

# Holographic Grating by Means of Polymer Liquid Crystals

Tomiki Ikeda, Satoshi Yoneyama, Takahiro Yamamoto, Makoto Hasegawa

## Abstract

Formation of intensity gratings was studied with two s-polarized (s+s) configuration in polymer liquid crystals (PLCs) containing a photochromic moiety (azobenzene) and a mesogenic unit (tolane, **T-AB**; cyanobiphenyl, **CB-AB**) by photoinduced alignment of PLCs. Remarkable differences were observed between the two PLCs. **T-AB** showed a faster response to the change in the diffraction intensity than **CB-AB**. In **T-AB**, alignment change took place faster than that of **CB-AB**. By introducing the tolane unit at the side chain, we obtained a diffraction efficiency of 30 % in the Raman-Nath regime

**Keywords** : holographic grating, polymer liquid crystal, azobenzene

## 1. Introduction

Novel materials for optical data storage have become of great interest in recent years with a rapid growth in information technology (IT). Holographic storage has been applied for data storage because using three-dimensional (3-D) storage techniques that can increase the information packing densities. Development of holography technology depends on the properties of recording materials. Ideal holographic materials show high diffraction efficiency, resolution and high-speed recording.

Polymer liquid crystals (PLCs) are known to be the high-performance materials for optical storage due to the large optical anisotropy and high stability below  $T_g$ . We previously reported the formation of holographic grating by means of photochemical phase transition of PLCs containing azobenzene moieties [1, 2]. Large modulation of the refractive index was induced by the photochemical

phase transition in LCs based on *trans-cis* photoisomerization of azobenzene molecules. The refractive-index modulation in PLCs arises from the 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 of  $|n_e - n_o|$  corresponds to birefringence ( $\Delta n$ ) of LC molecules. We previously studied the formation of refractive-index gratings by means of photoinduced alignment of PLCs containing azobenzene moieties. Diffraction efficiency ( $\eta$ ) and the modulation of the refractive index ( $\Delta n'$ ) were not very high (6 % and 0.04, respectively) on the grating formation [3]. However, it is expected that these values can be improved by molecular design of PLCs. One approach is to synthesize PLCs with a high value of  $\Delta n$ .

The  $\Delta n$  of LCs is mainly determined by  $\pi$ -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  $\Delta n$  and low viscosity. For LC displays, high  $\Delta n$  and low viscosity are very

Manuscript received August 7, 2001; accepted for publication August 25, 2001.

Corresponding Author : Tomiki Ikeda  
Chemical Resources Laboratory, Tokyo Institute of Technology 4259  
Nagatsuta, Midori-ku, Yokohama, Japan.

E-mail : tiked@res.titech.ac.jp Tel : +81 45-924-5240 Fax : +81 45-924-5275

useful in shortening response time through thinner cell gap requirement. Therefore, tolane LC compounds have been used for to obtain a quick response time of LC displays.

In this study, we investigated the formation of holographic grating using a PLC with an azobenzene moiety (photoresponsive unit) and a tolane moiety (mesogenic unit with a high  $\Delta n$ ) in the side chain.

## 2. Experiments

Fig. 1. shows the structure of PLCs used in this study. **T-AB** has a tolane unit and **CB-AB** possesses a cyanobiphenyl moiety. Thermodynamic properties and molecular weight of PLCs are shown in Fig. 1. Homogeneously aligned films with thickness between 600 nm and 1,600 nm were prepared by casting a solution in THF onto glass substrates, which had been coated with poly(vinyl alcohol) and rubbed to align mesogens. Formation of grating of the PLC was performed by the following procedure (Fig. 2. (A)). In this study, gratings were written at 488 nm and read out at 633 nm. The reading wavelength must be located outside the absorption band to avoid a destructive readout of the gratings. Writing beams were two linearly polarized beams from an Ar<sup>+</sup> laser. The direction of the electric field vector of the incident linearly polarized light was parallel to the direction of uniaxially aligned of mesogens, *i.e.*, s-polarization. The incident angle of writing beams was fixed at  $\theta = 7^\circ$  except for evaluation of the effect of fringe spacing.  $\eta$  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 writing beams. Photoinduced alignment change of the PLC was investigated as follows (Fig. 2. (B)). 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. After grating formation, the surface structure of the PLC films was investigated with an AFM (Shimadzu, SPM-9500 J2), and 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.

