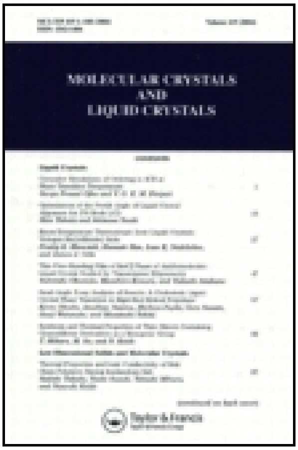

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochemical Switching of Liquid Crystals Under an Electric Field: Comparison of Photochemical Alignment Change in the Electric Field and Isothermal Phase Transition

Seiji Kurihara [a], Masahiko Nakano [a] & Takamasa Nonaka [a]
[a] Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, 2-39-1, Kumamoto, 860, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Seiji Kurihara , Masahiko Nakano & Takamasa Nonaka (1996): Photochemical Switching of Liquid Crystals Under an Electric Field: Comparison of Photochemical Alignment Change in the Electric Field and Isothermal Phase Transition, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 287:1, 155-167

To link to this article: http://dx.doi.org/10.1080/10587259608038752

Mol. Cryst. Liq. Cryst., 1996, Vol. 287, pp. 155–167
Reprints available directly from the publisher
Photocopying permitted by license only

Photochemical Switching of Liquid Crystals Under an Electric Field: Comparison of Photochemical Alignment Change in the Electric Field and Isothermal Phase Transition

SEIJI KURIHARA, MASAHIKO NAKANO and TAKAMASA NONAKA*

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, 2-39-1, Kumamoto 860, Japan

(Received January 23, 1996; in final form February 27 1996)

Photochemical alignment change was examined for a nematic liquid crystal (5CB) and a smectic liquid crystal (12CB). The distinct critical value of electric field on the molecular orientation as observed for the smectic liquid crystal. The transformation from a homogenous alignment to a homeotropic alignment in the electric field was induced by trans-cis photoisomerization of azobenzene derivatives. The amount of cis-form required for the transformation of the molecular alignment was smaller than that for photochemically induced isothermal phase transition.

Keywords: Photochemical phase transition, photochemical alignment change, azobenzene, optical switching, homeotropic, homogenous.

INTRODUCTION

Much attention has been focused with respect to the use of liquid crystals (LCs) in fields such as display devices, optical image recording systems and optical switchings. In particular, the photo-control of the orientation of LCs are extensively investigated,[1–14] e.g., the photochemical reaction of guest molecules in host LCs could cause a depression of a phase transition temperature from the LC phase to an isotropic phase of the LC systems, and consequently induced the isothermal phase transition at the irradiated sites. Time-resolved measurements have found that the photochemical phase transition occurs in a time range of 50 to 200 ms for low molecular weight nematic LC and polymeric LC systems.[8,9] Recently, Ikeda et al. reported on the switching of polarization of ferroelectric liquid crystals (FLCs) within a few milliseconds by means of cis-trans photoisomerization of azobenzene derivatives in an electric field.[10–14] The switching of polarization could be achieved by photochemical change in critical values of electric field on switching between two bistable states of FLCs. On the other hand, LCs such as conventional nematic and smectic LCs are also well known to respond to external forces such as a magnetic field and an electric field. Namely, the alignment of LC molecules can be controlled in accordance with the anisotropy of magnetic susceptibility and the dielectric constant. Therefore, the alignment change of the LC molecules is expected to be caused by photoisomerization of photoresponsive molecules resulting in a change in threshold values of the external forces. IN this paper, photooptical switching of the nematic and smectic LC systems in the electric field was investigated and compared with the photochemical isothermal phase transition of LC systems.

EXPERIMENTAL

Materials

Structures of host LCs and azobenzene derivatives used in this study are shown in Figure 1. 4-Cyano-4′-pentylbiphenyl (5CB) and 4-cyano-4′-dodecylbiphenyl (12CB), used as host LCs, were kindly provided by Chisso Co. and used without further purification. 4-Butyl-4′-methoxyazobenzene (BMAB) was synthesized according to the method described previously.[4] Other azobenzene derivatives were synthesized by the diazo-coupling reaction between 4-butylaniline and phenol in the presence of sodium nitrite and hydrochloric acid, and following alkylation of diazonium salts with alkyl halides. Structures of the azobenzene derivatives were confirmed by NMR, IR spectra and elemental analysis.

Data for BMAB: Yield, 79 per cent. ^{1}H NMR ($CDCl_3$ppm), δ 0.9 – 1.8 (*m*, 7H), 2.7 (*t*, 2H), 3.8 (*s*, 3H), 6.8 – 7.9 (*m*, 8H). Elemental analysis, calculated for $C_{17}H_{20}N_2O$, C 76.1, H 7.5, N 10.5; found, C 76.3, H 7.5, N 10.2.

