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Dynamics of Photochemical Phase Transition of Guest/Host Liquid Crystals with an Azobenzene Derivative as a Photoresponsive Chromophore

Jeong-Hee Sung, Shigenobu Hirano, Osamu Tsutsumi, Akihiko Kanazawa,†
Takeshi Shiono, and Tomiki Ikeda*

*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku,
Yokohama 226-8503, Japan*

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The dynamics of the photochemical phase transition process of guest/host liquid crystals (LCs) containing an azobenzene derivative as a photosensitive chromophore was studied. We proposed a model for the photochemical phase transition of the guest/host LCs and simulated the change in transmittance through LCs due to the phase transition on the basis of this model. Upon irradiation at 366 nm, the cis isomer was generated randomly in the irradiated site, and then the transmittance of the probe light was slightly decreased because of the disturbance of the alignment of the nematic (N) phase by the cis isomers. Upon further irradiation, the N-to-isotropic (I) phase transition took place in local domains, and the transmittance of the probe light decreased with the growth of these local I domains. In the simulations, three factors were found to affect significantly the dynamics of the photochemical phase transition and the change in transmittance of light: the number of I domains formed by irradiation, the growth rate of the I domains, and the threshold size of the I domains detected with the probe light.

Introduction

Liquid crystals (LCs) have been explored as photonic materials because they exhibited a large optical anisotropy that can be controlled by changing the alignment of LC molecules. Photoresponsive LC systems, therefore, are currently of interest in view of their applications as optical-switching and image-storing materials.[1−10]

We have reported that the photochemical nematic (N)-to-isotropic (I) phase transition of LCs can be induced by the photoisomerization of photochromic azo dyes.[10−12] The working principle of the photochemical phase transition is based on the change in the molecular shape of the photochromic guest molecules. For instance, the trans form of the azobenzene derivatives stabilizes the LC phase, because its molecular shape (rodlike) is similar to that of the host LC molecules. On the other hand, the cis isomer destabilizes the LC phase because its molecular shape is bent. Consequently, trans−cis photoisomerization of the guest azobenzene derivatives lowers the N-to-I phase transition temperature (T_{NI}).[10] If the system is held at a temperature between the T_{NI} of the trans isomer and the T_{NI} of the cis isomer and irradiated to induce the trans−cis photoisomerization, T_{NI} is gradually lowered with the accumulation of the cis isomer.[13] When T_{NI} falls below the irradiation temperature, the orientational relaxation of the mesogens from the LC state to the I state takes place, and the N-to-I phase transition is induced isothermally. In this (guest/host) system, the photochromic guest molecules act as a molecular switch driven by photons. We can assume that the principle of this phenomenon is the

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* To whom correspondence should be addressed. Tel.: 045-924-5240. Fax: 045-924-5275. E-mail: tikeda@res.titech.ac.jp. URL: http://www.res.titech.ac.jp/polymer/.

† Present address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan.

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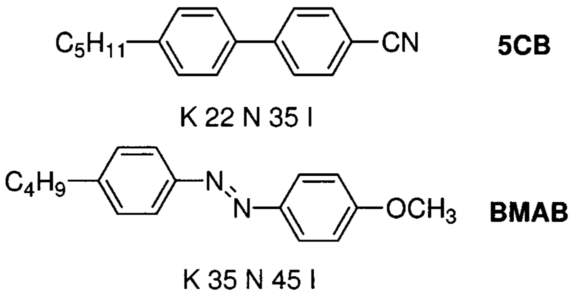

Figure 1. Chemical structures of the azobenzene derivative and the host liquid crystal used in this study.

change in structure of the whole molecular assembly induced by a small amount of the molecular switch incorporated into the system.

Because the photochemical phase transition of the LCs results in a change in the refractive indices and birefringences of materials, we can switch the transmittance of light with another light.[8-10] Thus, the guest/host LCs are applicable as optical-switching materials.[14-16] However, the interpretation of the photochemical phase transition mentioned above has been based on the static consideration in the photostationary state, and we have not fully understood the dynamics of the photochemical phase transition. To understand the optical-switching behavior, we need to reveal the dynamics of the photochemical phase transition of LC systems and the relationship between the phase transition and the change in the transmittance of light through LC materials. We consider that they can provide us with a key to the design of high-performance photonic materials. In this article, therefore, we studied the dynamic process of the photochemical phase transition of guest/host LCs with an azobenzene derivative as a photoresponsive chromophore. We proposed a model of the photochemical phase transition based on the trans−cis photoisomerization process of the azobenzene and the relaxation process of the mesogens and analyzed the dynamics of the change in light transmittance on the basis of this model.