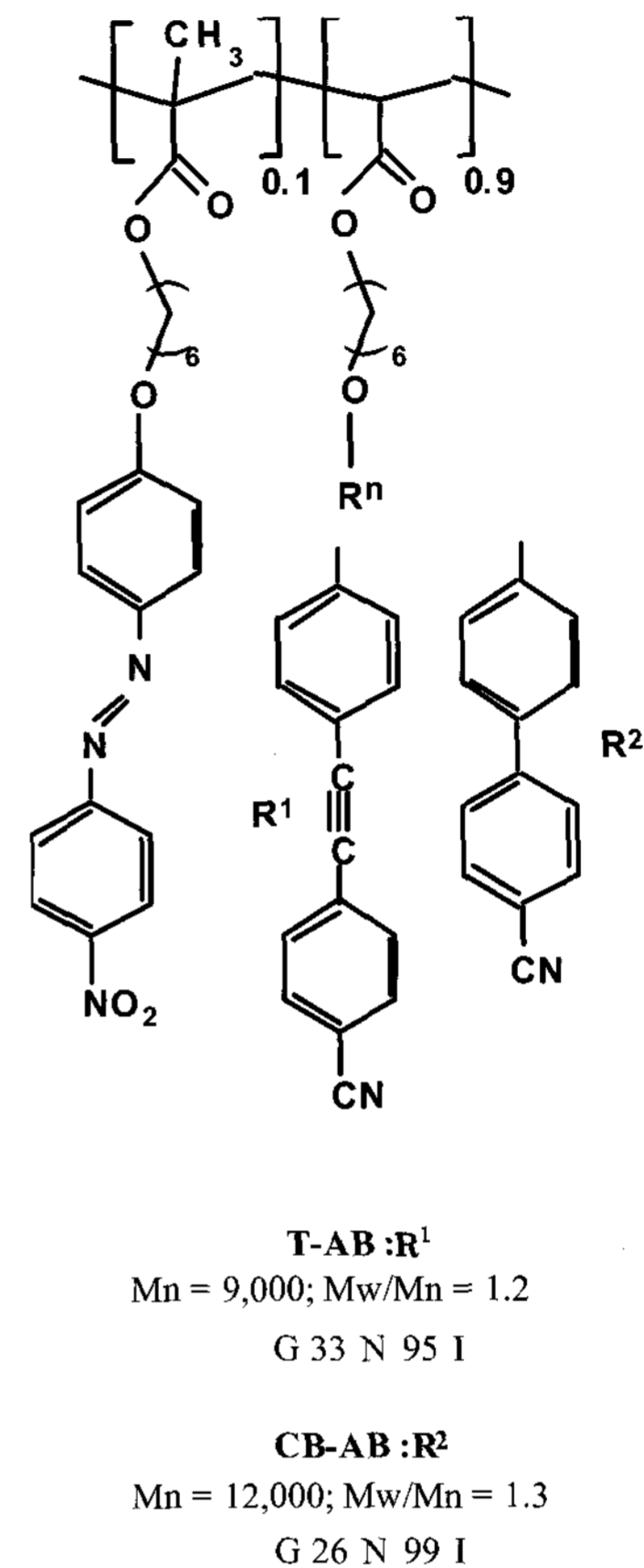


Fig. 1. Structure of PLCs used in this study.

## 3. Results and Discussion

### 3.1 Modulation of surface structure

Natansohn et al. [5], Tripathy et al. [6] and other research groups [7] explored the mechanism of surface relief gratings (SRGs) on azopolymer films. The behavior of the grating formation differs according to the polarization configuration of the writing beams. Two s-polarized (s+s) configuration produces a very small surface modulation, almost negligible (< few nm), and shows the smallest value of  $\eta$  (< 0.1 %) due to the SRG. We previously reported a phase-type grating in **CB-AB** films under the (s+s) configuration. It was found that the spatial modulation of the refractive index results from photoinduced alignment change based on *trans-cis-trans* photoisomerization of azobenzene moieties [3]. In this study, we explored the surface modulation of **T-AB** films

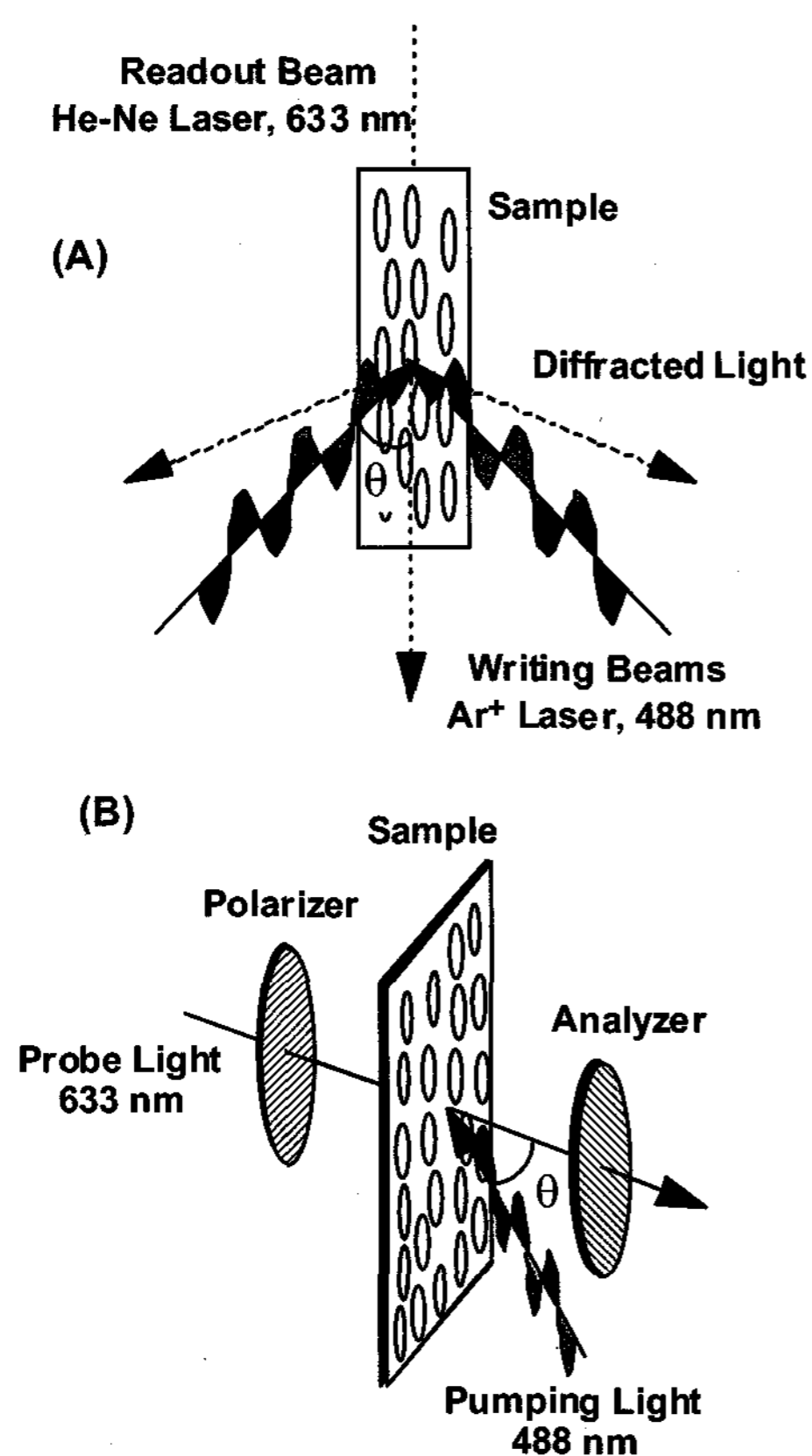


Fig. 2. Optical setup for the formation of gratings (A) and photoinduced alignment change (B).

