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High-Performance Material for Holographic Gratings by Means of a Photoresponsive Polymer Liquid Crystal Containing a Tolane Moiety with High Birefringence

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ABSTRACT: Formation of intensity gratings was studied with two s-polarized (s+s) writing beams in polymer liquid crystals (PLCs) containing a photochromic moiety (azobenzene) and a mesogenic unit (tolane, **T-AB**; cyanobiphenyl, **CB-AB**) by means of photoinduced change in alignment of PLCs. Remarkable differences were observed between these two PLCs. **T-AB** showed higher values of the diffraction efficiency (η) and a faster response than **CB-AB**. In photoinduced alignment behavior of the PLCs, **T-AB** exhibited a faster change in alignment than **CB-AB** with the value of η about 30% in the Raman−Nath regime and the maximum value for modulation of the refractive index ($\Delta n'$) of about 0.08. It was revealed that η and $\Delta n'$ are dependent on the structure of the mesogenic unit. In addition, we attempted the holographic image storage of three-dimensional (3-D) objects in the **T-AB** films. The 3-D object was reconstructed with high resolution (>5000 lines/mm).

Introduction

Novel materials for optical data storage have become of interest in recent years with a rapid expansion of information technology (IT). Holographic storage has been applied for data storage because the information packing densities can be increased by using three-dimensional (3-D) storage techniques. Holographic storage will enable fast data transfer because writing and reading of data can be carried out simultaneously. Development of holography technology depends on the properties of recording materials. Ideal holographic materials show high diffraction efficiency, high resolution, and high-speed recording.

Polymer liquid crystals (PLCs) are known as high-performance materials for optical storage due to their large optical anisotropy and high stability below glass transition temperature (T_g).[1−10] We previously reported the formation of holographic gratings by means of photochemical phase transition of PLCs containing azobenzene moieties.[2,3] Large modulation of the refractive index was induced by the photochemical phase transition in LCs based on trans−cis photoisomerization of azobenzene molecules.[9,11] The refractive index modulation in PLCs arises from difference in the refractive index between a nematic (N) phase and an isotropic (I) phase ($|n_e - n|$ or $|n_o - n|$), where n_e and n_o are the refractive index of LCs for an extraordinary ray and an ordinary ray, respectively, and n is the index of an I phase. To obtain a larger modulation of the refractive index in PLCs, $|n_e - n_o|$ should be used in place of $|n_e$ (or n_o) $- n|$. The difference $|n_e - n_o|$ corresponds to birefringence (Δn) of LC molecules. We previously studied the formation of refractive index (birefringence) gratings by means of photoinduced change in alignment of PLCs containing azobenzene moieties.[12] The diffraction efficiency (η) and the modulation of the refractive index ($\Delta n'$) were not very high (6% and 0.04, respectively) on the grating formation. However, it is expected that a further enhancement of these values can be achieved by molecular design of PLCs. One approach is to employ PLCs with a high value of Δn. In other words, a high value of η can be obtained with a slight change in alignment of mesogens when PLCs with a high value of Δn are used.

The Δn of LCs is mainly determined by π-electron conjugation, molecular shape, and order parameter. Thus, a more linearly conjugated LC would exhibit a larger optical anisotropy. Diphenylacetylene LC compounds (tolane derivatives) have been widely studied as low-molar-mass LCs with high Δn and low viscosity.[13] For LC displays, high Δn and low viscosity are very useful to shorten a response time through thinner cell gap requirement. Therefore, tolane LC compounds have been used to achieve a quick response in LC displays. Percec et al. and Hsu et al. reported new tolane-based LCs by using a Pd(0)/Cu(I)-catalyzed coupling reaction.[14−16]

In this paper, we studied the formation of holographic gratings in a PLC with an azobenzene moiety (photoresponsive unit) and a tolane moiety (mesogenic unit) in the side chain. We investigated the effect of Δn of PLCs on the intensity grating under an (s+s) polarization condition. The aims of this work are to enhance the values of η and $\Delta n'$ from the viewpoints of molecular structure of PLCs and to produce high-performance materials for holographic image storage.

Experimental Section

Materials. Structures of PLCs with an azobenzene moiety as well as their abbreviations used in this study are represented in Figure 1. These polymers were prepared using a procedure similar to the literature.[16,17] Thermodynamic properties and molecular weight of PLCs are shown in Figure 1.

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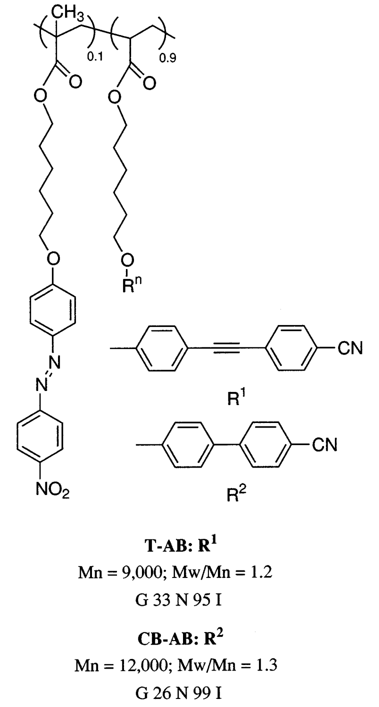

Figure 1. Chemical structures and properties of PLCs used in this study: M_n, number-average molecular weight; M_w, weight-average molecular weight; G, glass; N, nematic; I, isotropic phase.

