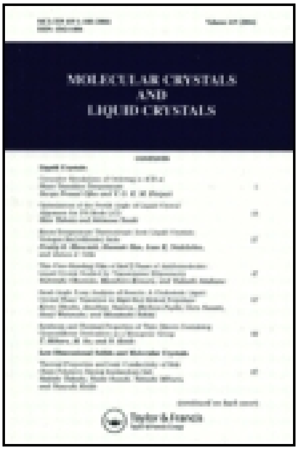

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Photochemically Induced Isothermal Phase Transition in Liquid Crystals. Effect of Interaction of Photoresponsive Molecules with Matrix Mesogens

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Photochemically Induced Isothermal Phase Transition in Liquid Crystals. Effect of Interaction of Photoresponsive Molecules with Matrix Mesogens

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The photoinduced phase transition behavior of liquid crystals (LCs) was investigated. The rate of the phase transition increased with increasing temperature and decreasing cell gap. The amount of isomerization of photoresponsive molecules to induce the phase transition was found to depend on the LC forming force and affinity of the photoresponsive molecule with the host mesogen. A larger amount of isomerization was required to induce the phase transition of LC matrix with higher T_{NI} or ΔS. Mesogenic azobenzene derivatives induced the phase transition effectively. These results indicate that the interaction between photoresponsive molecules and matrix mesogens is an important factor affecting the isothermal phase transition behavior.

INTRODUCTION

Photochromism is a topic of increasing interest because of its potential application to highly sensitive, tough and reversible optical image recording systems. Molecular aggregates like liquid crystals exhibit sometimes more than two stable states under appropriate conditions. Optical recording systems by means of a photochemically triggered phase transition between two stable states of liquid crystals were proposed; phase transition from liquid crystal to isotropic phases.[1-4] Although the recording systems based on heat-mode phase transition could be reversible, the best reversible recording systems will be achieved by the use of photochromic compounds. The advantage of the photon-mode recording over the heat-mode recording lies in superior resolution and the possibility of multiplex recording in the photon-mode recording.[5] Diffusion of heat worsens the resolution. A variety of information associated with the photon-mode recording (energy, polarization and coherency) is also an advantage of the photon-mode recording.[5] To achieve high sensitivity and a high signal-to-noise ratio (S/N) of the recording, methods other than direct reading of the photochemical reaction are to be developed. Vision is a good model. In visual cells, photons are absorbed by photoreceptors called retinal and photoisomerization of the photoreceptors takes place.[6] Photochemical reaction occurring at a local site of the visual cells causes a conformational change of the whole protein molecules, thus the photosignals are amplified.[6] We have applied this principle to optical recording systems and reported several examples.[7-11]

In a previous paper, we showed that the phase transition of 4-cyano-4′-*n*-pentylbiphenyl (5CB) could be induced isothermally by photoisomerization of a small amount of photoresponsive molecules doped in 5CB. The choice of 5CB was due to its colorlessness, chemical and photochemical stability. In this paper we report effects of thermodynamic properties of the host LCs and the structure of the photoresponsive molecules on the phase transition behaviors, together with the effects of temperature and concentration of the photoresponsive molecules.

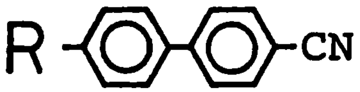
EXPERIMENTAL

Host liquid crystals (LCs) were purchased from Merck Co. and used without further purification. Azo derivatives were used as photoresponsive compounds. These compounds were prepared by a conventional method. One example, 4,4′-bis(propoxy)azobenzene, is given here. 4-Acetylaminophenol reacted with propyl bromide to give 4-propoxyanilide hydrochloride. Diazotization of the salt was followed by coupling with phenol and propylation with propyl bromide to give 4,4′-bis(propoxy)azobenzene. The structure of this compound was confirmed by NMR and IR. The structures and physical properties of compounds used in this study are listed in Table I and Table II. Thermal analyses were performed by DSC measurement (SEIKO SSC-5000) and microscopic observation (Mettler FP-80, FP-82 and OLYMPUS BH2).

Samples were prepared by placing mixtures of LC and an azo compound in a cell. The cell consisted of two parallel glass plates which were coated with polyimide and rubbed to obtain homogeneous alignment. The cell gap was ca. 10 μm. In Figure 1 is shown the schematic diagram of the apparatus used for simultaneous monitoring of both the photo-induced phase transition behavior and the isomerization behavior of the samples. The sample was thermostated and placed between two crossed polarizers. The polarizing directions of these two polarizers were set at an angle of 45° with respect to the orientation axis of the cell. A change in the transmittance of a He-Ne laser (633 nm, 5 mW) was monitored with a photodiode when the sample was irradiated with monochromatic light to bring about trans-cis photoisomerization of azobenzene derivatives doped in the host LCs. The photoisomerization behavior of the azobenzene derivatives was observed by monitoring the intensity of irradiated light passed through the sample and comparing the intensity without the sample.