Experimental Section

Materials. The structures of the host LC and the photoresponsive chromophore used in this study are shown in Figure 1. 4-Butyl-4′-methoxyazobenzene (BMAB) was synthesized as reported previously.[8a] 4-Cyano-4′-pentylbiphenyl (5CB) was obtained from Merck Ltd. and used as a photochemically inert host LC without further purification. The phase structures and phase transition temperatures of these compounds are also indicated in Figure 1.

Characterization of the LCs. LC behavior was examined on an Olympus model BH-2 polarizing microscope equipped with a Mettler hot-stage (models FP-90 and FP-82). The thermotropic properties of the LCs were determined with a differential scanning calorimeter (DSC, Seiko I&E SSC-5200 and DSC220C) at a heating rate of 1 °C/min. At least three scans were performed for each sample to verify reproducibility. The photoisomerization behavior of BMAB was observed with a UV−vis absorption spectrometer (JASCO, V-550).

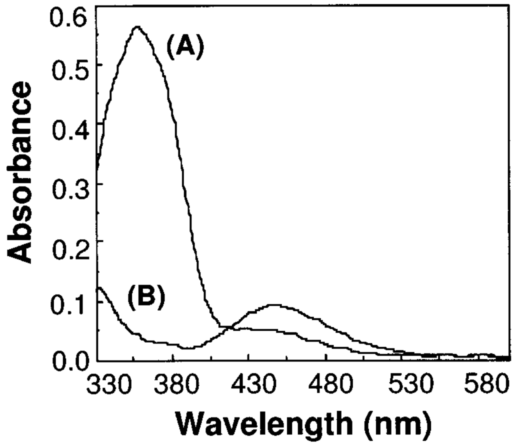

Figure 2. Absorption spectra of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) in a glass cell. (A) Before irradiation, (B) after irradiation at 366 nm for 60 s. The sample thickness was 2 μm.

Photochemical Phase Transition Behavior. BMAB and 5CB were dissolved separately in dichloromethane (spectroscopic grade), and the solutions were mixed together at the desired ratio. After the solvent was removed completely under vacuum, the LC mixture was inserted into a glass cell (cell gap = 2 μm) with a polyimide alignment layer. The samples were irradiated at 366 nm (85 μW/cm^2) with a 500-W high-pressure mercury lamp through glass filters (Toshiba, UV-D36C + UV-35 + IRA-25). The intensity of the probe light (NEC, GLG5370 He−Ne laser, 633 nm, 1 mW) transmitted through a pair of crossed polarizers between which the sample had been placed was measured with a photodiode.

Results and Discussion

Characterization of the Azobenzene LCs. The trans form of the azobenzene LCs showed absorption maxima at ~360 nm due to the $\pi-\pi^*$ transition and at ~450 nm due to the $n-\pi^*$ transition in 5CB (Figure 2). Irradiation at 366 nm induced a decrease in the $\pi-\pi^*$ band and an increase in the $n-\pi^*$ band. This indicates that the trans−cis photoisomerization of the azobenzene takes place in the N phase upon irradiation. When the irradiated sample was kept in the dark at room temperature for 1 day, the absorbance was restored because of cis−trans thermal back-isomerization.

Figure 3 shows the phase diagram of mixtures of BMAB and 5CB as a function of the mole fraction of BMAB. After the mixture reaches a minimum value of T_{NI} at a BMAB concentration of 1 mol %, T_{NI} increases gradually with mole fraction of BMAB. That is, the LC phase of the mixtures is stabilized when BMAB is doped at a concentration higher than 1 mol %.