Data for BHAB: Yield, 68 per cent. ^{1}H NMR ($CDCl_3$ ppm), δ 0.9 – 1.8 (*m*, 18H), 2.7 (*t*, 2H), 4.0 (*t*, 2H), 6.8 – 7.9 (*m*, 8H). Elemental analysis, calculated for $C_{22}H_{30}N_2O$, C 78.1, H 8.9, N 8.3; found, C 77.8, H 9.1, N 8.2.

Data for BDAB: Yield, 66 per cent. ^{1}H NMR ($CDCl_3$ ppm), δ 0.9 – 1.8 (*m*, 30H), 2.7 (*t*, 2H), 4.0 (*t*, 2H), 6.9 – 8.0 (*m*, 8H). Elemental anaysis, calculated for $C_{28}H_{42}N_2O$, C 79.6, H 10.0, N 6.6.; found, C 78.2, H 10.1, N 6.6.

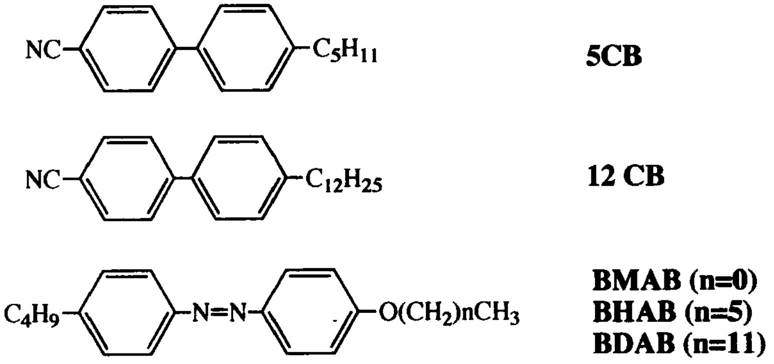

FIGURE 1 Structure of host liquid crystals and azobenzene derivatives.

The samples were abbreviated as nCB-Ax, where n is 5 for 5CB and 12 for 12CB. A and x refer to the abbreviation and the mol% of azobenzene derivatives dispersed in the host LCs, respectively.

Measurements

Thermal properties of the host LCs and the mixtures were examined by differential scanning calorimetry (DSC, Seiko I&E SSC-5020) and polarizing microscopic observation (Olympus BHSP; Mettler FP80 and FP82).

Samples were prepared by filling mixtures in cells which consisted of two parallel indium tin oxide (ITO) glass plates coated with polyimide and rubbed to obtain homogeneous alignment. The cell gap was 5 μm.

The sample was thermostated, placed between two crossed polarizers, and connected to a direct current(DC)power supply. The polarizing direction was set at an angle of 45° with respect to the orientation axis of the cell. The photooptical properties were measured with a 75-W high pressure mercury lamp equipped with a Toshiba cut filter UVD-36S for ultra violet (UV) light irradiation as an excitation lamp. A laser diode (670 nm, 10 mW) was used as an analyzing light source. Absorption spectra were measured on a Shimadzu UV-240 spectrophotometer. The change in transmittance of the light of the laser diode was measured with a photodiode.

Time-resolved measurements of photochemical switching were performed by using a Continuum NY60 Nd:YAG laser (the third harmonic, 355 nm; 4 mJ/pulse; pulse width, 10 ns fwhm) as an excitation light source. The sample was thermostated, placed between two crossed polariziers, and connected to the DC power supply. The polarizing direction was set at an angle of 45° with respect to the orientation axis of the cell. The light of the laser diode which passed through the sample mixture was focused onto the entrance slit of a Jabin-Ybon H20-UV monochomator. The change in transmittance was measured with a Hamamatsu R-928 photomultiplier and recorded with a Phillips PM3350A storage scope.

RESULTS AND DISCUSSION

Thermal properties of the azobenzene derivatives are given in Table 1. The endothermic peaks obtained by DSC measurements on heating were taken as the phase transition temperatures. It is well known that 5CB shows a nematic phase and 12CB shows a smectic phase as LC phases, respectively. The LC phases of both BMAB and BHAB were assigned as the nematic phase, while the LC phase of BDAB was assigned as the smectic phase on the basis of microscopic observation and DSC measurements. In addition, the temperature from the LC phase to an isotorpic phase was found to increase in the order of BMAB, BHAB and BDAB.