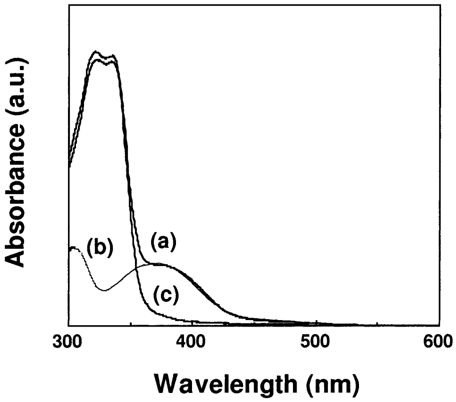

Figure 2. Absorption spectra of **T-AB** (a), **CB-AB** (b), and a tolane monomer (c) in $CHCl_3$.

We examined LC behavior of PLCs as reported previously.[2,3] Absorption spectra were recorded with a UV−vis absorption spectrometer (Japan Spectroscopic Co., V-550). Figure 2 shows absorption spectra of **T-AB** (a), **CB-AB** (b), and a tolane monomer (c) in $CHCl_3$. **T-AB** clearly exhibited two bands at about 330 and 380 nm, stemming from the mesogen and the chromophore, respectively. Homogeneously aligned films with thickness between 600 and 1600 nm were prepared by casting a polymer solution in THF onto glass substrates, which had been coated with poly(vinyl alcohol) and rubbed to align mesogens.

Optical Setup. Formation of gratings in the PLC and photoinduced alignment behavior of PLC were examined by the procedure already reported.[3a] In this study, gratings were written at 488 nm and read out at 633 nm. The reading wavelength has to be located outside the absorption band to avoid a destructive readout of the gratings. Writing beams were two linearly polarized beams from an Ar^+ laser. The direction of the electric field vector of the linearly polarized incident light was parallel to the direction of the uniaxial alignment of mesogens, i.e., s-polarization. The incident angle of the writing beams was fixed at $\theta = 7°$ except for the evaluation of the effect of fringe spacing. η was defined as the ratio of the intensity of the first-order diffraction beam to that of the transmitted beam through the film before irradiation of the writing beams. The photoinduced alignment change of PLCs was investigated as follows. The PLC film placed in a thermostated block was irradiated with linearly polarized light at 488 nm. The direction of polarization of the pumping light was parallel to that of alignment of mesogens. The intensity of the probe light at 633 nm from a He−Ne laser transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode. The optical setup used for the evaluation of switching behavior of a diffraction beam was the same as described above. Turning on and off the writing beams were controlled with a mechanical shutter with a response time of 31.3 ms.

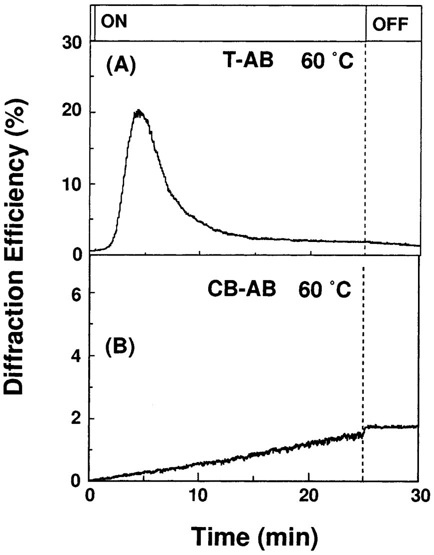

Figure 3. Change in the intensity of diffracted light in the **T-AB** (A) and **CB-AB** (B) films at 60 °C. Film thickness = 1200 nm; light intensity = 120 mW/cm^2.

Atomic Force Microscope (AFM) Measurements. After grating formation, the surface structure of the PLC films was investigated with an AFM (Shimadzu, SPM-9500 J2). Photoirradiation was performed at different temperatures (room temperature and 60 °C) for 10 min. After a grating was recorded at 60 °C, the films were cooled to room temperature, and their surface profiles were observed at room temperature.

Results and Discussion

Grating Formation in PLCs. Figure 3 shows the change in intensity of diffracted light as a function of irradiation time in the **T-AB** (A) and **CB-AB** (B) films (film thickness: 1200 nm). In this case, the grating formation was conducted at 60 °C (N phase), and the intensity of the writing beams was 120 mW/cm^2. In **T-AB**, the value of η showed a maximum at 60 °C: it reached up to 20% after 4 min as shown in Figure 3A. This value is largest and 200 times as large as those reported so far under the (s+s) polarization condition.[18,19] The intensity of the diffracted light increased first with irradiation time, and then it decreased. This behavior may be due to an increase at first, followed by a decrease, of difference in the refractive index between bright and dark areas of the interference patterns. Similar behavior has been already observed when high-intensity writing beams were employed.[2,3,12] In contrast, in the **CB-AB** film, the value of η increased slowly during irradiation of the writing beams at 60 °C as shown in Figure 3B. The time taken to reach a maximum value of η (4%) was about 1 h. We already reported the effect of temperature on the grating formation in

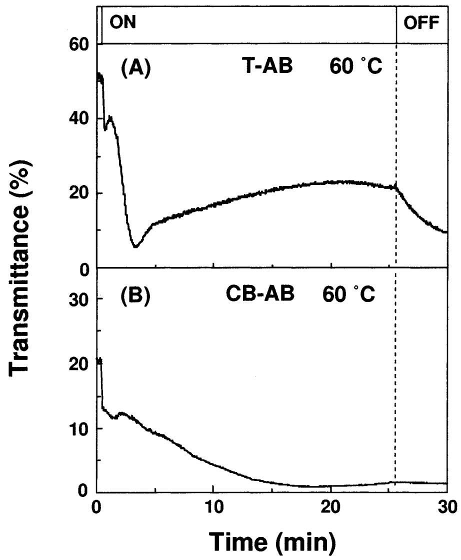

Figure 4. Change in the intensity of probe light in the **T-AB** (A) and **CB-AB** (B) films at 60 °C. Film thickness = 1200 nm; light intensity = 120 mW/cm^2.