Photochemical Phase Transition Behavior of the BMAB/5CB Mixture. We observed the photochemical phase transition behavior of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) at 32 °C during photoirradiation at 366 nm (85 μW/cm^2) with the polarizing microscope (Figure 4). Before irradiation, a homogeneous bright view was observed in the polarizing micrograph (Figure 4A), meaning that the sample exhibited a homogeneously aligned N phase. This homogeneous N phase remained unchanged for ~80 s of irradiation. After irradiation for >80 s, dark spots appeared in the N phase, and they developed quickly (Figure 4C). The formation of the dark spots indicates that the photochemical N-to-I phase transition has occurred in local

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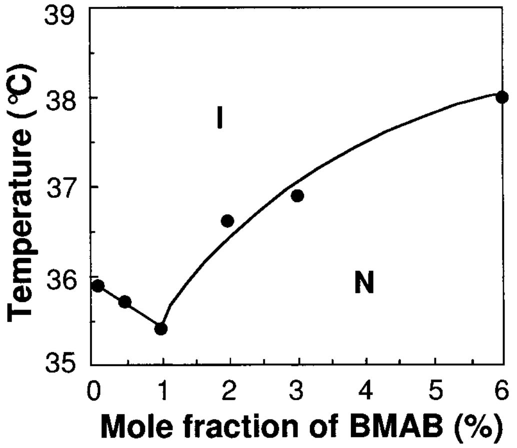

Figure 3. Phase diagram of the BMAB/5CB mixture as a function of the concentration of doped BMAB. Abbreviations: N, nematic; I, isotropic.

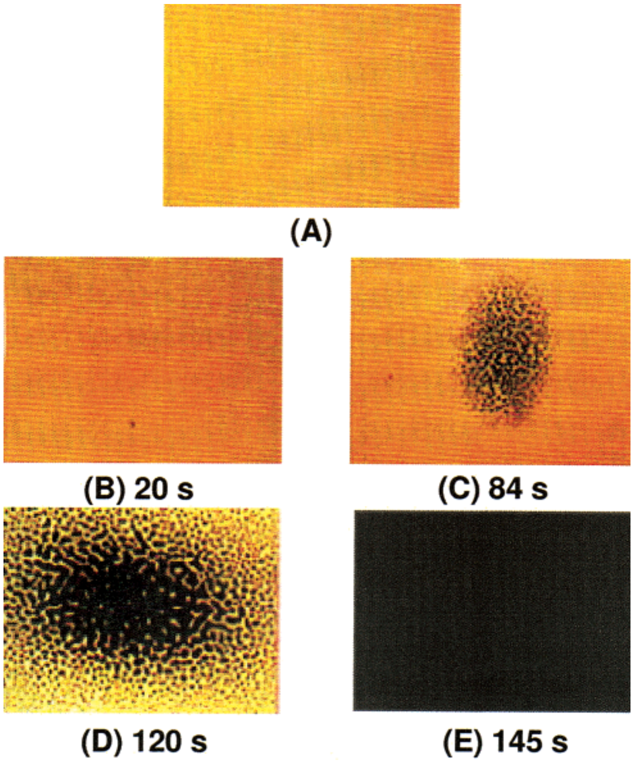

Figure 4. Optical textures observed during photochemical phase transition of the BMAB/5CB mixture ([BMAB] = 3.0 mol %). (A) Before irradiation, (B–E) after irradiation at 366 nm. Irradiation times are indicated in the figure.

regions. Upon further irradiation, the number and size of the I domains increased (Figure 4D), and eventually the N-to-I phase transition took place throughout the whole irradiated area (Figure 4E).

To evaluate the dynamics of the photochemical phase transition quantitatively, we measured the change in transmittance of light at 633 nm through crossed polarizers between which the sample had been placed (Figure 5). The transmittance of the probe light depends on the molecular alignment of the mesogens. When the mesogens are aligned in the N phase, the probe light can be transmitted through the crossed polarizers because of the birefringence of the sample. When the alignment of the mesogens becomes random (I phase), however, no transmittance of the probe light can be observed. Therefore, the dynamic process of the photochemical phase transition (orientational relaxation of the mesogens) can be evaluated by observing the change in transmittance of the probe light.

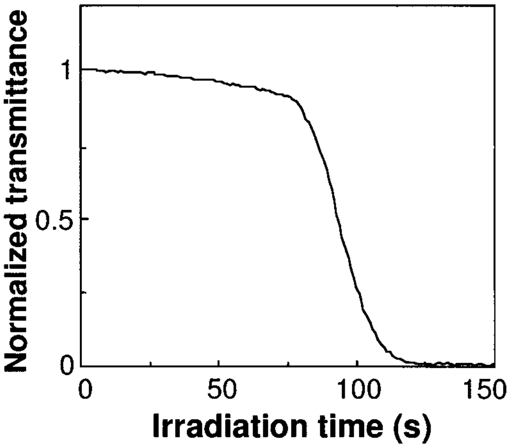

Figure 5. Change in normalized transmittance of the probe light upon photoirradiation of the BMAB/5CB mixture ([BMAB] = 3.0 mol %). Photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

As shown in Figure 5, before irradiation, the probe light could transmit through the crossed polarizers because of the birefringence of the sample. Upon irradiation at 366 nm (85 μW/cm^2), the transmittance of the probe light was scarcely changed for 75 s, and then it decreased steeply. The transmittance vanished completely at the irradiation time of 128 s, indicating that the photochemical phase transition in this mixture had completely taken place at this time.