Table 2 listed thermal properties of the mixtures consisting of host LCs and azobenzene derivatives. All mixtures containing 5CB as the host LC showed the nematic phase as the LC phase. The phase transition temperature from the nematic phase to the isotropic phase (T_{NI}) increased with increasing BMAB concentration. On the other hand, the mixtures containing 12CB as the host LC showed the

TABLE 1

Thermotropic properties of host LCs and azobenzene derivatives

Sample	Phase Transition Temperature(°C)				ΔHc	ΔSc
	K	*S*	*N*	*I*	(KJ/mol)	(J/mol•K)
5CB	•	—	21.5 •	35.5 •	0.45	1.46
12CB	•	47.1 •	—	57.9 •	4.34	13.1
BMAB	•	—	32.1 •	47.3 •	0.27	0.84
BHAB	•	—	44.7 •	73.0 •	0.64	1.85
BDAB	•	65.1 •	—	75.8 •	7.60	21.8

TABLE 2

Thermotropic properties of 5CB and 12CB doped with various azobenzene derivatives

Sample	Azo. deriv.	Content of Azo. deriv.(mol%)	Temperature(°C)				ΔH_{SI}	ΔS_{SI}
			K	• *S*	• *N*	• I	(KJ/mol)	(J/mol•K)
5CB-BMAB3	BMAB	3	•	—	24.7 •	35.5 •	0.32	1.4
5CB-BMAB5	BMAB	5	•	—	24.4 •	36.2 •	0.32	1.0
12CB-BMAB1	BMAB	1	•	46.3 •	—	57.5 •	4.37	13.2
12CB-BMAB3	BMAB	3	•	45.8 •	—	57.2 •	3.97	12.0
12CB-BMAB5	BMAB	5	•	45.5 •	—	56.8 •	3.75	11.4
12CB-BMAB10	BMAB	10	•	43.9 •	—	55.2 •	3.54	10.8
12CB-BMAB15	BMAB	15	•	42.8 •	—	54.3 •	3.14	9.6
12CB-BMAB20	BMAB	20	•	41.7 •	—	53.5 •	2.71	8.3
12CB-BHAB5	BHAB	5	•	45.3 •	—	56.3 •	4.06	12.3
12CB-BDAB5	BDAB	5	•	44.5 •	—	58.0 •	4.56	13.8

smectic phase. The phase transition temperature from the smectic phase to the isotropic phase (T_{SI}) decreased with increasing BMAB concentration. However, both the transition enthalpy and transition entropy changes of all mixtures at T_{NI} or T_{SI} decreased with increasing BMAB concentration. Doping of BMAB provided more or less the disorder of the host LC phases. Furthermore, the polarizing microscopic observation revealed the phase separation of the mixtures containing BMAB higher than 15 mol%.

The doping of BHAB decreased the T_{SI} of the mixtures, whereas BDAB increased the T_{SI} of the mixtures despite the fact that both the T_{NI} of BHAB and the T_{SI} of BDAB were higher than the T_{SI} of 12CB. The length of the alkoxy groups is closely related to the interaction between 12CB and the azobenzene derivative, and is one of the important factors in the preparation of the LC mixture systems.

Figure 2 shows the changes in transmittance of 5CB-BMAB3 as a function of the applied DC voltage at Tred($= T/T_{NI}$)$=0.980$ and 0.990 at which 5CB-BMAB3 exists in the nematic phase. In addition, 5CB-BMAB3 was in the homogenous alignment where 5CB and BMAB molecules are aligned in the plane of the ITO glass plates in the direction parallel to the rubbing treatment without application of DC voltage. By applying DC voltage the transmittance of 5C-BMAB3 decreased gradually,

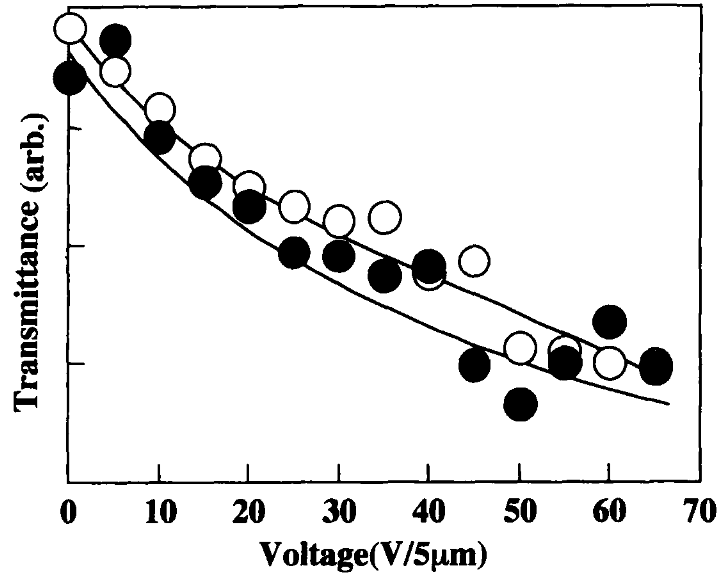

FIGURE 2 Changes in transmittance of 5CB-BMAB3 by applying DC voltage at Tred = 0.980(○) and 0.990(●).

indicating transformation of molecular alignment according to the nature of its own dipole moment. The dipole moment of 5CB is oriented almost parallel to the long axis of the molecules. In addition, it is known that the electrical alignment change of nematic LCs can be induced by applying several volts per micrometer. Therefore, the alignment of 5CB-BMAB3 was transformed by applying DC voltage from the homogeneous alignment to a homeotropic alignment where the molecules were aligned out of the glass plates parallel to the direction of the electric field. 5CB-BMAB5 exhibited similar changes in transmittance to those of 5CB-BMAB3. However, the slope of the changes in the tansmittance of the 5CB-BMAB mixtures was gentle compared to that of the 12CB-BMAB mixtures described later.