to discuss the spatial modulation of the refractive index. Grating formation was performed under different conditions: T-AB films in an N phase (60 °C) and those in a glassy state (25 °C). Photoirradiation was performed at light intensity of 80 mW/cm<sup>2</sup> for 10 min. The details of the surface modulation is shown in Fig. 3. The periodic structure of the surface relief was about 2.0  $\mu\text{m}$  wide in each case while its height was about 12 nm (60 °C, A) and 7 nm (25 °C, B), respectively. In the N phase, the value of  $\eta$  was 31 % while it was less than 1 % in glassy state (Fig. 4.(A)). This difference is attributable to the modulation of refractive index based on orientation of mesogens in the PLC film. Fig. 4.(B) shows the change in the transmittance upon photoirradiation of the T-AB film with 1,600 nm thickness under different temperatures. The transmittance brought about little changed on irradiation of the pumping beam at room temperature. On the other hand, the transmittance gradually decreased and finally reached zero on irradiation of light at 60 °C. This means that the birefringence disappeared and a large modulation of

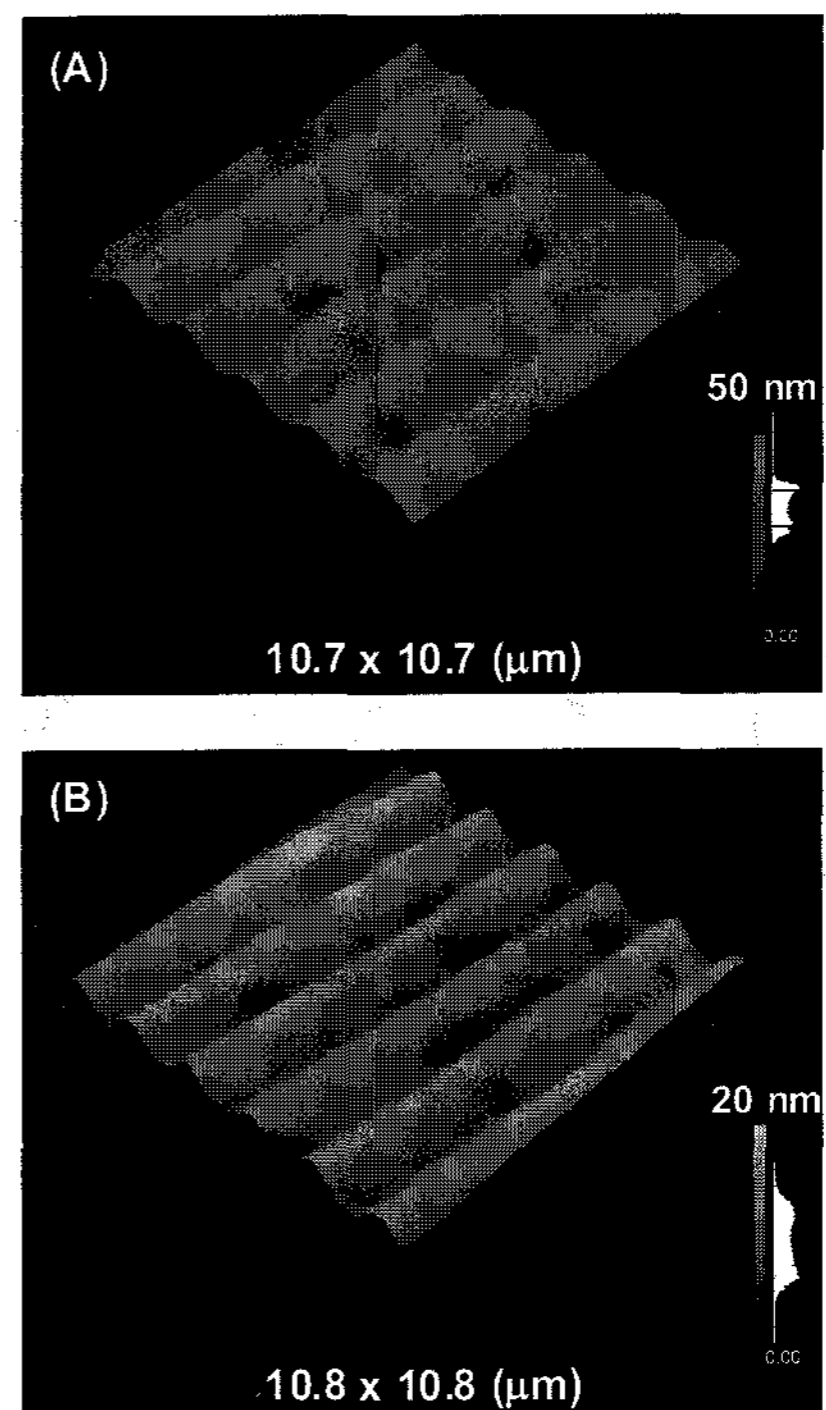


Fig. 3. SRGs recorded in an N phase (A) and a glassy state (B) in the T-AB film.