Model of the Photochemical Phase Transition Process. From these results, we assumed a model of the photochemical phase transition process in the guest/host system (Figure 6). This model is composed of the following sequence of the events: In an early stage of the photochemical phase transition, the cis isomer, which plays a role as a nucleus of the I phase, is generated randomly in the irradiated site (Figure 6B). At this stage, the concentration of the cis isomer is not sufficient to induce the N-to-I phase transition over the whole irradiated area. The photochemical phase transition, thus, takes place in local domains around the cis isomers, while the domains containing no cis isomer still remain in the N phase. Just after photoirradiation, this local phase transition could be directly observed by polarizing microscopy (Figure 4B). Upon irradiation at 366 nm, the I domain grows (Figure 6C), and the transmittance of the probe light decreases with the growth of the I domain, because the probe light cannot transmit through the I domain under this experimental setup. We, therefore, can assume that the transmittance of the probe light depends on the area of the N domain. Eventually, the N-to-I phase transition is induced throughout the whole irradiated area (Figure 6E), and the transmittance of the probe light decays completely.

To examine whether this model is appropriate, we used it to simulate the change in the transmittance of the probe light as a function of time. When both areas of the N and the I domains are obtained at a prescribed time interval, we can simulate the change in the transmittance of the probe light during the photochemical phase transition. In the simulation of the growth of

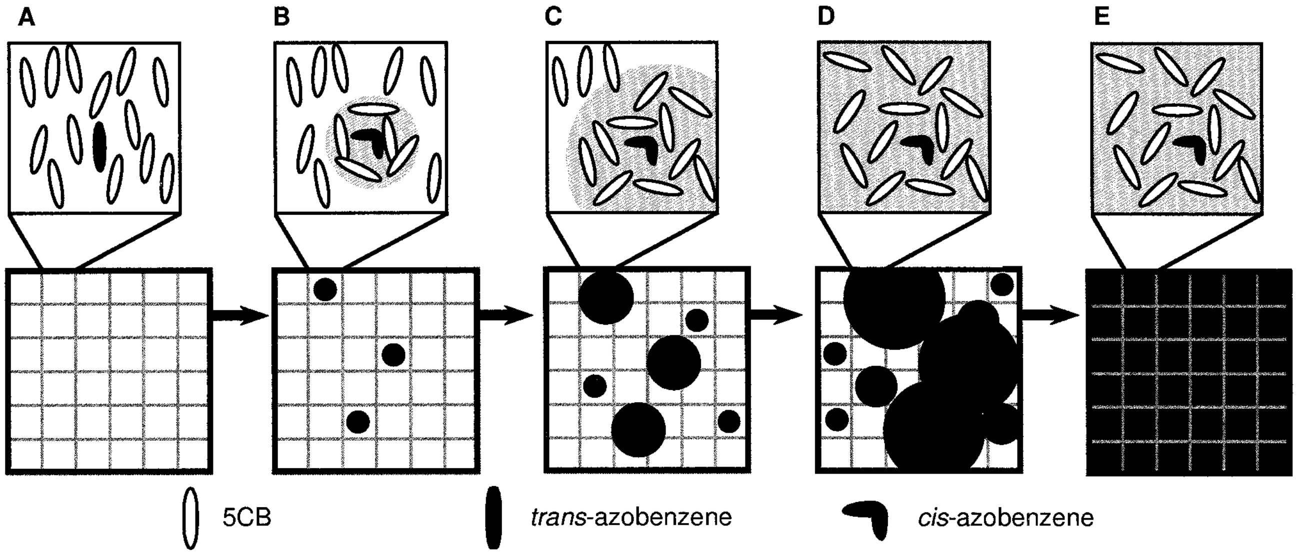

Figure 6. Schematic illustration of a model of the photochemical N-to-I phase transition. Expansion of the local domain is shown in the top of the figure. (A) Before irradiation, the LC mixture shows a homogeneously aligned N phase. (B) Just after irradiation, trans−cis photoisomerization of BMAB occurs, and a local N-to-I phase transition takes place around the cis isomer. (C, D) The I domain grows by the diffusion of the I phase. (E) Upon further irradiation, the I phase eventually propagates throughout the entire irradiated area.