Figure 3 shows the changes in the transmittance of 12CB-BMAB10 as a function of the applied voltage at Tred $(=T/T_{SI}) = 0.980$, 0.990 and 0.995 at which 12CB-BMAB10 is in the smectic phase. Contrary to the 5CB-BMAB mixtures, 12CB-BMAB10 was found to show distinct critical voltages of the electric field on the transformation of the molecular alignment from the homogenous alignment to the homeotropic alignment. Although the transmittance remained nearly constant by application of DC voltage up to $V = 40\ V/5\mu m$ at Tred $= 0.98$, it decreased steeply above this voltage and became 0. In addition, it seems that the critical voltage of the transformation of alignment is dependent on temperature. In order to discuss the transformation of the moelcular alignment under the electric field, the intersection of the initial transmittance value and the tangent of changes in the transmittance was defined as the critical voltage (*Vc*) as depicted in Figure 3. In Figure 4, *Vc* for 12CB-BMAB10 was plotted as a function of temperature, Tred. It is clearly seen that *Vc* decreases with increasing temperature. The threshold values of the magnetic field

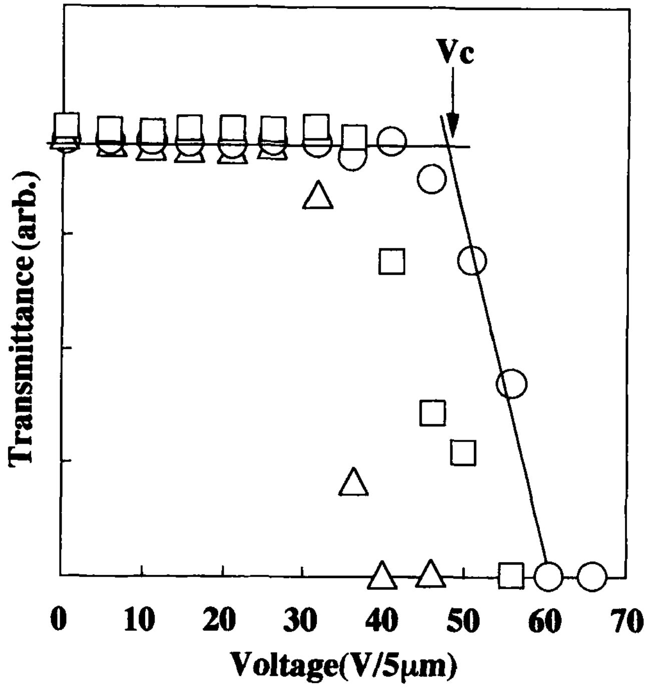

FIGURE 3 Changes in transmittance of 12CB-BMAB10 by applying DC voltage at Tred = 0.980(○), 0.990(□) and 0.995(△).

and the electric field on the LC molecular orientation is known to be proportional to the square root of the elastic constant.[15,16] Therefore, the decrease in *Vc* with increasing temperature may be closely related to the decrease in the elastic constant with increasing temperature.

Figure 5 shows *Vc* of 12CB containing various concentrations of BMAB at Tred = 0.990. *Vc* was found to decrease with increasing the concentration of BMAB doped up to 15 mol%. The doping of BMAB disordered the smectic phase resulting in the decrease in the entropy change as given in Table 2. The decrease in *Vc* signifies that the doping of BMAB also causes the decrease in the elastic constant of the 12CB-BMAB system. On the other hand, the increase in *Vc* was observed at 20 mol% of BMAB. The microscopic observation revealed the phase separation of BMAB in the systems containing BMAB higher than 15 mol%. The increase in *Vc* at 20 mol% of BMAB may be attributed to the phase separation of BMAB.

BMAB is in a trans-form when BMAB is dispersed in 12CB in the dark, whereas UV irradiation brings about the photoisomerization of BMAB to a cis-form. Many studies on the isothermal phase transition of LC systems induced by photoisomerization of photoresponsive molecules such as azobenzene derivatives were reported. The photo-induced isothermal phase transition of the LC systems was interpreted in terms of the depression of the phase transition temperature of the LC systems due to the changes in the molecular shape of the photoresponsive molecules on irradiation. Namely, the photoisomerization in the host LCs affects the ordering of the host LC