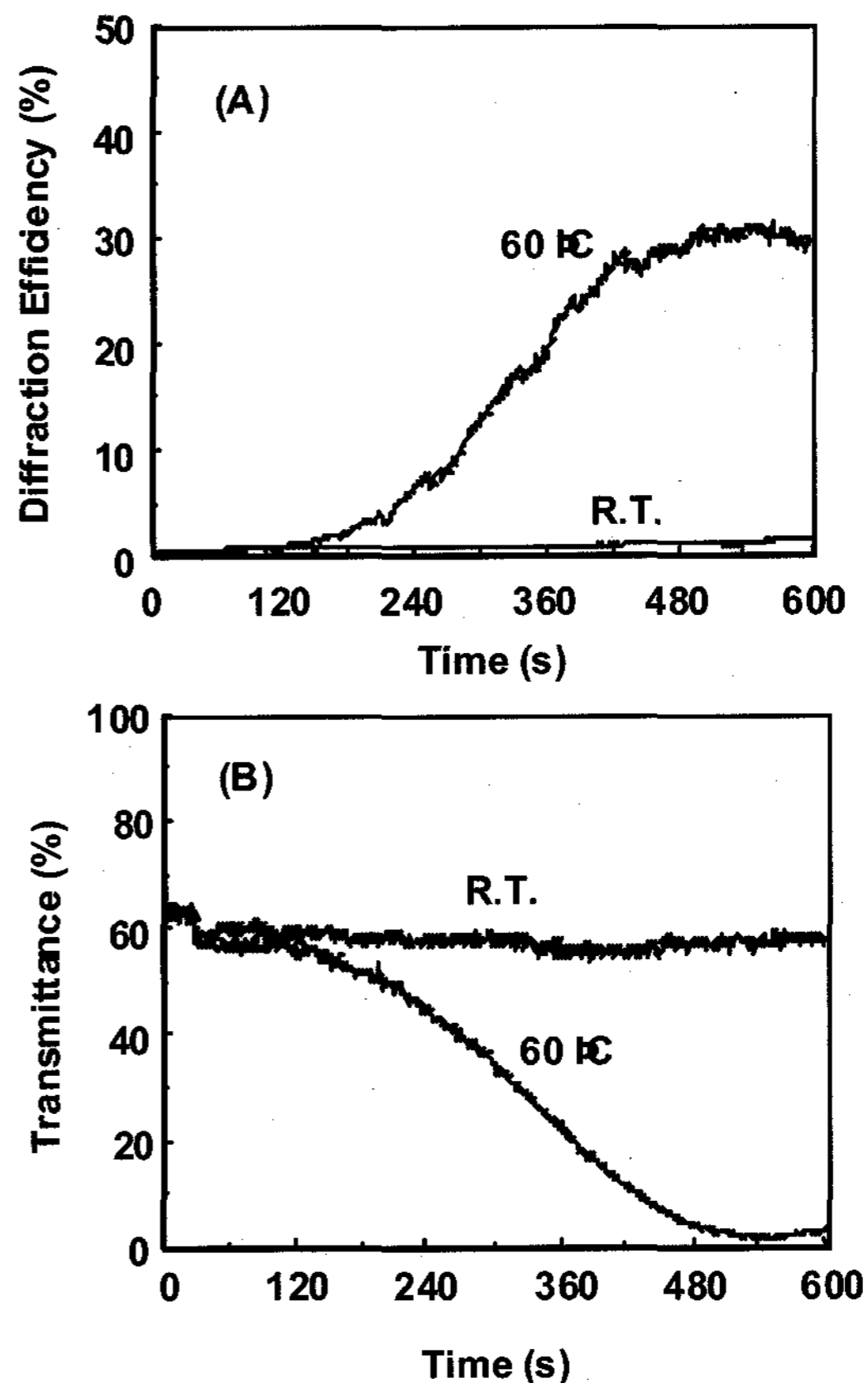
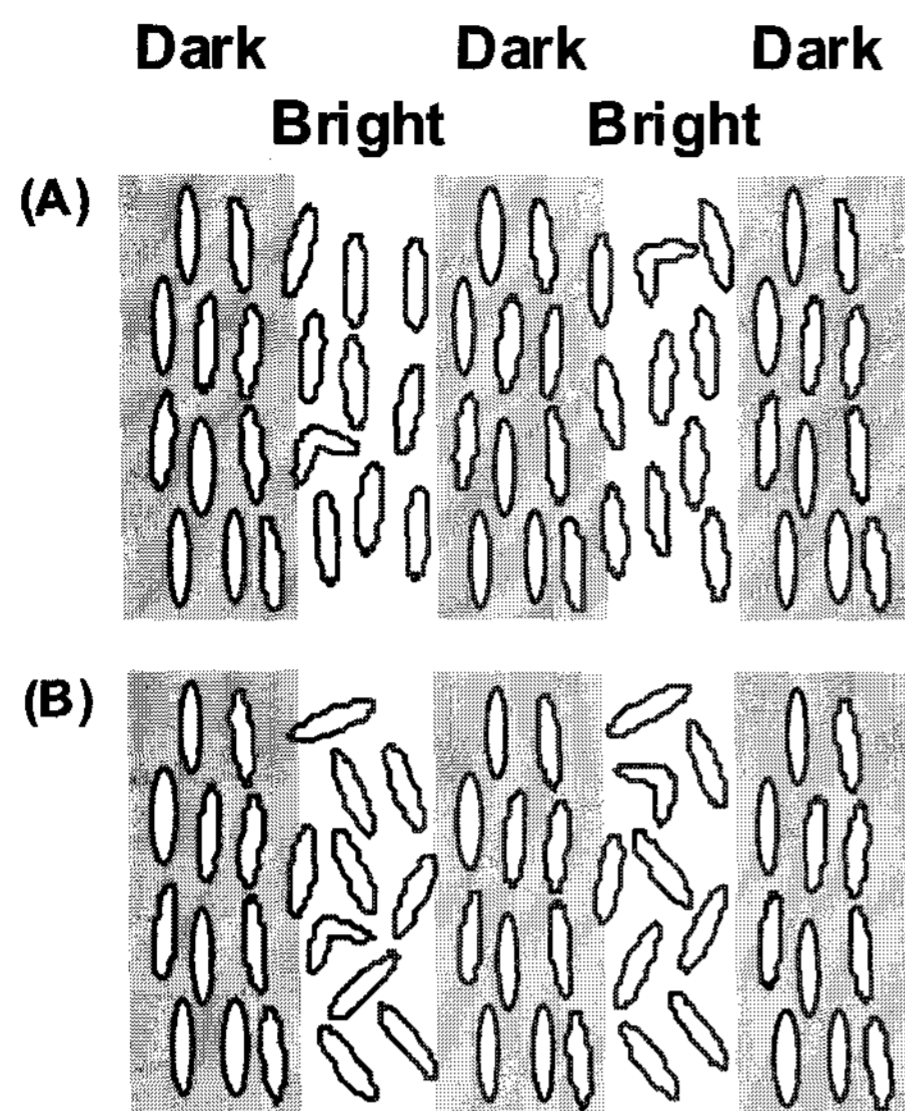
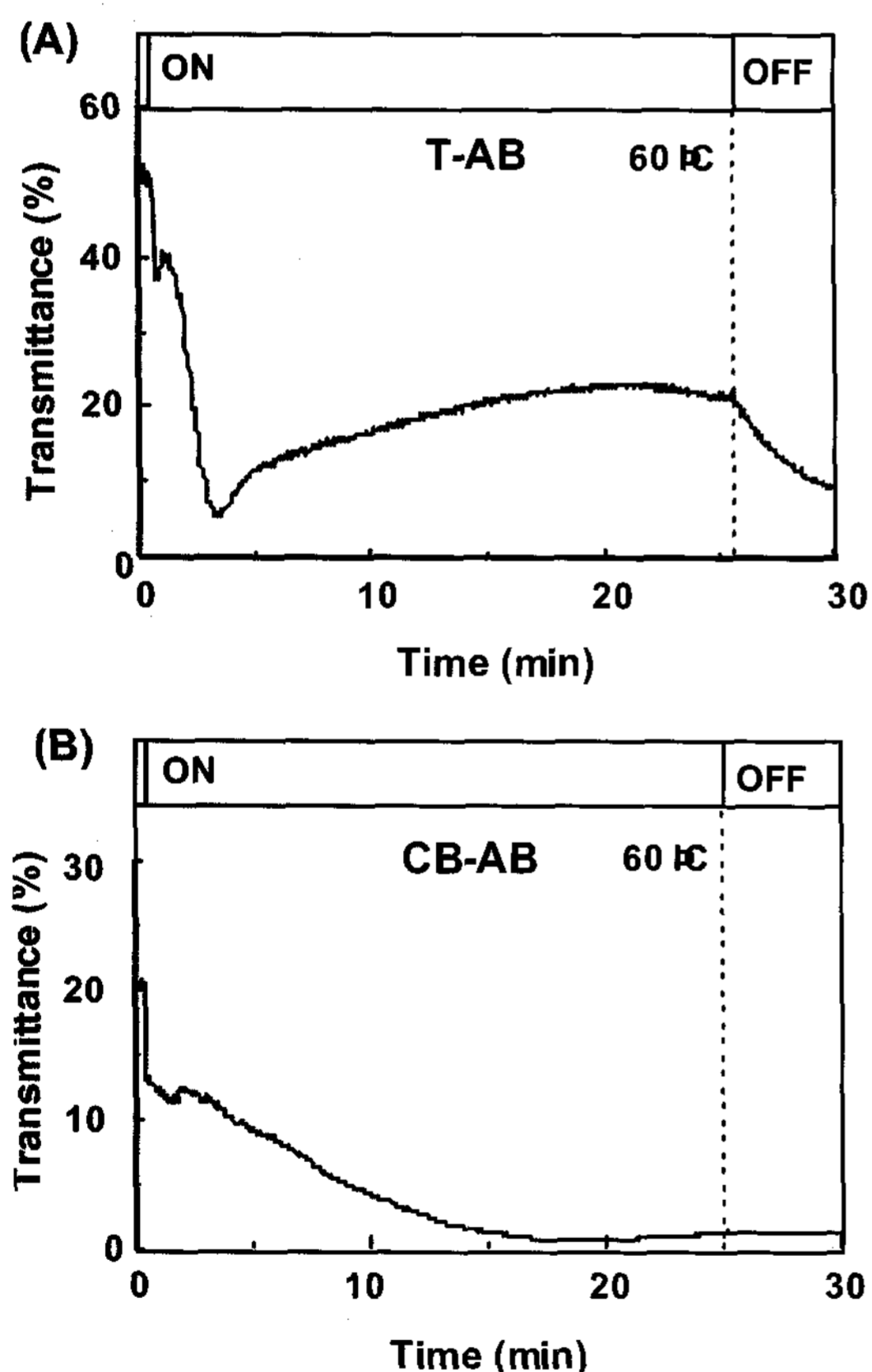