the I domain, we need to consider two parameters: the rate of formation of cis isomers and the growth rate of an I domain. Here, we assumed that the cis isomers act as the nucleus of an I domain as mentioned before, so that the number of the I domains can be estimated by the amount of the cis isomer, which can be determined directly by absorption spectroscopy.[17] In this study, we estimated the energy absorbed by the system by the absorbance of the sample and the irradiated light intensity, and we obtained the amount of the cis isomer from the absorbed energy and the quantum yield of the trans−cis photoisomerization. In the simulation, therefore, only the growth rate of the I domain was used as a variable parameter. To simplify the calculation, we assumed that the shape of the cross section of the probe light is a square with a size of 40 μm × 40 μm and that the I domain is a circle with a radius of $r(t)$ that is a function of irradiation time. The normalized transmittance [$T(t)$] of the probe light is expressed in terms of the normalized total area (A) of the I domains as

$$T(t) = 1 - \frac{A}{(40 \times 10^3)^2} = 1 - \frac{\sum \pi [r_i(t)]^2}{1.6 \times 10^9} \qquad (1)$$

If the value of $r(t)$ can be described properly as a function of irradiation time, then the dynamics of the photochemical phase transition can be simulated appropriately. Here, we define the quantity $\mathrm{d}r(t)/\mathrm{d}t$ as the growth rate of the I domain. By analogy with the diffusion equation, we can assume that $r(t)$ is a first-order function of irradiation time, which means that the growth rate of the I domain [$\mathrm{d}r(t)/\mathrm{d}t$] is constant throughout the photochemical phase transition.[18] Figure 7 shows the results of the simulation for the response time of the photochemical N-to-I phase transition of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) as a function of the growth rate of the I domains. The response time was defined as the time necessary for the transmittance to decay completely to 0. An increase in the growth rate improved the response time of the photochemical phase transition. In agreement with the experimental results shown in Figure 5, the transmittance of the probe light decayed completely at 128 s. From a comparison of the experimental observations and the results of the simulation, we obtained a value of 1.5 nm/s as the growth rate of the I domain. Furthermore, we simulated the response time with this growth rate as a function of the concentration of the cis isomer, namely, the light intensity. When we employed 1.5 nm/s as the fixed growth rate of the I domain, the simulation always agreed with the observations (Table 1).

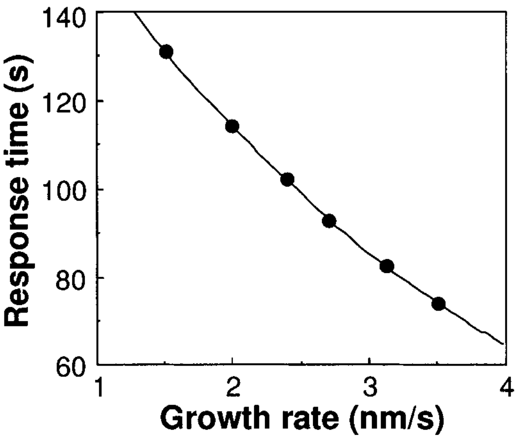

Figure 7. Simulation of the response time of the photochemical N-to-I phase transition of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) as a function of the growth rate of the I domain.

The growth rate of the I domain can be related to the diffusion of cis isomers and host LC molecules. Hara et al. reported the diffusion coefficient of the cis isomer of an azobenzene derivative (methyl red, MR) in NLC.[19] The diffusion coefficients of cis-MR parallel and per-

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[17] Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1993**, *26*, 151.

[18] When other functions such as quadratic functions and exponential functions were employed, we could not obtain good fits to the experimental results.

Table 1. Response Time of the Photochemical N-to-I Phase Transition as a Function of Light Intensity[a]

light intensity (μW/cm^2)	response time (s)	
	observed	simulated
170	48	46
85	128	131
40	532	542

[a] Growth rate of the I domain was 1.5 nm/s.