CB-AB: the value of η increased with temperature at first and then decreased with temperature, giving a maximum value (6%) at 80 °C in **CB-AB**.[12] This temperature dependence of η has been interpreted as the mobility of mesogens increases with temperature, which results in a faster response with increased η. The decrease in η may be due to disorganization of the phase structure at high temperature.[12]

Photoinduced Alignment Behavior of PLCs. To discuss the formation of gratings in PLCs, it is necessary to explore not only the grating formation behavior but also the photoinduced change in alignment behavior of PLCs. Figure 4 shows the photoinduced alignment in the **T-AB** and **CB-AB** films. The transmittance (T) of probe light passed through a pair of crossed polarizers, with a uniaxially aligned film between them, is defined by eq 1:[20]

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

where d is the film thickness, Δn is the birefringence of PLC films, and λ is the wavelength of the probe light (633 nm). The experimental conditions were the same as those of the preceding section (at 60 °C; light intensity, 120 mW/cm^2). In the initial state, the calculated values of Δn of the PLC films ($d = 1200$ nm) were 0.14 (**T-AB**), and 0.08 (**CB-AB**). The transmittance of the probe light decayed upon irradiation of linearly polarized light, gradually increased, and finally became saturated in **T-AB**. This result indicates that a photoinduced alignment change of the PLC is induced by trans−cis−trans isomerization cycles of the azobenzene moieties.[10,12] On the other hand, in **CB-AB**, the intensity of the probe light decreased slowly during irradiation of pumping light, and no photoinduced alignment change was induced under this experimental condition. This difference may be due to a degree of trans−cis−trans isomerization cycles of the azobenzene moieties. In the **T-AB** film, the photoisomerization cycles of the azobenzene moieties can proceed more effectively than those in **CB-AB** because of low viscosity of mesogens composed of tolane moieties.

Spatial Modulation of Refractive Index. It is obvious that the value of η is greatly enhanced in the PLC containing a tolane moiety. In practical applications, η is a very important factor. So the effect of spatial modulation of the refractive index ($\Delta n'$) on the formation of gratings was explored. The value of η is defined in the Raman−Nath (thin) diffraction regime by eq 2:[21]

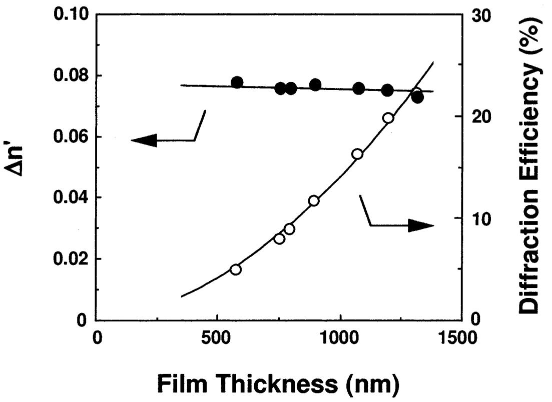

Figure 5. Effect of film thickness on the diffraction efficiency (○) and the modulation of refractive index ($\Delta n'$) (●) in **T-AB** at 60 °C. Photoirradiation was carried out at 488 nm at an incident angle of $\theta = 7°$. Light intensity = 120 mW/cm^2.

$$\eta = (\pi d \Delta n'/\lambda)^2 \tag{2}$$

where d is the film thickness, $\Delta n'$ is the degree of spatial modulation of the refractive index, and λ is the wavelength of the reading beam. Figure 5 shows the effect of the film thickness on the value of η in the **T-AB** film. The value of η increased with increasing the film thickness. The value of $\Delta n'$ was evaluated by eq 2 using the values of η and d with an assumption that the gratings formation in this study is entirely due to refractive index modulation of materials, and the contribution of surface modulation is negligible (see below). The value of $\Delta n'$ was almost constant regardless of the film thickness: 0.08. This value is larger than those reported previously for other holographic materials like photopolymers.[22]

Modulation of Surface Structure. Natansohn et al., Tripathy et al., and others explored the mechanism of surface relief gratings (SRG) on azopolymer films.[18,19,23−27] The behavior of the SRG formation differs according to the polarization configuration of the writing beams.[18,19] Two s-polarized (s+s) configuration produces a very small surface modulation, nearly negligible (< few nanometers), and shows the smallest value of η (<0.1%) due to SRG. In this study, we explored the surface modulation of the **T-AB** films under the (s+s) configuration to discuss the origin of $\Delta n'$. As described above, ideal holographic materials show high diffraction efficiency and high photosensitivity. In the Raman−Nath regime, the theoretical $\eta_{\max}$ is 33.9%.[28] In this study, the value of η approached the maximum value of 33.9% with an increase in the film thickness while the value of $\Delta n'$ remained unchanged. To obtain η values as close as possible to the theoretical $\eta_{\max}$, it would be necessary to use the **T-AB** films with the thickness more than 1500 nm provided that the value of $\Delta n'$ is 0.08. Furthermore, the minimum light intensity required to induce the alignment change in **CB-AB** was 70 mW/cm^2. Considering those factors, we performed the grating formation under different conditions from those of the preceding sections (Figures 3−5). Namely, the film thickness was 1600 nm, which is thicker by 400 nm than before, and the light intensity was 80 mW/cm^2.