Fig. 4. Change in diffraction efficiency (A) and in transmittance through crossed polarizers in the T-AB film.



**Fig. 5.** Schematic illustration of grating formation in PLCs in a glassy state (25 °C; A) and an N phase (60 °C; B).



**Fig. 6.** Change in transmittance of probe light in **T-AB** (A) and **CB-AB** (B) films (film thickness, 1,200 nm).

refractive index was induced upon photoirradiation at 60 °C. The plausible mechanism of grating formation in **T-AB** is schematically illustrated in Fig. 5. At room

temperature, *trans-cis* photoisomerization of azobenzene moieties is induced in the bright areas of the interference patterns. This photoisomerization gives rise to the generation of diffracted beams with a periodic change in the refractive index. At 60 °C, the difference in the refractive index between the bright and dark areas increases because the orientational relaxation proceeds while  $\eta$  becomes large. In **CB-AB** films, under the same conditions, the relief height was about 10 nm and the value of  $\eta$  was 2 % in the N phase. These differences are dependent on photoinduced alignment behavior based on *trans-cis-trans* isomerization cycles of azobenzene moiety. In any event, the ratio of the height of relief to the film thickness was very small (less than 1.0 %), and the contribution of the surface modulation to the spatial modulation of the refractive index was negligible in **T-AB** films similarly to **CB-AB** films.