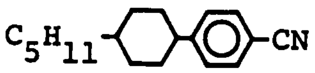
TABLE I

Thermodynamic properties of host liquid crystals doped with 5 mol% of BMAB.

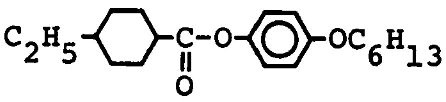


Abbrev.	R	T_{NI} °C	ΔH_{NI} kJ/mol	ΔS_{NI} J/mol·K
5CB	C_5H_{11}	39.1	0.30	0.96
6CB	C_6H_{13}	32.9	0.24	0.77
7CB	C_7H_{15}	45.7	0.36	1.13
ECH206	1)	46.2	0.33	1.04
PCH5	2)	56.4	0.86	2.60
3OCB3)	OC_3H_7	66.0	0.19	0.56
5OCB	OC_5H_{11}	71.4	0.37	1.08
6OCB	OC_6H_{13}	77.5	0.56	1.59
11OCB	$OC_{11}H_{23}$	85.5	2.41	6.73

1)



2)



3) 3OCB is a monotropic liquid crystal.

TABLE II

Thermodynamic properties of azobenzene derivatives.

Abbrev.	R_1	R_2	Temp. °C
BMAB	CH_3O	C_4H_9	K 32 N 42 I
1AB1	CH_3O	CH_3O	K 163 I
1AB3	CH_3O	C_3H_7O	K 117 I
1AB8	CH_3O	$C_8H_{17}O$	K 98 N 101 I
1AB12	CH_3O	$C_{12}H_{25}O$	K 103 I
3AB3	C_3H_7O	C_3H_7O	K 148 I
8AB8	$C_8H_{17}O$	$C_8H_{17}O$	K 99 N 113 I

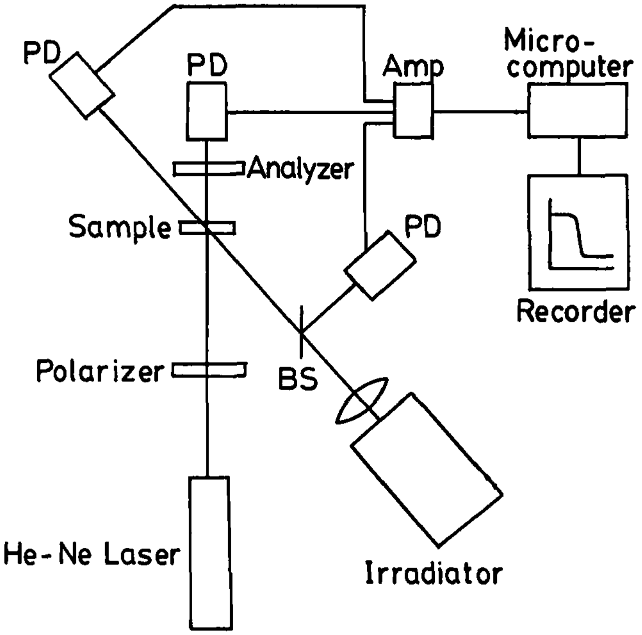


FIGURE 1 Schematic diagram of the apparatus used for measuring of the phase transition behaviors. PD, photodiode; BS, beam-splitter.

RESULTS AND DISCUSSION

1. Influence of environmental conditions

In order to explore the effects of such factors as temperature, concentration of the photoresponsive compounds doped in the host LC, and cell gap on the photoinduced phase transition behavior, 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-butyl-4′-methoxyazobenzene (BMAB) were used as the host LC and the photoresponsive molecule, respectively.

Figure 2 shows the temperature dependence of the transmittance of 5CB alone loaded in a homogeneously aligned cell with a thickness of 10.5 μm on cooling. The transmittance increased steeply at 36°C. This steep increase is due to the isotropic (*I*)–nematic (*N*) transition. Further cooling gave a periodic change in the transmittance owing to interference. In the course of heating the same trend was observed.

The transmittance of the He-Ne laser light, I_t, is expressed in the form of

$$I_t = I_0 \cdot \sin^2(\pi \cdot d \cdot \Delta n/\lambda) \tag{1}$$

where I_t is the intensity of the light transmitted through the two crossed polarizers, I_0 is the intensity of the incident light. The variables d, Δn and λ are the sample thickness, the birefringence and the wavelength of the incident light, respectively. The value of $d \cdot \Delta n/\lambda$ can be written as

$$d \cdot \Delta n/\lambda = m + \tfrac{1}{2} \tag{2}$$

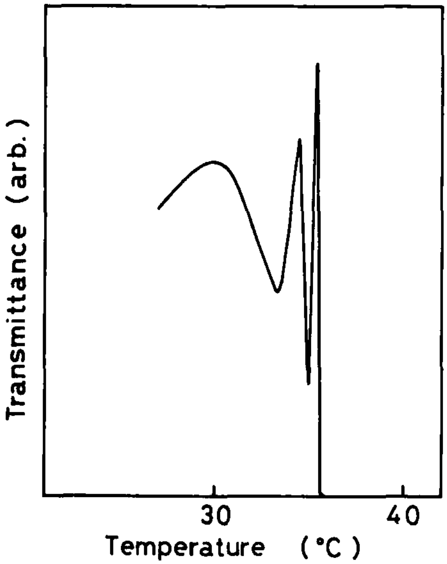


FIGURE 2 Temperature dependence of transmittance of a He-Ne laser through 5CB in a homogeneous cell with a thickness of 10.5 μm on cooling.