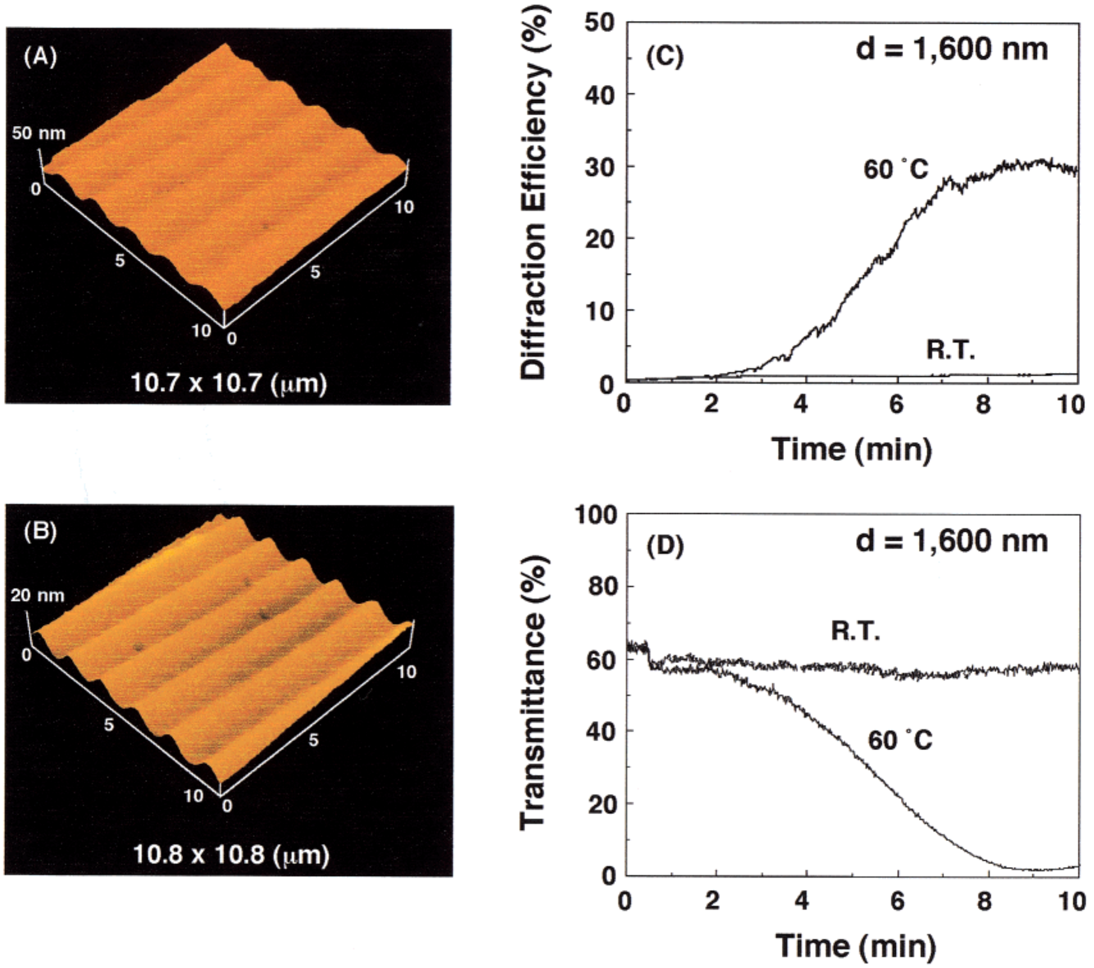

Figure 6. AFM 3-D views of the gratings recorded in an N phase (A) and a glassy state (B) in the **T-AB** film, change in the intensity of diffracted light in the **T-AB** film upon photoirradiation (C), and change in transmittance of probe light in the **T-AB** film (D). AFM observation was carried out at room temperature. Photoirradiation was performed at an incident angle of $\theta = 7°$ ($\Lambda = 2.0$ μm). Film thickness = 1600 nm; light intensity = 80 mW/cm^2.

Two different phases were examined: an N phase at 60 °C and a glassy state at 25 °C. Details of the surface modulation are shown in Figure 6. The periodic structure of the SRG was about 2.0 μm wide in each case while its height was about 12 nm (60 °C, A) and 7 nm (25 °C, B). In the N phase, the value of η was 31% while it was less than 1% in a glassy state (C) under this experimental condition. This difference may arise from the $\Delta n'$ due to the photoinduced alignment change of mesogens in the PLC film. Figure 6D shows the change in transmittance upon photoirradiation at different temperatures. The transmittance little changed at 25 °C, while it gradually decreased and finally reached zero at 60 °C. This means that the birefringence disappeared and a large value of $\Delta n'$, which is necessary to obtain a high value of η, was induced upon photoirradiation. However, the alignment change of mesogens was not completed in this case as is evidenced by the lack of the stationary value of the transmittance seen in Figure 4A. This result indicates that high diffraction efficiency can be achieved with a slight change in alignment of mesogens when PLCs with a high value of birefringence are used.