### 3.2 Photoinduced alignment behavior of PLCs

To discuss the formation of grating in PLCs, it is necessary to explore not only the grating formation behavior but also photoinduced alignment behavior of PLCs. Fig. 6 shows the photoinduced alignment in the **T-AB** and **CB-AB** films. Transmittance ( $T$ ) of probe light passed through crossed polarizers, with the uniaxially film between them, is defined by eq (1):

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

where  $d$  is film thickness,  $\Delta n$  is birefringence of PLC films and  $\lambda$  is wavelength of the probe light, respectively. The experiment was performed at 60 °C (N phase) on the films with thickness of 1,200 nm, and intensity of the pumping light was 120 mW/cm<sup>2</sup>. In the initial state, the calculated values of  $\Delta n$  of PLC films (**T-AB** and **CB-AB**) were 0.14 and 0.08, respectively. The transmittance of the probe light decayed on irradiation of linearly polarized light and gradually increased, finally became saturated for **T-AB**. This result indicates that photoinduced alignment change of the PLC was induced by *trans-cis-trans* isomerization cycles of the azobenzene moieties [8]. While in **CB-AB**, the intensity of the probe light decreased slowly during irradiation of pumping light and the photoinduced alignment change was not induced under this experimental condition. This difference is probably due to a degree of *trans-cis-trans*

isomerization cycles of azobenzene moieties. In the **T-AB** film, the photoisomerization cycles of azobenzene moieties proceeded effectively than those in **CB-AB** because of low viscosity of mesogens composed of tolane moieties.

### 3.3 Spatial modulation of refractive index

It is obvious that the diffraction efficiency is greatly enhanced with a PLC containing a tolane moiety. In practical applications,  $\eta$  is a very important factor. Therefore the effect of spatial modulation of the refractive index ( $\Delta n'$ ) on the formation of grating was explored.  $\eta$  is defined in the Raman-Nath (thin) diffraction regime by eq (2):

$$\eta = (\pi d \Delta n' / \lambda)^2 \quad (2)$$

where  $d$  is film thickness,  $\Delta n'$  is a degree of spatial modulation of the refractive index and  $\lambda$  is wavelength of the reading beam, respectively. Fig. 7. shows the effect of the film thickness on the value of  $\eta$  in the **T-AB** film.  $\eta$  increased with increasing film thickness and  $\Delta n'$  was evaluated using eq (2) with values of  $\eta$  and  $d$ . The value of  $\Delta n'$  was almost constant regardless of the film thickness: 0.08. This value is larger than those reported so far for other holographic materials, such as photopolymers [9].

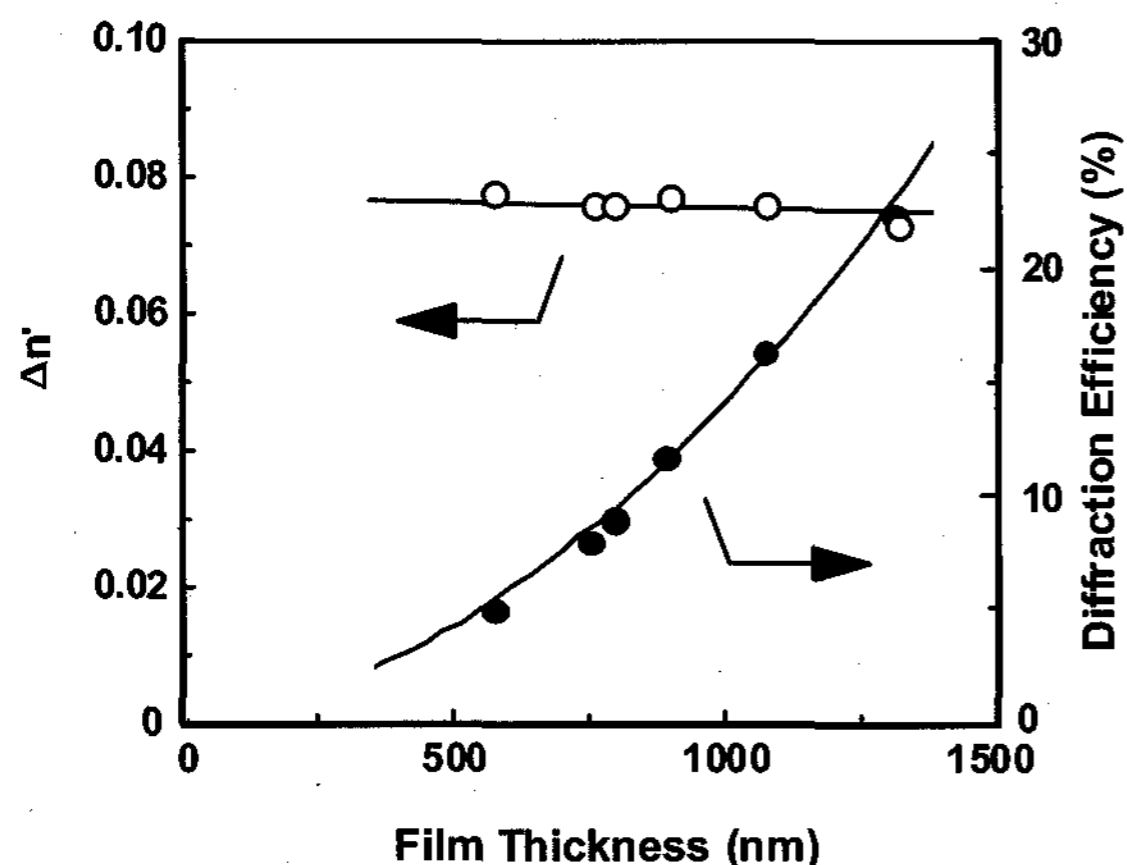


Fig. 7. Effect of film thickness on the diffraction efficiency (J) and the modulation of the refractive index (E) in **T-AB** at 60 °C. (a).