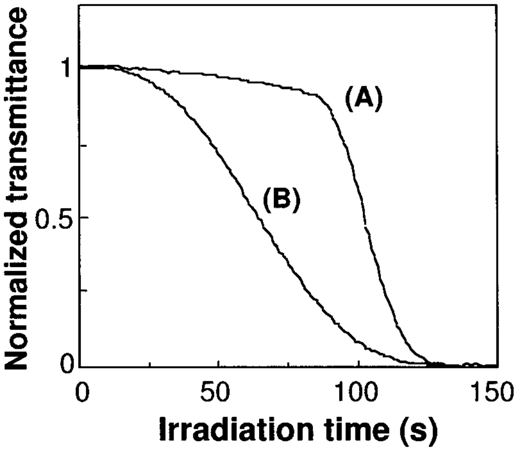

Figure 8. Change in normalized transmittance of the probe light upon photoirradiation of BMAB/5CB ([BMAB] = 3.0 mol %). (A) Observed, (B) simulated. In the observations, photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

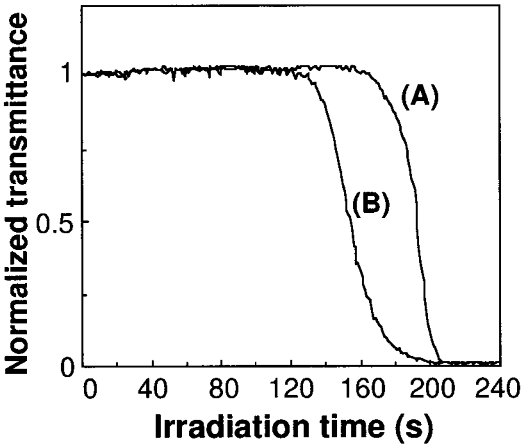

Figure 9. Photoinduced change in the normalized transmittance of the probe light with different wavelength in BMAB/5CB ([BMAB] = 3.0 mol %). (A) At 830 nm from a diode laser, (B) at 633 nm from a He−Ne laser. Photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

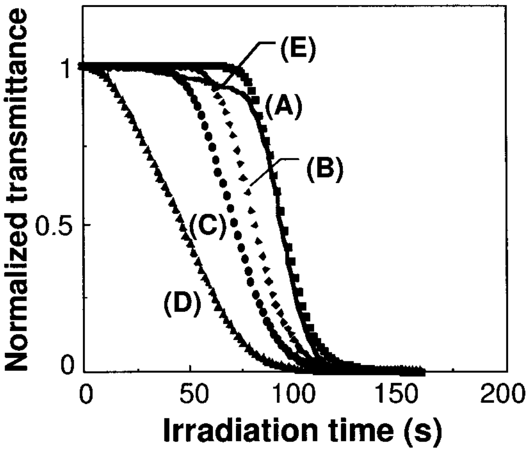

Figure 10. Simulation of the change in the normalized transmittance of the probe light as a function of the threshold size of the I domain. (A) L = 400 nm, (B) L = 200 nm, (C) L = 100 nm, (D) L = 0 nm, (E) observed. Photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

pendicular to the optic axis are 3×10^{-11} and 2×10^{-11} m^2/s, respectively. Furthermore, those of a NLC (methoxybenzylidene butylaniline, MBBA) are 7×10^{-11} m^2/s (parallel) and 5×10^{-11} m^2/s (perpendicular). From those results, the root-mean-square diffusion velocity of the cis isomer can be estimated as 8 μm/s for parallel and 6 μm/s for perpendicular motion, and those of the NLC are 12 μm/s (parallel) and 10 μm/s (perpendicular). These values are larger than the growth rate of the I phase (1.5 nm/s) by a factor of approximately 10^3. This means that the molecular diffusion is much faster than the growth of the I phase and that a sufficient number of the cis isomers diffuse into the I domain.

Effect of the Size of the I Domains on the Change in Transmittance. As shown in Figure 8, the simulated profile did not agree completely with the observed results; in the observed profile (Figure 8A), the transmittance of the probe light did not change until 75 s after irradiation, whereas in the simulation (Figure 8B), it decreased gradually even in the initial stages. We assumed that the probe light cannot recognize the I domain when the size of the I domain is too small (smaller than the wavelength). To confirm this assumption, we observed the photochemical phase transition behavior using probe lights with different wavelengths (Figure 9). When we used a probe light at 833 nm from a diode laser, the transmittance of the probe light did not change until 170 s after irradiation (Figure 9A). These results suggest that there is a threshold size of the I domain that depends on the wavelength of the probe light and that the probe light cannot recognize the I phase when the I domain is smaller than this threshold size. The size of the I domain, therefore, is also an important factor in analyzing the photochemical phase transition of LCs, and we employed it as the third parameter in our simulations.