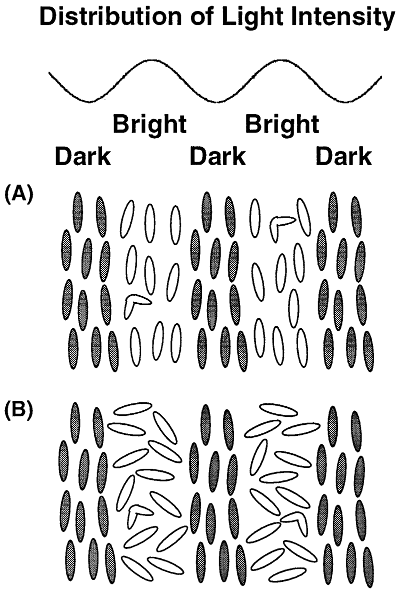

Figure 7. Schematic illustration of a plausible mechanism of the grating formation in a glassy state (25 °C) (A) and in an N phase (60 °C) (B).

The plausible mechanism of the grating formation in **T-AB** is schematically illustrated in Figure 7. At 25 °C (below T_g, A), trans−cis photoisomerization of azobenzene moieties is induced in bright areas of the interference patterns. This photoisomerization results in a periodic change in the refractive index due to the formation of *cis*-azobenzenes, which leads to a slight modulation of the film surface. At 60 °C (N phase, B),

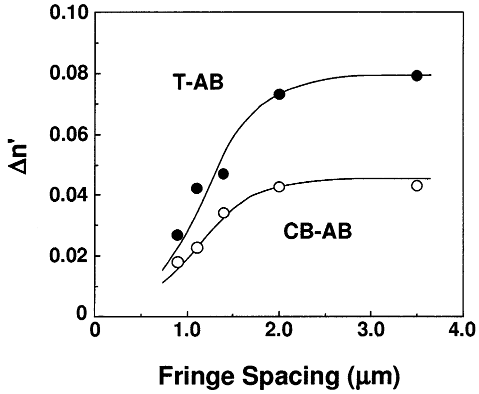

Figure 8. Influence of the fringe spacing on the value of $\Delta n'$ in **T-AB** at 60 °C (●) and **CB-AB** at 80 °C (○). Film thickness = 1200 nm; light intensity = 120 mW/cm^2.

the modulation of the film surface is similarly induced; however, the difference in the refractive index between the bright and dark areas increases because an alignment change of mesogens takes place in the bright areas, leading to a large value of η. In the **CB-AB** films, under the same conditions, the relief height was about 10 nm and the value of η was 2% in an N phase. These differences mainly arise from the photoinduced alignment behavior of mesogens based on trans–cis–trans isomerization cycles of the azobenzene moiety. In any event, the ratio of the height of the relief to the film thickness was very small (less than 1.0%), and the contribution of SRG to the $\Delta n'$ was negligible in the **T-AB** films similarly to the **CB-AB** films.

The effect of the fringe spacing (Λ) on the value of $\Delta n'$ was investigated. By changing the incident angle (θ) of the writing beams from 4° to 16°, Λ was varied from 3.5 to 0.9 μm. Figure 8 shows the dependence of $\Delta n'$ on the value of Λ. Photoirradiation was performed at 60 °C (**T-AB**) and 80 °C (**CB-AB**), at which each film showed a maximum value of η. It was found that the value of $\Delta n'$ was small when the fringe spacing was 0.9 μm in both PLC films. On the other hand, when the Λ was larger than 2.0 μm, the maximum value of $\Delta n'$ reached more than 0.08 in the **T-AB** film. In the **CB-AB** film, the maximum value of $\Delta n'$ was 0.04. This difference could result from the difference in Δn of the mesogenic molecules themselves. In general, the value of Δn of tolane derivatives is larger than that of cyanobiphenyl derivatives, and the value of Δn of **T-AB** is about 1.8 times as large as that of **CB-AB** as described above. Therefore, it is reasonable that the value of $\Delta n'$ of **T-AB** was larger than that of **CB-AB** in the grating formation due to the photoinduced refractive index modulation of PLCs.

Optical Switching Behavior. We have already reported that both holographic data storage and dynamic holography can be achieved in the PLC films.[2,3] However, in the previous studies the performance in the dynamic holography was insufficient: the value of η was on the order of 10^{-3}%, and the response time was several seconds. Therefore, we attempted to improve the dynamic nature of the grating formation using the **T-AB** film with high birefringence and low viscosity. Figure 9 shows the results of the dynamic grating formation (A) and the photoinduced refractive index modulation (B) in the **T-AB** film at 91 °C. Upon irradiation of the writing beams (120 mW/cm^2), the intensity of the diffraction beam increased immediately and attained a maximum value within 50 ms. Furthermore, an increase in the intensity of the diffraction beam and a decrease in transmittance of the probe beam proceeded synchronously. Therefore, the dynamic grating formation could be due to the photoinduced refractive index modulation in the PLC film. When the writing beams were turned off, the diffraction beam rapidly decayed. The decay process of the diffraction light also coincided with the increase in the transmittance, which corresponds to the recovery of the N phase. In this study, the rise and decay times were defined as the time necessary to increase or decrease to 90% or 10% of the maximum intensity, respectively. It was estimated that rise and decay times were about ~30 ms and ~500 ms, respectively. In the decay process, the thermal recovery of the N phase results from two processes: thermal cis–trans isomerization of the azobenzene moieties and reorientation of mesogens. It has been reported that the cis–trans thermal isomerization is the rate-determining step in the thermal recovery of the N phase of azobenzene LCs.[9] The cis–trans thermal isomerization proceeds effectively in the azobenzene with a strong acceptor; thus, the thermal recovery of the N phase occurred very quickly in this system. The other factor of an effective recovery of the N phase is reorientation of mesogens. The mobility of mesogens in the PLCs is correlated to the viscosity of the mesogens. As described above, the