The effect of fringe spacing ( $\Lambda$ ) on the value of  $\Delta n'$  was investigated. By increasing the incident angle ( $\theta$ ) of the writing beams ( $\lambda$ ) from 4° to 16°,  $\Lambda$  was varied from

3.5 to 0.9  $\mu\text{m}$  as evaluated by eq (3).

$$\Lambda = \lambda / (2 \sin \theta) \quad (3)$$

Fig. 8. shows the dependence of  $\Lambda$  on the value of  $\Delta n'$ . Photoirradiation was performed at 60 °C (**T-AB**) and 80 °C (**CB-AB**). It was found that  $\Delta n'$  was small when the fringe spacing was 0.9  $\mu\text{m}$  for both PLC films. On the other hand, when the  $\Lambda$  was greater than 2.0  $\mu\text{m}$ , the maximum value of  $\Delta n'$  reached up to 0.08 in the **T-AB** film. In the **CB-AB** film, the maximum value of  $\Delta n'$  was 0.04. It is probable that such difference results from the difference of  $\Delta n$  of the mesogenic molecules. In general,  $\Delta n$  of tolane derivatives is larger than that of cyanobiphenyl derivatives. As described above,  $\Delta n$  of **T-AB** is about 1.8 times as large as that of **CB-AB**. Therefore, in the **T-AB** film,  $\Delta n'$  was larger than that of **CB-AB** on the grating formation by means of photoinduced refractive index change of PLCs.

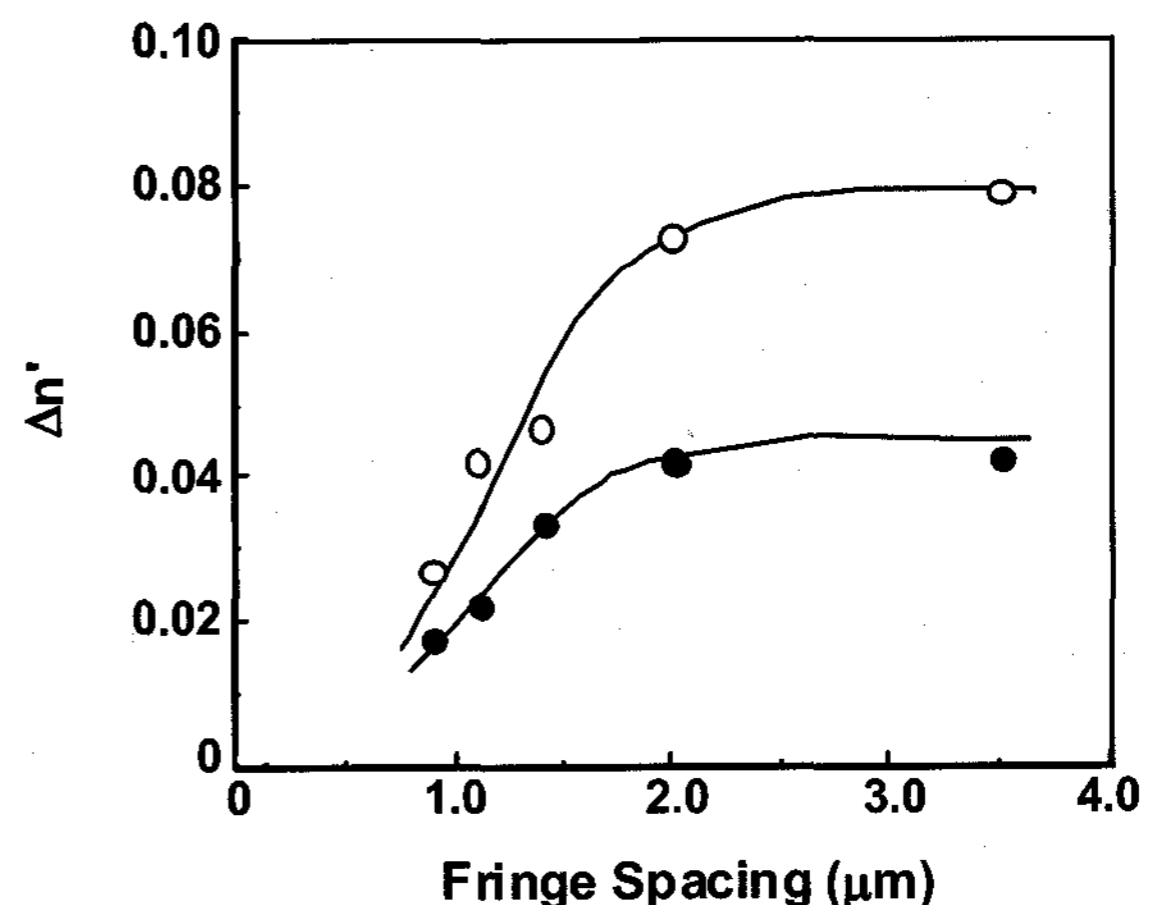
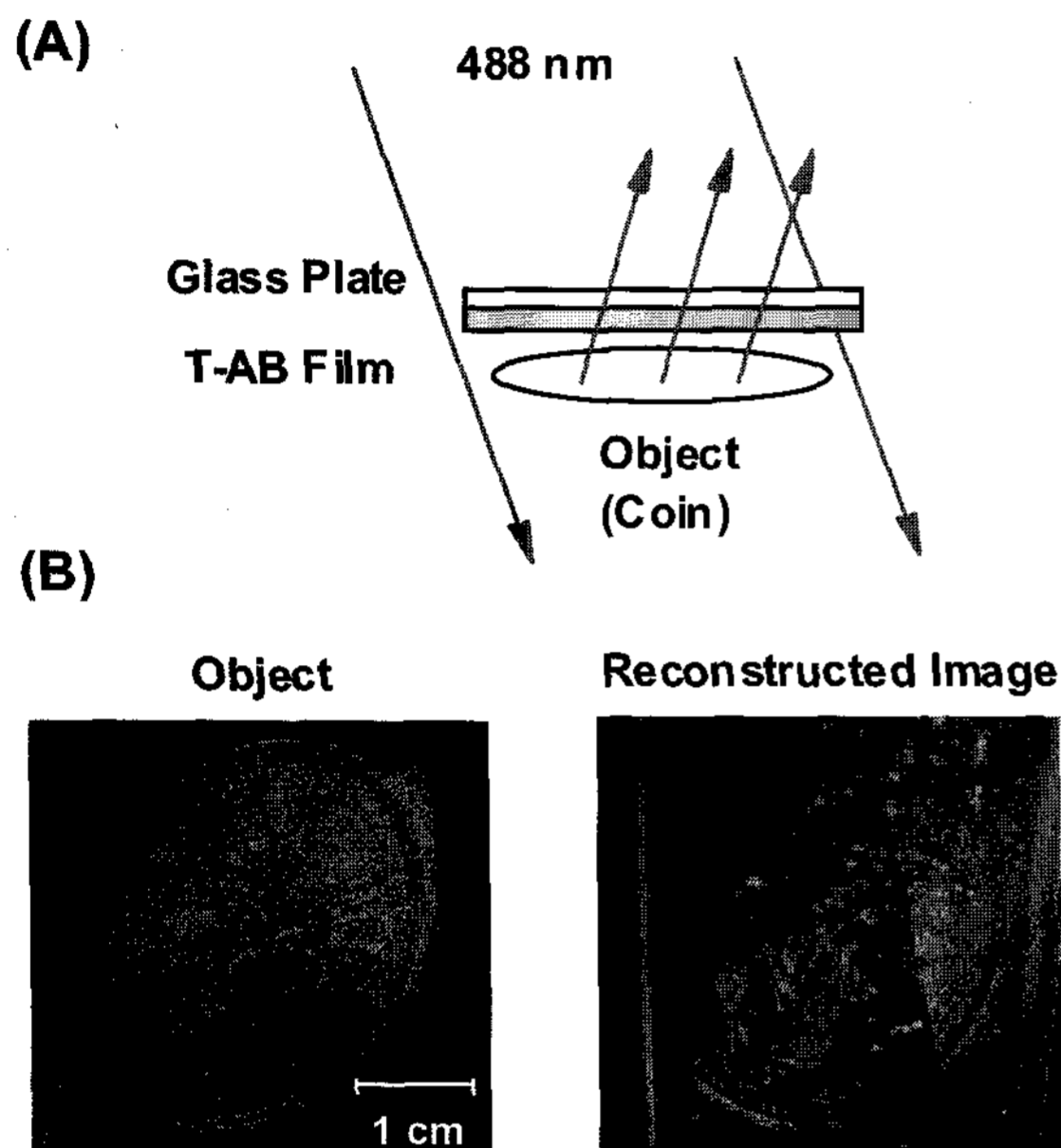