Figure 10 shows the change in the transmittance of the probe light simulated with various minimum domain sizes. We employed a square domain with a length of L (L = 0, 100, 200, and 400 nm) as the minimum domain that can be detected by the probe light, and we assumed that the transmittance of each domain becomes 0 when the I domain has completely covered the area expressed by $L \times L$ (nm^2). When the minimum size of the I domain was 400 nm × 400 nm, we could obtain a profile similar to that observed. In the initial stages of the phase transition, however, the simulated profile still did not agree completely with the observations (Figure 10E).

Effect of the Change in the Order Parameter of the N Phase. In the model, it was assumed that the transmittance of the probe light in the N domains is not affected by the cis isomers generated in those areas

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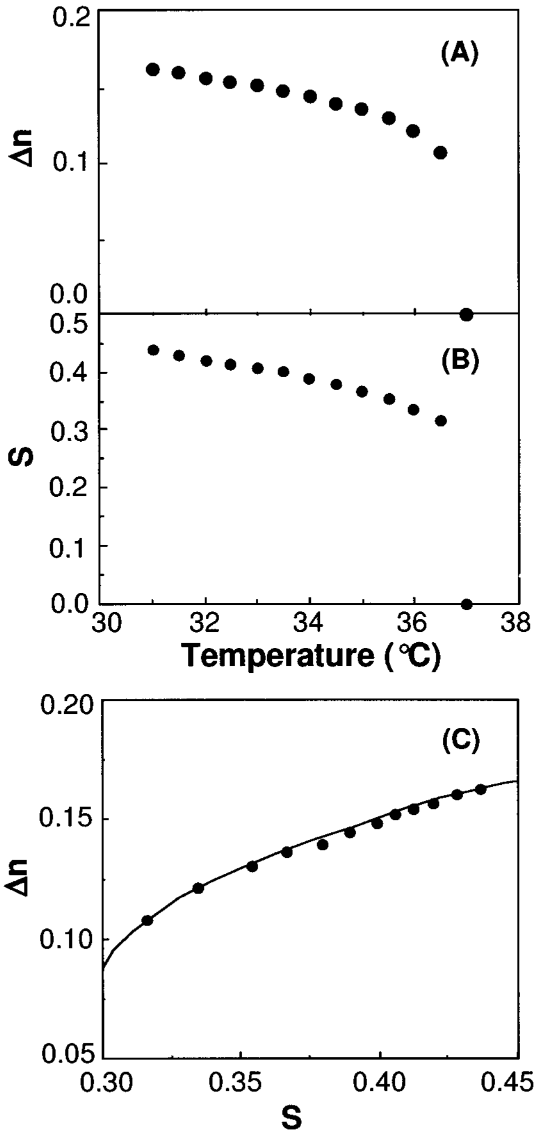

Figure 11. Changes in (A) Δn and (B) S of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) as functions of temperature and (C) relationship between S and Δn in a thermal N-to-I phase transition.

by irradiation. However, *cis*-azobenzene disturbs the alignment of the LC molecules, and the orientational order of the N phase decreases upon formation of the cis isomers. That is, the transmittance of the probe light in the N domains depends on the concentration of cis isomers.

The intensity of transmitted light (I) through a pair of crossed polarizers is given by

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

where Δn is the birefringence of the LCs, d is the thickness of the LC sample, λ is the wavelength of the probe light, and I_0 is the intensity of the incident light. When the Δn value of the BMAB/5CB mixture is given as a function of irradiation time, the transmittance, I/I_0, can be determined using eq 2.

To simulate the temporal change of I using eq 2, we need to obtain the change in Δn of the LCs resulting from the formation of cis isomer as a function of irradiation time. However, it is difficult to measure the change in Δn as a function of irradiation time directly. We obtained the relationship between the change in Δn and the irradiation time as follows: First, we measured the changes in the order parameter (S) and Δn of the mixture as functions of temperature, as shown in Figure 11A and B. The S can be defined by eq 3 in the case where the transition moment is oriented parallel to the molecular long axis[20]

