been evaluated by the use of the nanosecond laser pulse with special reference to the comparison of the photon-mode phase transition with the heat-mode process. The isothermal phase transition of the BMAB/SCB mixture was induced photochemically with a single pulse of the laser of 10 ns FWHM in a time scale of ~100 ms at $T_{\text{red}} = 0.998$. On the other hand, HOAB/SCB did not exhibit the phase transition, although the change in transmittance of the He-Ne laser light was observed.

The photochemical isothermal phase transition can be interpreted in terms of the lowering of the phase transition temperature brought about by accumulation of the *cis* form of the dopant. This depression of the phase transition temperature may be a function of the concentration of the *cis* form photochemically produced in the mixtures. The idea of the "impurity"-induced depression of the phase transition temperature of the mixture well explains the effects of temperature, dopant concentration and laser power on the photochemical isothermal phase transition of the guest/host mixtures.

REFERENCES

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
2. K. Kondo, H. Takezoe, A. Fukuda, E. Kuze, K. Flatischler and K. Skarp, *Jpn. J. Appl. Phys.*, **22**, L294 (1983).
3. A. Sasaki, *Mol. Cryst. Liq. Cryst.*, **139**, 103 (1986).
4. S. Tazuke and T. Ikeda, *The Effects of Radiation on High-Technology Polymers*, Reichmanis, E.; O'Donnell, J. H., Eds., ACS Symposium Series 381, Washington DC, chapter 13 (1989).
5. W. Haas, J. Adams and J. Wysocki, *Mol. Cryst. Liq. Cryst.*, **7**, 371 (1969).
6. W. E. Haas, K. F. Nelson, J. E. Adams and G. A. Dir, *J. Electrochem. Soc.*, **121**, 1667 (1974).
7. E. Sackman, *J. Am. Chem. Soc.*, **93**, 7088 (1971).
8. K. Ogura, H. Hirabayashi, A. Uejima and K. Nakamura, *Jpn. J. Appl. Phys.*, **21**, 969 (1982).
9. G. Attard and G. Williams, *Nature*, **326**, 544 (1987).
10. V. P. Shibaev, S. G. Kostromin, N. A. Plate, S. A. Ivanov, V. Yu. Vetrov and I. A. Yakovlev, *Polym. Commun.*, **24**, 364 (1983).
11. H. J. Coles and R. Simon, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 43 (1984).
12. H. J. Coles and R. Simon, *Polymer*, **26**, 1801 (1985).
13. M. Eich, J. H. Wendorff, B. Reck and H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, **8**, 59 (1987).
14. M. Eich and J. H. Wendorff, *Makromol. Chem. Rapid Commun.*, **8**, 467 (1987).
15. C. B. McArdle, *Liquid Crystals*, **2**, 573 (1987).
16. S. Tazuke, S. Kurihara and T. Ikeda, *Chem. Lett.*, 911 (1987); S. Kurihara, T. Ikeda and S. Tazuke, *Jpn. J. Appl. Phys.*, **27**, L1791 (1988); S. Kurihara, T. Ikeda and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, **178**, 117 (1990); T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol.*

- Cryst. Liq. Cryst.*, **182B**, 357 (1990); T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, **182B**, 373 (1990).
17. T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, *Chem. Lett.*, 1679 (1988); T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, *Macromolecules*, **23**, 36 (1990) and *Macromolecules*, **23**, 42 (1990); T. Ikeda, H. Itakura, C. H. Lee, F. M. Winnik and S. Tazuke, *Macromolecules*, **21**, 3536 (1988); T. Ikeda, C. H. Lee, T. Sasaki, B. Lee and S. Tazuke, *Macromolecules*, **23**, 1691 (1990); T. Ikeda, S. Kurihara, D. B. Karanjit and S. Tazuke, *Macromolecules*, **23**, 1990).
18. M. Irie, *Molecular Models of Photoresponsiveness*, Montagnoli, G.; Erlanger, B. F., Eds., NATO ASI series A68, Plenum, New York, p. 291 (1983).
19. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959); **15a**, 287 (1960); **16a**, 816 (1961).
20. P. Knight, E. Wyn-Jones and G. J. T. Tiddy, *J. Phys. Chem.*, **89**, 3447 (1985).