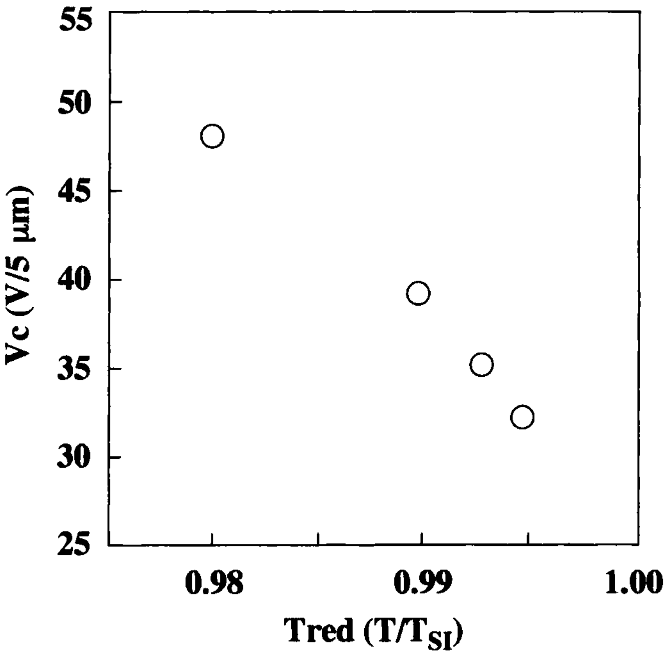

FIGURE 4 Temperature dependence of *Vc* of 12CB-BMAB10.

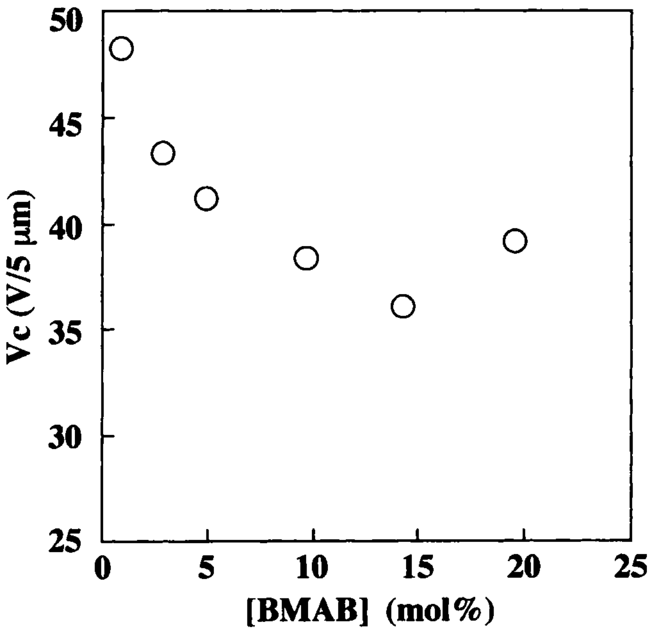

FIGURE 5 BMAB concentration dependence of *Vc* at Tred = 0.990.

phases. In addition, the elastic constant was closely related to the ordering of the LC phases as described above. Therefore, the transformation from the homogenous alignment to the homeotropic alignment is expected to be induced by photoisomerization of BMAB in 12CB with respect to the change in the elastic constant of the systems under the electric field.

Figure 6 shows the absorption spectra of BMAB before and after UV irradiation. BMAB in ethanol before irradiation is in the trans-form with a rod shape showing an absorption maximum at 355 nm. The UV irradiation brought about not only the decrease in the absorbance at 355 nm, but also the increase in the absorbance longer than 430 nm. This is due to the photoisomerization of BMAB from the trans-form to the cis-form with bulky structure by UV irradiation. The change in the absorption spectra of 12CB-BMAB3 is given in Figure 6B when 12CB-BMAB3 is irradiated with UV light in the smectic phase (Tred = 0.99) for 30 min. The irradiation caused a similar change in the absorption spectra to that in ethanol. Therefore, the photoisomerization of BMAB was also brought about in the smectic phase by UV irradiation.

UV irradiation of 12CB-BMAB3 was performed at Tred = 0.98 with or without application of DC voltage and the result is shown in Figure 7. In this figure, transmittance of the light of the laser diode through the sample cell is plotted as a function of the irradiation time. Before UV irradiation, 12CB-BMAB3 was in the smectic state, thus birefringence was detected at time 0. The transmittance remained almost constant under UV irradiation without application of DC voltage, indicating that the isothermal phase transition could not be induced photochemically. On the other hand, a rapid decrease in transmittance was observed by UV irradiation in the electric field. This implies that the transformation from the homogenous alignment to the homeotropic alignment can be induced by photoisomerization of BMAB. Photoisomerization to the cis-form with bulky structure caused the decrease in the threshold voltage of the sample resulting the alignment change in the electric field. The decrease in the threshold voltage may be related to the change in the elastic constant.