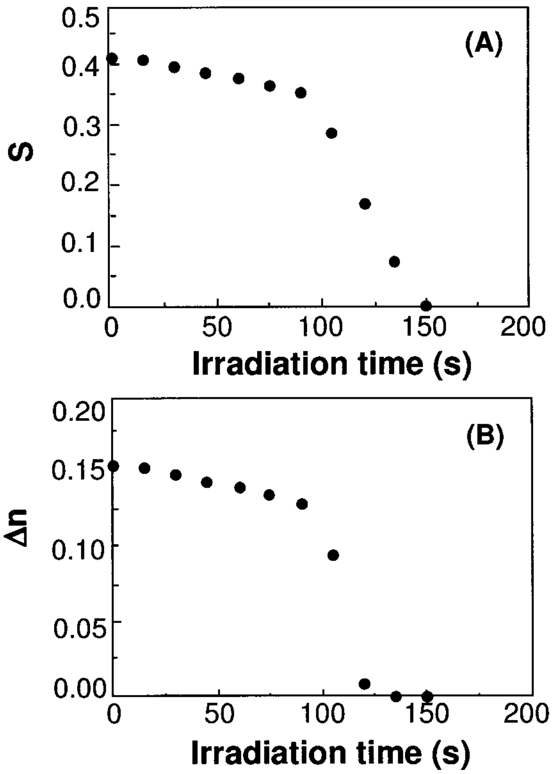

Figure 12. (A) Change in S of the BMAB/5CB mixture ([BMAB] = 3.0 mol %) upon photoirradiation and (B) change in Δn obtained from the S-Δn relationship as a function of irradiation time. Photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

$$S = \frac{R - 1}{R + 2} \tag{3}$$

where R is the dichroic ratio determined by polarized absorption spectroscopy. For a symmetrical system, R can be given by

$$R = \frac{A_{\parallel}}{A_{\perp}} \tag{4}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances at 366 nm parallel and perpendicular to the optical axis of the molecule, respectively. From Figure 11A and B, we obtained the relationship between S and Δn in a thermal N-to-I phase transition of this mixture (Figure 11C).

Next, the change in S of the mixtures upon photoirradiation was measured by polarized absorption spectroscopy (Figure 12A). The change in Δn due to the formation of *cis*-azobenzene could then be obtained from the S−Δn relationship as a function of irradiation time (Figure 12B).

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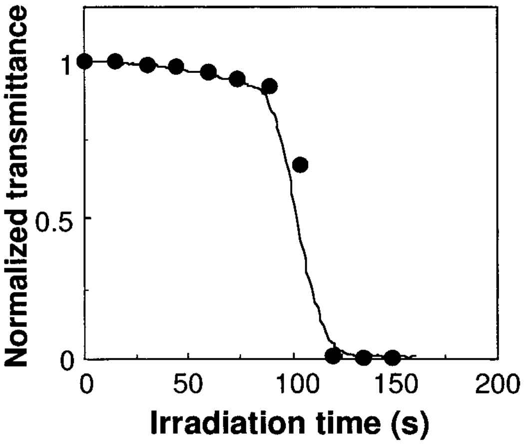

Figure 13. Change in normalized transmittance of the probe light upon photoirradiation of the BMAB/5CB mixture ([BMAB] = 3.0 mol %). ●, calculated; solid line, observed. Photoirradiation at 366 nm (85 μW/cm^2) was performed at 32 °C.

When we took into account the change in Δn in the N domains, the simulated profile of the transmittance agreed well with the observations, as shown in Figure 13. This result indicates that the decrease in transmittance in the initial stage results from the decrease in S in the N phase because of the photoisomerization of BMAB.

In the manner mentioned above, we can correlate the dynamic behavior of the photochemical phase transition of binary LC mixtures with the change in transmittance of the probe light. In the initial stages of the photochemical phase transition, the N-to-I phase transition does not take place because of the low concentration of the cis isomer, but the orientational order of the N phase is affected by the cis isomers. Thus, the transmittance of the probe light is slightly decreased by photoirradiation. Upon photoirradiation, the cis isomers accumulate in the N phase, and then the N-to-I phase transition takes place in local domains. Just after the formation of local I domains, however, the size of the I domains is too small to be recognized by the probe light. When the I domains grow large enough (larger than the wavelength of the light), the transmittance decays rapidly. We clarified that, in this stage, three factors are important in the photochemical phase transition process of the guest/host LC systems: (1) the rate of formation of the I domains upon irradiation, (2) the growth rate of the I domains, and (3) the threshold size of the I domains to be recognized by light. When we obtain those factors, we can understand the dynamics of the change in transmittance resulting from the photochemical phase transition clearly.

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