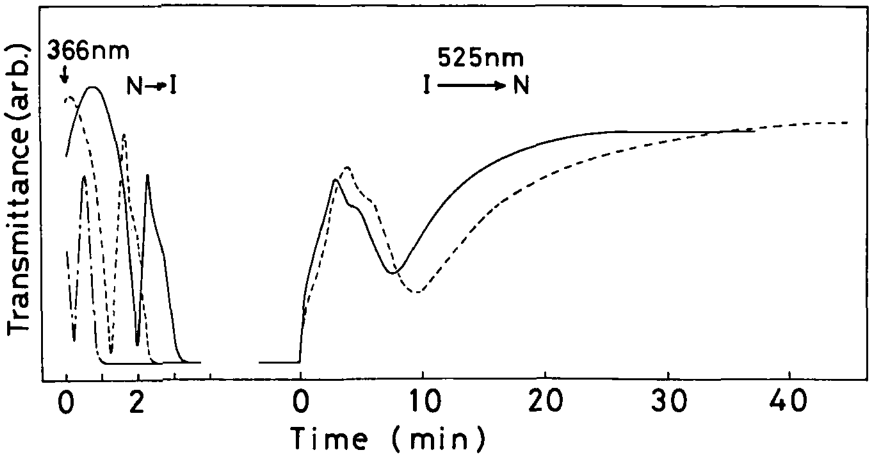


FIGURE 3 Phase transition behaviors of 5CB/BMAB induced by trans-cis isomerization at various temperature. (——), 27°C; (— — — —), 30°C; (— - —), 33°C.

where *m* is the order of interference. The evaluated value of *m* based on Equation 2 under the above condition was two, which agreed with the *m* value obtained from Figure 2. The changes in transmittance associated with photoirradiation to bring about trans-cis isomerization of BMAB doped in 5CB (5 mol%) are shown in Figure 3. Before photoirradiation, the system was nematic. The transmittance changed periodically and became zero when the system was irradiated at 366 nm to cause the trans → cis photoisomerization of BMAB. It is clear that phase transition of the whole system from *N* to *I* occurred. A reversible phase transition, *I* → *N*, could be induced by irradiating at 525 nm to cause the reverse cis → trans photoisomerization. Profiles of the changes in the transmittance are similar to that observed for 5CB when the temperature was varied (Figure 2). The complicated shape in Figure 3 is again due to interference. This is also supported by the effect of the cell gap. According to Equation 2, the order of interference, *m*, should depend on the cell gap based on Equation 2. As shown in Figure 4, the shape depended on the cell gap and interference was not observed with a 2.5 μm cell. As described later, the same cell gap dependence was observed for the 5OCB/BMAB mixture.

The irradiation time required to induce the phase transition depended on the temperature and the cell gap. The irradiation time for the *I* → *N* transition was longer than that for the *N* → *I* transition. The longer time for this *I* → *N* transition may be attributed to the low extinction coefficient of $n \rightarrow \pi^*$ transition associated with the cis form of BMAB ($\varepsilon_{525} \sim 300$) compared to $\pi \rightarrow \pi^*$ ($\varepsilon_{366} \sim 25000$). Secondly, the *I* → *N* transition is a process from a disordered state to an ordered one, thus disadvantageous in view of entropy.

In order to discuss the phase transition behavior quantitatively, we defined the rate of the photochemically-induced phase transition, τ^{-1}, as the reciprocal of the response time, τ, which is the time taken to reduce the transmittance across the polarizers to 10% of the maximum value (Figure 4). In Figure 5(a), τ^{-1} is plotted