Figure 8 shows the changes in transmittance of 12CB-BMAB5 by UV irradiation at Tred = 0.98 with and without application of DC voltage. Before irradiation, 12CB-BMAB5 was in the smectic state. Contrary to 12CB-BMAB3, the transmittance was decreased by UV irradiation without the electric field, which is attributed to the isothermal phase transition of 12CB-BMAB5. The isothermal phase transition of LC systems can be interpreted as the depression of the phase transition temperature by accumulation of the cis-form of BMAB acting as an impurity on the system. The irradiation was performed at Tred = 0.98 for both 12CB-BMAB3 and 12CB-BMAB5. The amount of cis-form of BMAB after prolonged irradiation of 12CB-BMAB3 was not enough to bring about the isothermal phase transition, while a sufficient amount of the cis-form to depress the phase transition temperature to the irradiation temperature was produced by UV irradiation of 12CB-BMAB5. On the other hand, UV irradiation in the electric field decreased the transmittance more rapidly compared to that without the electric field. There was no difference in the photoisomerization behavior of BMAB with and without the electric field. This implies that the amount of cis-form for BMAB required for the alignment change in

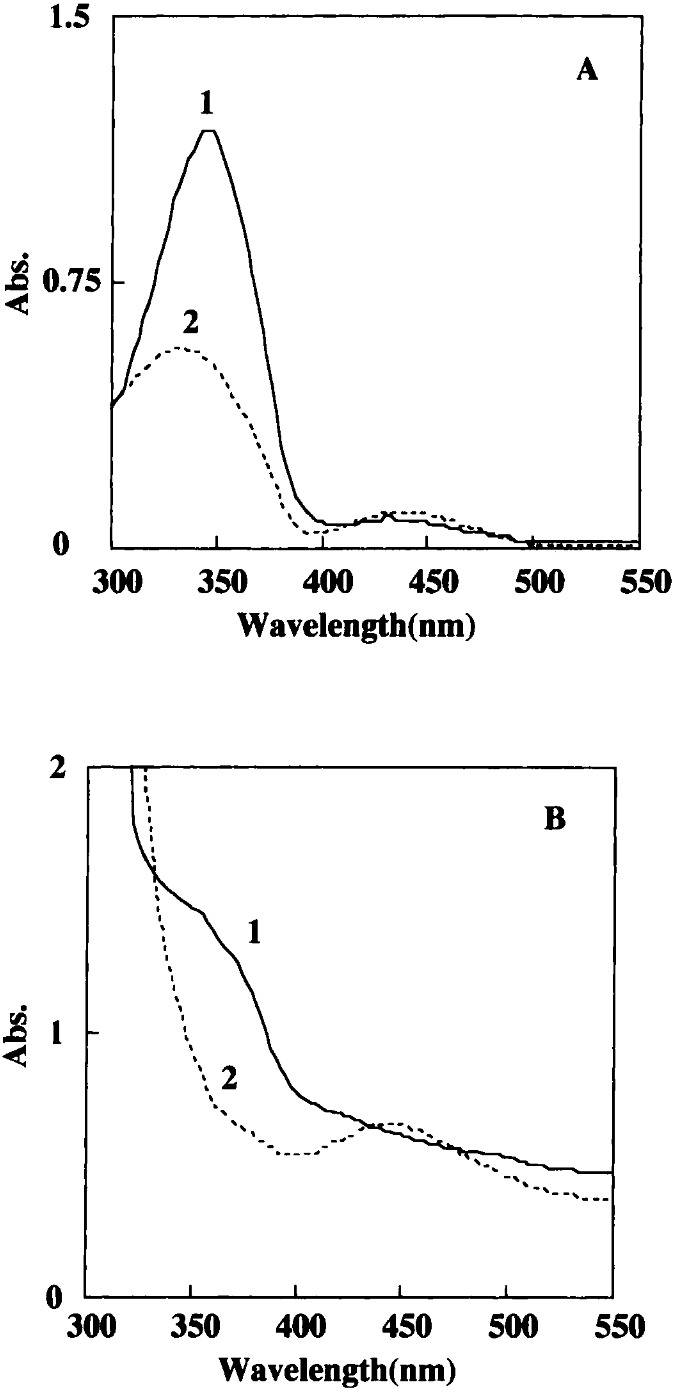

FIGURE 6 Changes in absorption spectra of BMAB in ethanol (A) and 12CB(B). 1, in the dark; 2, irradiated with a high pressure mercury lamp.

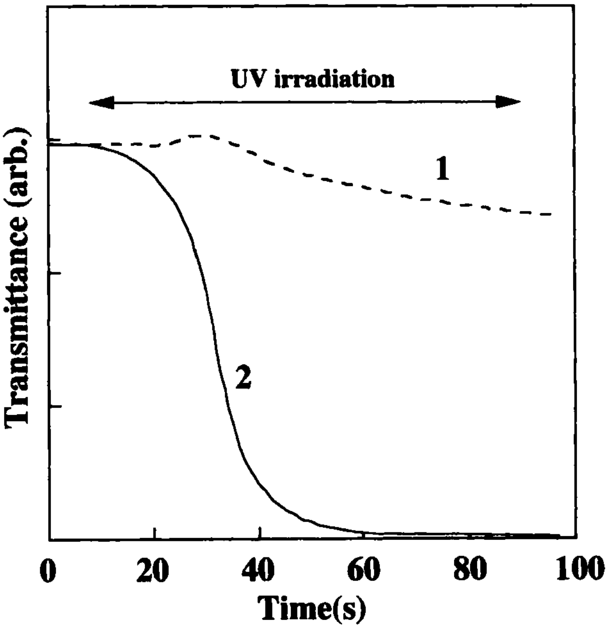

FIGURE 7 Changes in transmittance of 12CB-BMAB3 by UV irradiation with a high pressure mercury lamp at Tred = 0.98, 1, DC = 0V/5 μm; 2, DC = 40V/5μm.