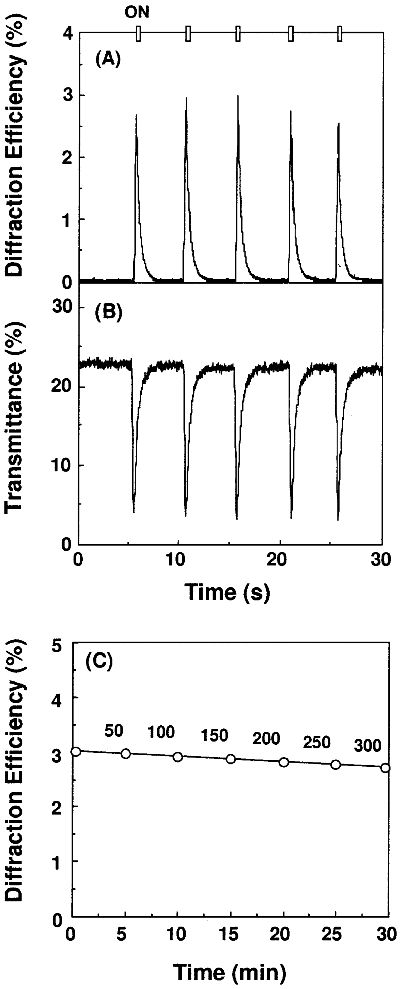

Figure 9. Change in the intensity of probe light for diffraction signal (A), transmittance (B), and stability of optical switching (C). Irradiation was performed at 488 nm at 91 °C for 31.3 ms. The writing beams intersected in the **T-AB** film at an incident angle of $\theta = 7°$. Light intensity = 120 mW/cm^2. Each number in (C) corresponds to the cycles of the laser irradiation.

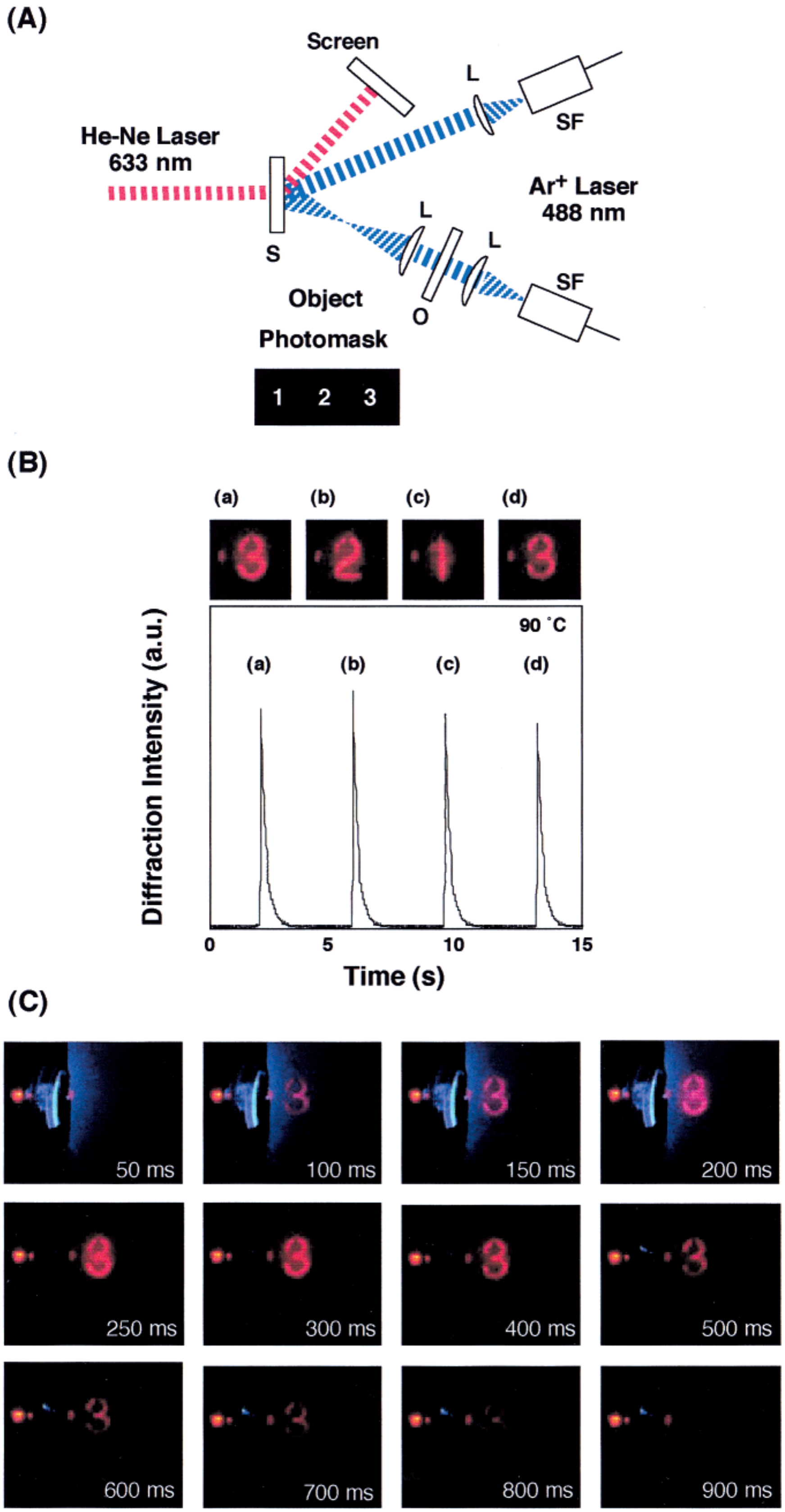

Figure 10. Dynamic control of 2-D holographic images with the **T-AB** film: (A) optical setup; (B) change in the diffraction intensity; (C) images on the screen taken at the time indicated in each picture.

viscosity of **T-AB** is lowered by introduction of the tolane unit. It is reasonable, therefore, that the reorientation of the mesogens in **T-AB** takes place effectively. In this study, despite the low temperature, the response times are almost the same as those obtained at high temperature.[3c] This result indicates that the **T-AB** film is more effective than other PLC films. Furthermore, these cycles could be repeated without any significant change in the value of $\eta_{\max}$ and the sensitivity of the material during the experiment (Figure 9C).