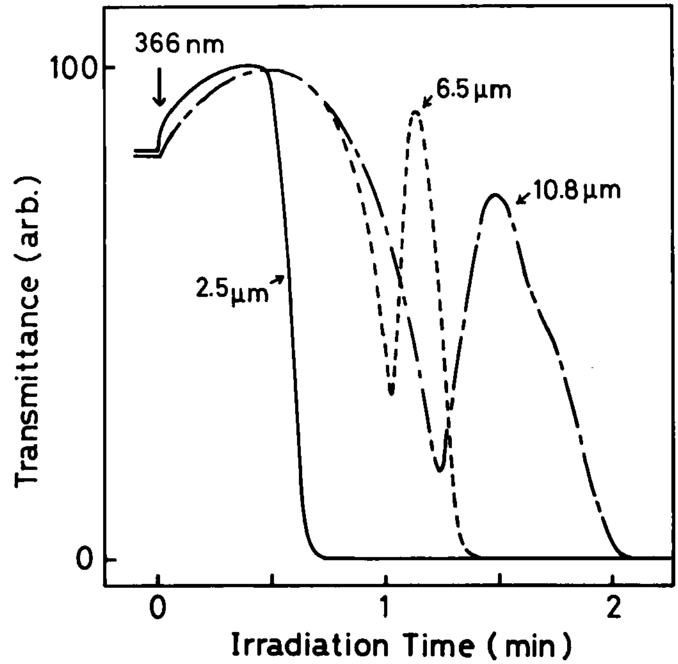
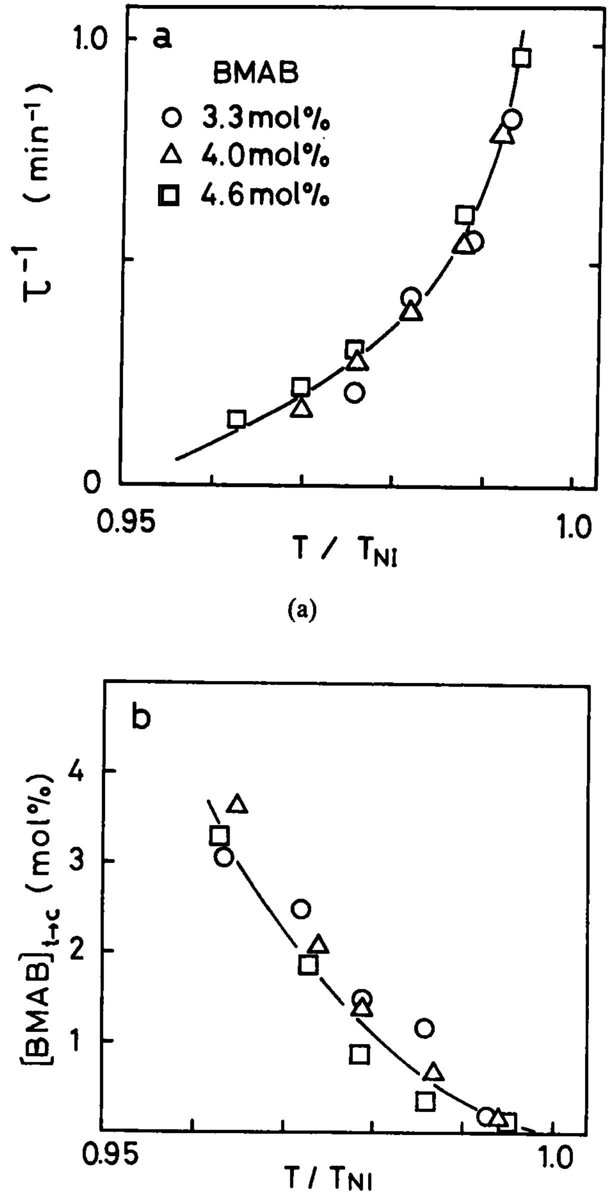


FIGURE 4 Phase transition behaviors of 5CB/BMAB at various cell gaps. Irradiation was performed at $T/T_{NI} = 0.99$.

as a function of reduced temperature, $T_{red}(= T/T_{NI})$, where T_{NI} is the $N \rightarrow I$ transition temperature. It was found that τ^{-1} increased monotonously with temperature and at temperatures close to T_{NI} the phase transition occurred most effectively. The amount of BMAB isomerized by the time when the phase transition was completed decreased with temperature as shown in Figure 5(b). At $T/T_{NI} = 0.99$, only 0.3 mol% of BMAB to the whole system was enough to induce the phase transition when trans → cis isomerization took place. Figure 6 shows the concentration dependence of BMAB on the phase transition of the 5CB/BMAB mixture at $T/T_{NI} = 0.99$. The rate at a concentration of 1 mol% was higher than those which were more than 3 mol%. Phase separation of the mixture into BMAB and 5CB domains could not be observed below 10 mol% of BMAB. Hence the concentration dependence of BMAB arose from the simple inner filter effect of BMAB.

Not only the shape of the change in the transmittance described above but also the response of the photo-induced phase transition depended on the cell gap as shown in Figure 7. 5CB and 5OCB were used as host LCs and doped with 5 mol% of BMAB as the trigger molecule. Figure 7(a) shows τ^{-1} as a function of the cell gap for the $N \rightarrow I$ transition, and τ^{-1} for the $I \rightarrow N$ transitions is given in Figure 7(b). Absorption of the incident light at the surface layer of the cell may be the origin of the cell gap dependence on τ^{-1}.