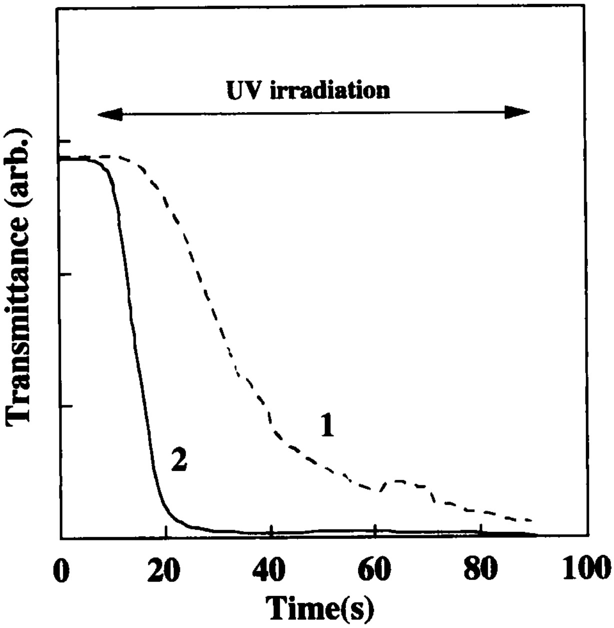

FIGURE 8 Changes in transmittance of 12CB-BMAB5 by UV irradiation with a high pressure mercury lamp at Tred = 0.98. 1, DC = 0V/5μm; 2, DC = 40V/5μm.

the electric field is smaller than that for the isothermal phase transition. Therefore, the alignment change can be induced more effectively than the isothermal phase transition.

In order to investigate the photochemical switching behavior, time resolved observation of changes in transmittance was performed by using a nanosecond pulsed laser. Figure 9 shows the time-resolved change in transmittance of 12CB-BMAB5 at Tred = 0.99 induced by one laser pulse. The UV irradiation with a high pressure mercury lamp caused the isothermal phase transition of 12CB-BMAB5 without the electric field. However, no significant change in transmittance occurred after one pulse irradiation of Nd:YAG laser on 12CB-BMAB5 without the electric field, indicating the phase transition could not be induced. Contrary to this result, the rapid decrease in transmittance was induced by one laser pulse irradiation in the electric field, and the transmittance became 0 after 50 ms. The result is interpreted in terms of the amount of the cis-form required for the phase transition or the alignment change. The amount of cis-form required for the alignment change is smaller than that for the isothermal phase transition. Therefore, the alignment change could be achieved by one pulse of Nd:YAG laser.

Figure 10 shows the strcutural effect of azobenzene derivatives on the photochemical switching behavior. The response time of the photochemical switching of 12CB-BMAB5 was longer than others. The photochemical switching is related to the decrease in the elastic constant by photoisomerization of azobenzene derivatives. Therefore, the photoisomerization rate of azobenzene derivatives in the LC molecules and resulting influence on the elastic constant are considered to be important

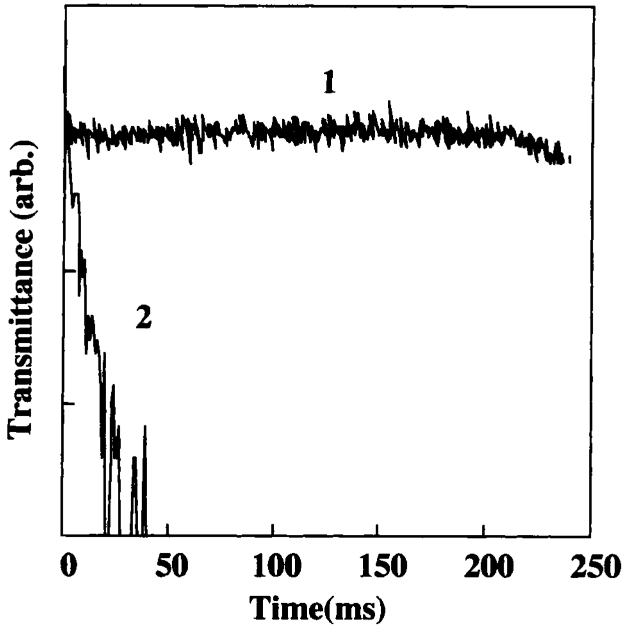

FIGURE 9 Time-resolved observation of change in transmittance of 12CB-BMAB5 at Tred = 0.99. 1, DC = 0V/5μm; 2, 40V/5μm; laser power, 4 mJ/pulse; pulse width, 10 ns.