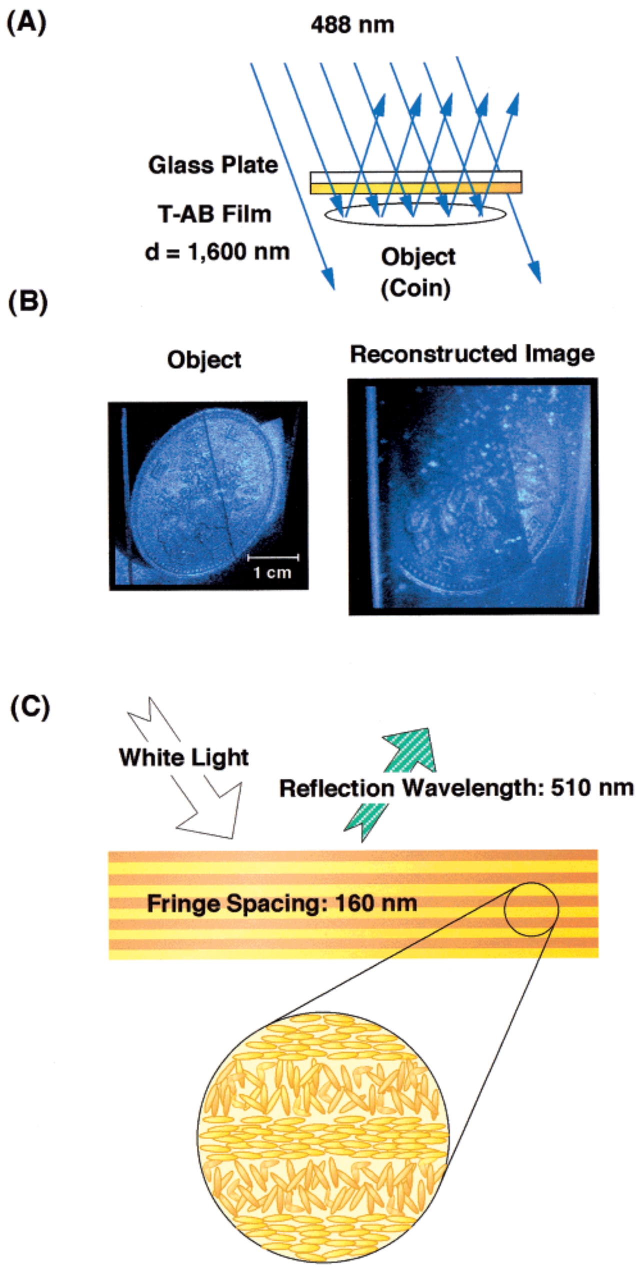

Figure 11. Optical setup for holographic 3-D image storage by reflection-type geometry (A), reconstructed image from the hologram stored in the **T-AB** film (B), and a plausible structure of the reflection-type grating (C). The hologram was reconstructed by the same setup without the object.

We attempted the dynamic control of the holographic image storage in the PLC films. A photomask with figures was employed as an object (Figure 10A). The image storage was conducted at 90 °C. It was found that the holographic image was stored, reconstructed, and erased within 1 s (Figure 10B,C). This fact clearly indicates that the dynamic control of the image storage is possible using the present PLC film.

Holographic Image Storage. On the basis of these results, we attempted holographic image storage of three-dimensional (3-D) objects in the **T-AB** film with a reflection-type optical setup. Generally, reflection holograms are characterized by a higher spatial frequency (>5000 lines/mm) than transmission-type holograms (1500 lines/mm) since they are recorded with interference fringes in the thickness direction. The optical setup used is shown in Figure 11A. We employed a coin shown in Figure 11B as an object. The intensity of the writing beams was 100 mW/cm^2. Figure 11B also shows the reconstructed image. It is evident that the object was reconstructed with high resolution (>5000 lines/mm) in the **T-AB** film. In the reflection holograms, the interference patterns are formed parallel to the sample film and the glass substrate. The SRG was not observed by polarizing microscopy and AFM measurements. The mechanism of the formation of the reflection-type gratings in the PLC film is schematically illustrated in Figure 11C. Just after irradiation, an alignment change is induced by isomerization cycles of azobenzene moieties in bright areas of the interference patterns. This behavior results in the generation of reflection light with a periodic change in the refractive index. The recording and erasure of images were reversible by controlling temperature. The stored image remained unchanged after 2 years when the films were preserved at room temperature.

Conclusion

In summary, we explored the formation of holographic gratings in a PLC containing a tolane moiety with high Δn. It was found that the grating formation is strongly affected by the structure of the mesogenic unit. The PLC with a tolane moiety showed a faster response for the change in the diffraction intensity than the analogue with a cyanobiphenyl unit. This behavior is due to the photoinduced alignment change of mesogens in PLCs, which is based on the photoisomerization cycles of the azobenzene moiety. The effect of Δn of PLCs on the formation of gratings indicates that a considerable enhancement of η can be achieved by using a PLC with a tolane moiety. Furthermore, η and $\Delta n'$ showed the largest values of 31% and 0.08, respectively, in the (s+s) polarization configuration. These values are equal to or larger than those under other polarization conditions. In addition, we could perform a rapid switching of diffracted light and the holographic 3-D image storage. We believe that these results will contribute to the development of various holographic applications such as optical data storage and 3-D display.