On the $N \rightarrow I$ transition, τ^{-1} of the 5CB/BMAB mixture is higher than that



(a)

(b)

FIGURE 5 Rates of phase transition of 5CB/BMAB (a) and the amount of BMAB reacted (b) as a function of T/T_{NI}. $[BMAB]_{t\to c}$: mol fraction of BMAB reacted to the whole systems. (○), BMAB 3.3 mol%; (△), BMAB 4.0 mol%; (□), BMAB 4.6 mol%.

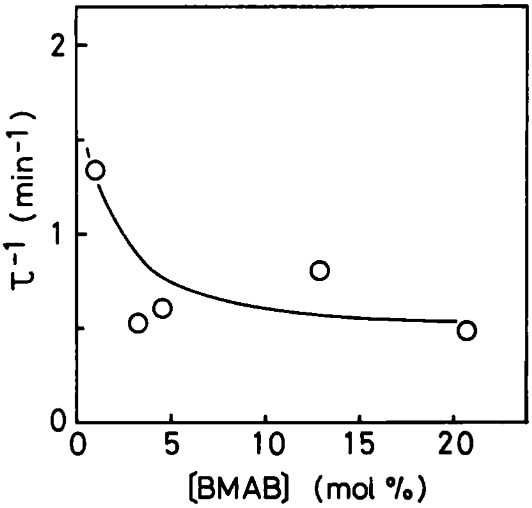


FIGURE 6 Concentration dependence of BMAB on the phase transition behavior of 5CB/BMAB mixture at T/T_{NI} = 0.99.

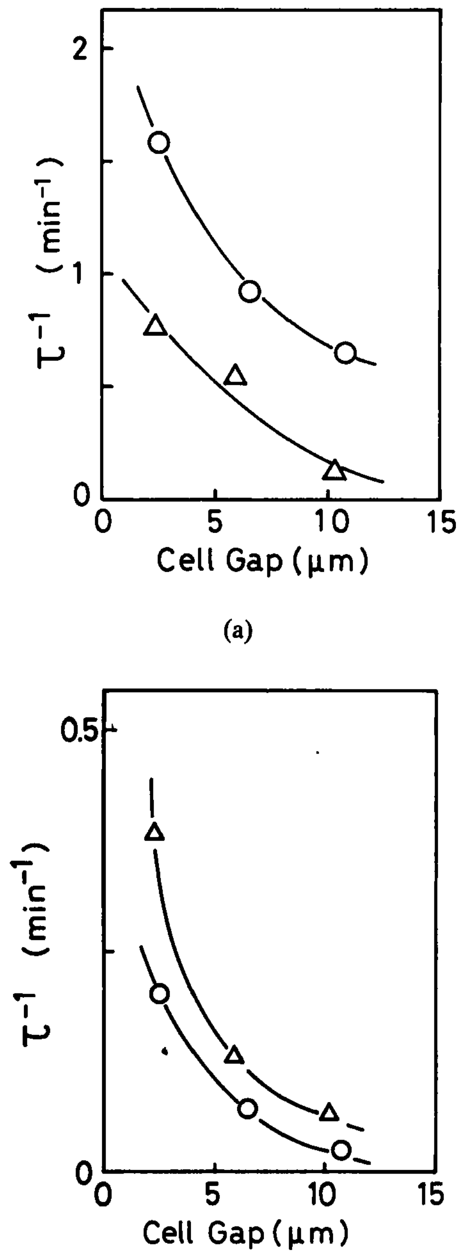
observed for the 5OCB/BMAB mixture. This arose from the difference in the LC forming force between 5CB and 5OCB, as described later. Contrary to the $N \rightarrow I$ transition, τ^{-1} for the 5CB/BMAB mixture is lower than that for the 5OCB/BMAB mixture in the $I \rightarrow N$ transition. This phenomenon may be interpreted on the same basis as the temperature dependence of the phase transition. Although τ for the $N \rightarrow I$ transition of the 5CB/BMAB mixture became shorter as the temperature approached T_{NI} of the system, τ increased with the temperature in the $I \rightarrow N$ transition.

2. Effects of the matrix

The phase transition behavior was observed on various LC matrices doped with 5 mol% of BMAB. Figure 8 shows τ^{-1} as a function of T_{NI} of the system. τ^{-1} was evaluated at T/T_{NI} of 0.99. It is evident that the higher the T_{NI} of the LC matrix, the lower the τ^{-1} of the phase transition becomes. Eventually, 11OCB with T_{NI} = 84.5°C did not exhibit the photochemical phase transition. According to the Maier-Saupe theory,[12]

$$Tc = A \cdot n^2/4.54 \cdot k \qquad (3)$$

where A is a constant representing the strength of the dispersion force, $n = N/V$ is the concentration of molecules and k is Boltzmann's constant. The LC forming force of the LC matrix with a higher T_{NI} is considered to be stronger so that a larger perturbation is required for the phase transition to take place. In addition, host LCs may be divided into two groups in our study, depending on their isothermal phase transition behavior: the OCB series and others.



(a)

(b)

FIGURE 7 Cell gap dependence of the rates of the photo-induced phase transition in 5CB (○) and 5OCB (△) doped with 5 mol% of BMAB. For *N* → *I* transition (a) and *I* → *N* transition (b).