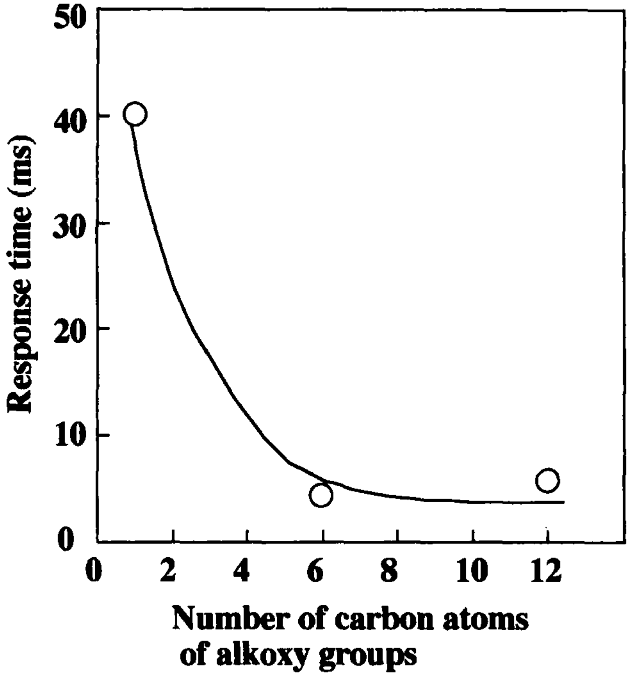

FIGURE 10 Response time of the photochemical alignment change of 12CB containing 5mol% of azobenzene derivatives. The samples were irradiated by one pulse of Nd:YAG laser with the application of *Vc* at Tred = 0.99.

factors in determining the photochemical switching behavior. There was no significant difference in the photoisomerization behavior of azobenzene derivatives. Therefore, it seems that the photoisomerization of BHAB and BDAB with longer alkoxy groups affects more effectively the elastic constant compared to that of BMAB with a methoxy group. In addition, doping of BDAB increased T_{SI} as well as the entropy change at the phase transition from the smectic phase to the isotropic phase, indicating the stabilization of the smectic phase by doping BDAB. The stabilization of the LC phase may be related to the slightly longer response time of 12CB-BDAB5 compared to that of 12CB-BHAB5.

CONCLUSION

The switching of molecular alignment of the LC systems can be achieved by photoisomerization of azobenzene dopants in the electric field. The comparison of the photoirradiation with and without the electric field revealed that the alignment change in the electric field can be induced more effectively than the isothermal phase transition without the electric field. The response time of the alignment change could be induced in several milliseconds. In addition, the response time depended on the strcuture of the azobenzene derivatives.

References

1. K. Ogura, H. Hirabayashi, A. Uejima and K. Nakamura, *Jpn. J. Appl. Phys.*, **21**, 969 (1982).
2. M. Eich and J. H. Wendorff, Makromal. *Chem. Rapid. Commun.*, **8**, 467 (1987).
3. K. Anderle, R. Birenheide, M. Eich and J. H. Wendorff, ibid, **10**, 477 (1989).
4. S. Kurihara, T. Ikeda and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, **178**, 117 (1990).
5. T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, *Macromolecules*, **23**, 36 (1990); ibid, **23**, 42 (1990).
6. S. Kurihara, T. Ikeda, S. Tazuke and J. Seto, *J. Chem. Soc. Faraday Trans.*, **87**, 3251 (1991).
7. K. Ichimura, T. Hayashi, H. Akiyama and N. Ishizuki, *Langmuir.*, **9**, 3298 (1993).
8. S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim and S. Tazuke, *J. Chem. Soc. Chem. Commun.*, 1751 (1990).
9. T. Sasaki, T. Ikeda and K. Ichimura, *Macromolecules*, **25**, 3807 (1992).
10. T. Ikeda, T. Sasaki and K. Ichimura, *Nature*, **361**, 428 (1993).
11. T. Sasaki, T. Ikeda and K. Ichimura, *J. Am. Chem. Soc.*, **116**, 625 (1994).
12. T. Sasaki and T. Ikeda, *J. Phys. Chem.*, **99**, 13002 (1995).
13. T. Sasaki and T. Ikeda, *J. Phys. Chem.*, **99**, 13008 (1995).
14. T. Sasaki and T. Ikeda, *J. Phys. Chem.*, **99**, 13023 (1995).
15. K. Okano and S. Kobayashi, ed. "Ekisho-Kisohen", Baihukan (1985).
16. S. Chandrasekhar, "Liquid Crystals. 2nd Ed.", Cambridge University Press (1992).