References and Notes

(1) (a) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 59. (b) Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 467. (c) Eich, M.; Wendorff, J. H. *J. Opt. Soc. Am. B* **1990**, *7*, 1428. (d) Anderle, K.; Wendorff, J. H. *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 51.

(2) (a) Hasegawa, M.; Yamamoto, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Adv. Mater.* **1999**, *11*, 675. (b) Hasegawa, M.; Yamamoto, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **1999**, *11*, 2745. (c) Hasegawa, M.; Yamamoto, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Mater. Chem.* **1999**, *9*, 2765.

(3) (a) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **1999**, *103*, 9873. (b) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Mater. Chem.* **2000**, *10*, 337. (c) Yamamoto, T.; Yoneyama, S.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Appl. Phys.* **2000**, *88*, 2215. (d) Yamamoto, T.; Ohashi, A.; Yoneyama, S.; Hasegawa, M.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **2001**, *105*, 2308.

(4) (a) Hvilsted, S.; Andruzzi, F.; Ramanujam, P. S. *Opt. Lett.* **1992**, *17*, 1234. (b) Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H. W.; Ramanujam, P. S. *Macromolecules* **1995**, *28*, 2172.

(5) Berg, R. H.; Hvilsted, S.; Ramanujam, P. S. *Nature (London)* **1996**, *383*, 505.

(6) Rasmussen, P. H.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 4738.

(7) Andruzzi, L.; Altomare, A.; Ciardelli, F.; Solaro, R.; Hvilsted, S.; Ramanujam, P. S. *Macromolecules* **1999**, *32*, 448.
(8) Wang, C.; Fei, H.; Qiu, Y.; Yang, Y.; Wei, Z.; Tian, Y.; Chen, Y.; Zhao, Y. *Appl. Phys. Lett.* **1999**, *74*, 19.
(9) (a) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873. (b) Tsutsumi, O.; Shiono, T.; Ikeda. T.; Galli. G. *J. Phys. Chem. B* **1997**, *101*, 1332.
(10) (a) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 349. (b) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 1104. (c) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 4457. (d) Wu, Y.; Zhang, Q.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Nagase, Y. *Macromolecules* **1999**, *32*, 3951.
(11) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *119*, 7791.
(12) Yoneyama, S.; Yamamoto, T.; Hasegawa, M.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Mater. Chem.* **2001**, *11*, 3008.
(13) Takatsu, H.; Takeuchi, K.; Tanaka, Y.; Sasaki, M. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 279.
(14) (a) Pugh, C.; Percec, V. *Chem. Mater.* **1991**, *3*, 107. (b) Pugh, C.; Percec, V. *Polym. Bull. (Berlin)* **1990**, *23*, 177. (c) Pugh, C.; Percec, V. *Mol. Cryst. Liq. Cryst.* **1990**, *178*, 193.
(15) (a) Percec, V.; Rodenhouse, R. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 15. (b) Percec, V.; Johansson, G.; Rodenhouse, R. *Macromolecules* **1992**, *25*, 2563.
(16) Hsieh, C.-J.; Wu, S.-H.; Hsieh, G.-H.; Hsu, C.-S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1077.
(17) Angeloni, A. S.; Caretti, D.; Carlini, C.; Chiellini, E.; Galli, G.; Altomare, A.; Solaro, R. *Liq. Cryst.* **1989**, *4*, 513.
(18) (a) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136. (b) Lagugné Labarthet, F.; Rochon, P.; Natansohn, A. *Appl. Phys. Lett.* **1999**, *75*, 1377. (c) Lagugné Labarthet, F.; Buffeteau, T.; Sourisseau, C. *J. Phys. Chem. B* **1999**, *103*, 6690.
(19) (a) Kim, D. Y.; Tripathy, S. K.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166. (b) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835.
(20) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V. In *Handbook of Liquid Crystals;* Wiley-VCH: Berlin, 1998; Vol. 1, p 771.
(21) Hicher, H. J.; Gunther, P.; Pohl, D. W. In *Laser Induced Dynamic Grating*; Springer-Verlag: Berlin, 1986.
(22) Gambogi, W. J.; Weber, A. M.; Trout, D. J. *Proc. SPIE* **1993**, *2043*, 2.
(23) (a) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. *J. Phys. Chem.* **1996**, *100*, 8836. (b) Barrett, C. J.; Rochon, P. L.; Natansohn, A. *J. Chem. Phys.* **1998**, *109*, 1505.
(24) Li, X. T.; Natansohn, A.; Rochon, P. *Appl. Phys. Lett.* **1999**, *74*, 3791.
(25) Kumar, J.; Li, L.; Jiang, X. L.; Kim, D. Y.; Lee, T. S.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *72*, 2096.
(26) Jiang, X. L.; Li, L.; Kumar, J.; Kim, D. Y.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *72*, 2502.
(27) (a) Viswanathan, N. K.; Balasubramanian, S.; Li, L.; Kumar, J.; Tripathy, S. K. *J. Phys. Chem. B* **1998**, *102*, 6064. (b) Viswanathan, N. K.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9*, 1941.
(28) Kogelnik, J. *Bell Syst. Technol. J.* **1969**, *48*, 2909.

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