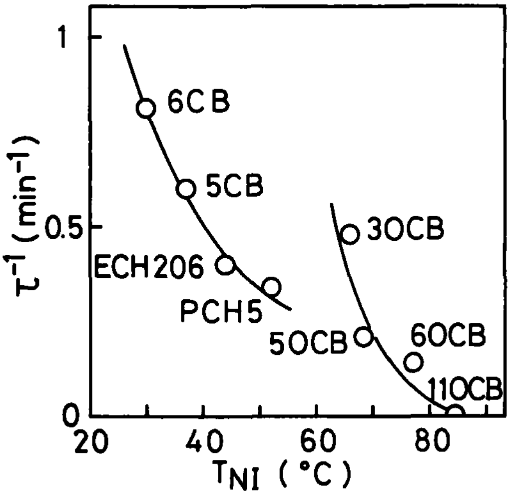


FIGURE 8 Rates of the phase transition in various matrix LCs as a function of T_{NI} at T/T_{NI} = 0.99. BMAB, 5.0 mol%. Cell gap ~ 10 μm.

The difference in the phase transition behavior can be clearly seen in Figure 9 in which τ^{-1} is plotted as a function of ΔS. The values of τ^{-1} observed in the OCB series are lower than those of the CB series. The properties of 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkoxy-4′-cynobiphenys have been studied in detail by Gray et al.[13-15] 4-*n*-Alkoxy-compounds possess higher melting temperatures and considerably higher $N \rightarrow I$ transition temperatures than 4-*n*-alkyl derivatives. Figure 10 shows the transition temperatures as a function of the change in entropy for the

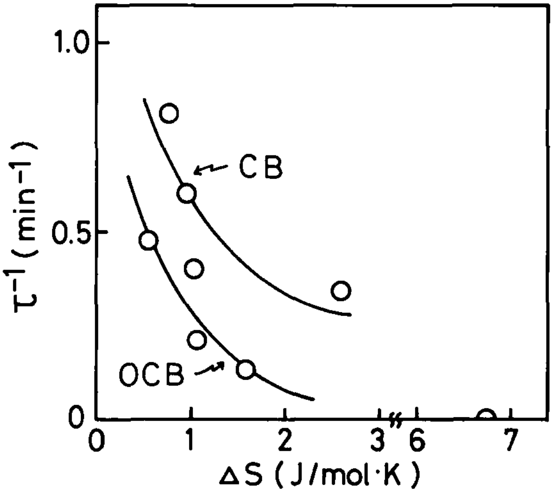


FIGURE 9 Rate of the phase transition in various matrix as a function of ΔS at T/T_{NI} = 0.99. Cell gap ~ 10 μm.

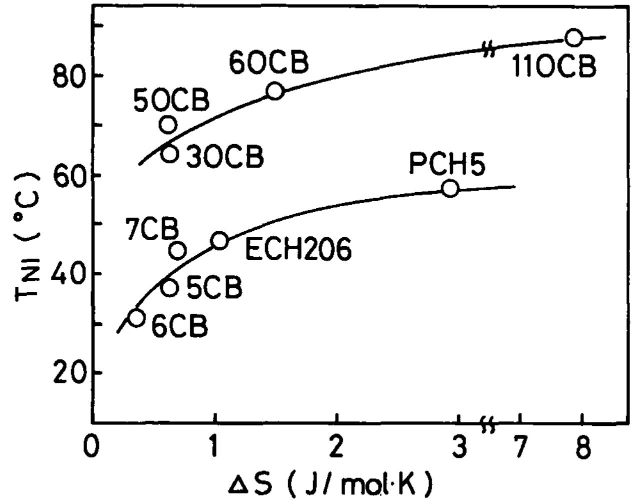


FIGURE 10 Relation of T_{NI} and ΔS for various LC's used in our study.

$N \rightarrow I$ transition. As in the case of Figure 8, two series are present, depending on the kind of substituents. The attachment of the alkoxy group to the aromatic ring is considered to allow conjugate interactions of the alkoxy group with the ring.[16] According to recent studies on cyanobiphenyls,[17,18] there is a strong tendency for the cyanobiphenyl derivatives to form loose molecular pairs in such a way that an antiparallel alignment of the CN dipoles occurs. The intermolecular interaction of the OCB series is stronger than that of the CB series because of the conjugate interaction. The difference in the intermolecular interaction between the OCB and CB series may be responsible for the different behavior of τ^{-1}, as shown in Figure 8. The amount of BMAB isomerized ($[\mathrm{BMAB}]_{t\rightarrow c}$) when the phase transition occurred is plotted against T_{NI} in Figure 11. The amount was estimated by Equation 4.

$$[\mathrm{BMAB}]_{t\rightarrow c} = [\mathrm{BMAB}]_{\mathrm{doped}} \cdot (A_0 - A_T)/(A_0 - A_\infty) \qquad (4)$$

where $[\mathrm{BMAB}]_{\mathrm{doped}}$ is the concentration of BMAB doped in the matrix, and A_0, A_T and A_∞ are the absorbances at the maximum of BMAB before irradiation, at time τ and after prolonged irradiation when the photostationary state is achieved. $[\mathrm{BMAB}]_{t\rightarrow c}$ is found to increase with increasing T_{NI}. This result clearly indicates that the T_{NI} dependence of the matrix predominantly arose from the LC forming force, but not from an increase of thermal cis-trans back isomerization rate of BMAB.[19]

3. Effects of structure of photoresponsive molecules

In Figure 12 is shown a comparison of the phase transition behaviors between two systems where different photoresponsive molecules were doped in 5CB; BMAB

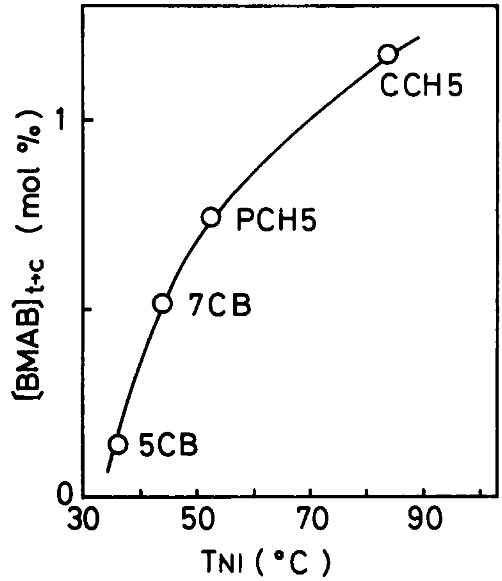


FIGURE 11 Amounts of isomerized BMAB required for $N \rightarrow I$ transition.

and azobenzene (AB). The phase transition behavior of 5CB doped with AB was explored by irradiation at 313 nm. The extinction coefficient of AB at 313 nm ($\varepsilon \sim 22000$) was similar to that of BMAB at 366 nm. Although the intensity of the incident light was somewhat different between 313 nm (1.9×10^{-9} einstein/cm^2 · s) and 366 nm (2.7×10^{-9} einstein/cm^2 · s), the rate of the phase transition was

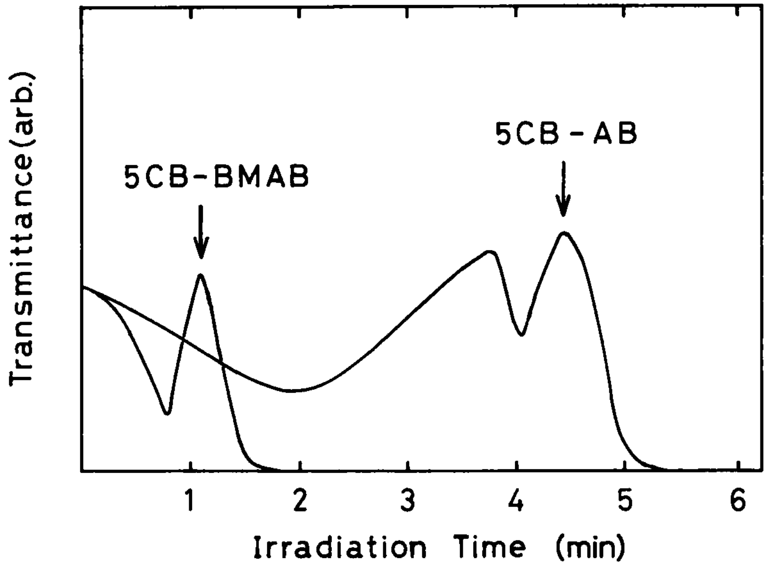


FIGURE 12 Phase transition behaviors of 5CB induced by photoisomerization of BMAB or AB at T/T_{NI} = 0.99. Cell gap = ca. 7 μm.

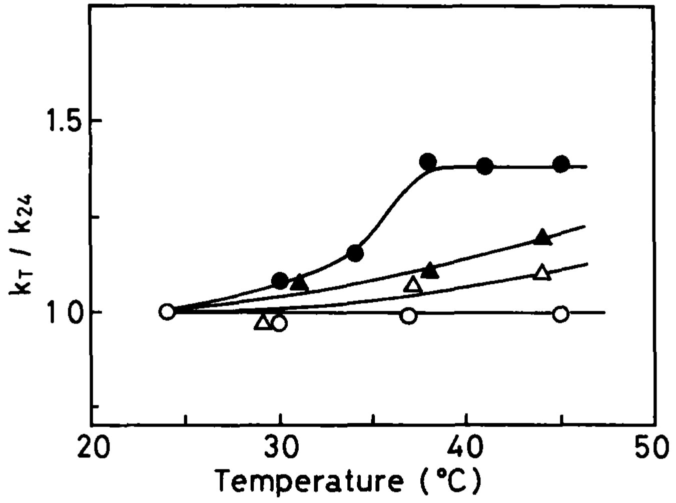


FIGURE 13 Temperature dependence of k_T/k_{24} in *n*-hexane and 5CB. k_T and k_{24} are rates of photoisomerization at *T*°C and 24°C, respectively. (●), BMAB in 5CB; (▲), AB in 5CB (○); BMAB in *n*-hexane; (△), AB in *n*-hexane.

much higher for the 5CB/BMAB mixture than for the 5CB/AB mixture. It can be thought that BMAB is more effective as the trigger than AB. Figure 13 shows the relative rates of trans-cis (k_T/k_{24}) of BMAB and AB in different media, *n*-hexane and 5CB, where k_{24} and k_T indicate the rates of photoisomerization measured at 24°C and *T*°C, respectively. The temperature dependence of k_T/k_{24} for BMAB in 5CB was significantly different from that of the others. Above the T_{NI} of 5CB, photoisomerization of BMAB in 5CB proceeded in a similar manner to that in *n*-hexane, while below the T_{NI}, it was suppressed to a remarkable extent. On the other hand, AB exhibited similar rate profiles both in 5CB and in *n*-hexane. These results imply that the intermolecular interaction between the trigger molecule and the host matrix is an important factor for the phase transition.

The structural effects of the trigger molecules on the photo-induced phase transition were investigated for various 4,4′-disubstituted azobenzene derivatives—BMAB and 4,4′-dialkoxyazobenzene. In order to discuss the effect of trigger molecules quantitatively, we normalized τ^{-1} to the rate of trans → cis isomerization of azobenzenes doped in 5CB. The rates of the isomerization were evaluated at $T/T_{NI} = 0.99$ and from the absorbance change in the initial stage of the photoirradiation.

Figure 14 shows the effect of the alkyl spacer length in 4-methoxy-4′-alkoxyazobenzenes (1ABn) on the rate of the phase transition of 5CB. It seems likely that an optimum spacer length for the photo-induced phase transition may exist. Table III shows τ^{-1} and the efficiency of various azobenzene derivatives for the phase transition. The efficiency is defined as the amount of the isomerized azobenzene derivatives required to induce the $N \rightarrow I$ transition of the mixtures. Mesogenic azobenzene derivatives were found to be more effective trigger molecules than the others. In fact, the efficiency of 1AB8, 8AB8 and BMAB is less than 30% and that of the others is more than 30%.

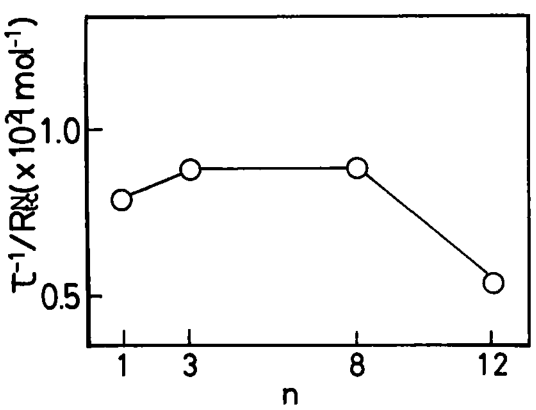


FIGURE 14 Effect of the alkyl spacer length in 1ABn on the rates of phase transition of 5CB.

CONCLUSION

Three kinds of factors affecting the photo-induced phase transition behaviors have been explored in our study. One is the physical environmental effects: temperature, cell gap and concentration of the photoresponsive molecules doped in LCs. Although these factors cannot affect the mode of interaction between the photore-

TABLE III

Photoinduced phase transition behaviors of 5CB doped with 1 mol% of various azobenzene derivatives at T/T_{NI} of 0.99

Abbrev.	τ^{-1} (min^{-1})	efficiency (%)
BMAB	1.01	24.0
1AB1	0.65	34.4
1AB3	0.69	33.3
1AB8	0.78	29.5
1AB12	0.51	38.1
3AB3	0.72	30.5
8AB8	0.68	28.8

sponsive molecule and matrix mesogens, the rate of the phase transition increased with increasing temperature and decreasing the cell gap. Therefore we should elucidate carefully the effects of the interaction between the photoresponsive molecule and the matrix mesogen on the photo-induced phase transition.

Secondly, the intermolecular interaction between the mesogens was found to be crucial to the phase transition. The LC forming force, as a result of the interaction, is reflected by such thermodynamic properties of the LCs as T_{NI} and ΔS. A larger perturbation was required to induce the phase transition of an LC matrix with higher T_{NI} or higher ΔS.

The last important factor was the affinity of photoresponsive molecules with matrix mesogens. It seems likely that an optimum spacer length for the photo-induced phase transition may exist. Furthermore, mesogenic azobenzenes induced the phase transition effectively. The results obtained in the present study enable us to design highly efficient photoresponsive molecules for the photo-induced phase transition of LC systems.

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