Fig. 8. Effect of the fringe spacing on  $\Delta n'$  in **T-AB** at 60 °C (E) and **CB-AB** at 80 °C (J).

### 3.4 Holographic image storage

Based on these results, we attempted holographic image storage of a three-dimensional (3-D) object in the **T-AB** film with reflection-type optical setup, as is shown in Fig. 9 (A), and a coin was used as an object. Fig. 9 (B) also shows the reconstructed image. It is evident that the object was reconstructed with high resolution (>5,000 lines/mm). It is speculated that the mechanism of image storage would be attributable to the photoinduced refractive-index modulation in the PLC film. In

reflection-type holograms, the interference patterns were formed parallel to the sample film and glass substrate. SRG was not observed with POM and AFM measurements. The recording and erasure of the images are reversible by controlling the temperature. The stored image remained unchanged after 15 months when the films were preserved at room temperature.



**Fig. 9.** Optical setup for holographic image storage of the object (coin) (A) and the reconstructed image from the reflection-type hologram stored in the T-AB film (B).

#### 4. Conclusions

In summary, we explored the formation of holographic gratings in a PLC containing a tolane moiety with high  $\Delta n$ . It was found that the grating formation was strongly affected by the structure of the mesogenic unit. The PLC with a tolane moiety showed a faster response to the change in the diffraction intensity than the analog with a cyanobiphenyl unit. This behavior was due to the photoinduced alignment change of PLCs, which is based on the photoisomerization cycles of the azobenzene moiety. The effect of  $\Delta n$  of PLCs on the formation of gratings indicates that a considerable enhancement of  $\eta$  can be achieved by using PLC with a tolane moiety. Furthermore,  $\eta$  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 were able to perform the holographic 3-D image storage. We believe that these results will contribute greatly to the development of various holographic applications such as optical data storage and 3-D display.

#### References

- [1] (a) M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono and T. Ikeda, "A Dynamic Grating Using a Photochemical Phase Transition of Polymer Liquid Crystals Containing Azobenzene Derivatives," *Adv. Mater.*, vol. 11, pp. 675-677, 1999. (b) M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono and T. Ikeda, "Photochemically Induced Dynamic Grating by Means of Side Chain Polymer Liquid Crystals," *Chem. Mater.*, vol. 11, pp. 2764-2769, 1999. (c) M. Hasegawa, T. Yamamoto, A. Kanazawa, T. Shiono and T. Ikeda, "Real-Time Holographic Grating by Means of Photoresponsive Polymer Liquid Crystals with a Flexible Siloxane Spacer in the Side Chain," *J. Mater. Chem.*, vol. 9, pp. 2765-2769, 1999.
- [2] (a) T. Yamamoto, M. Hasegawa, A. Kanazawa, T. Shiono and T. Ikeda, "Phase-Type Gratings Formed by Photochemical Phase Transition of Polymer Azobenzene Liquid Crystals: Enhancement of Diffraction Efficiency by Spatial Modulation of Molecular Alignment," *J. Phys. Chem. B*, vol. 103, pp. 9873-9878, 1999. (b) T. Yamamoto, M. Hasegawa, A. Kanazawa, T. Shiono and T. Ikeda, "Holographic Gratings and Holographic Image Storage via Photochemical Phase Transition of Polymer Azobenzene Liquid-Crystal Film," *J. Mater. Chem.*, vol. 10, pp. 337-342, 2000. (c) T. Yamamoto, S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, "Holographic Gratings in the Optically Isotropic Phase of Polymer Azobenzene Liquid-Crystal Film," *J. Appl. Phys.*, vol. 88, pp. 2215-2220, 2000. (d) T. Yamamoto, A. Ohashi, S. Yoneyama, M. Hasegawa, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, "Phase-Type Gratings Formed by Photochemical Phase Transition of Polymer Azobenzene Liquid Crystal. 2. Rapid Switching of Diffraction Beams in Thin Films," *J. Phys. Chem. B*, vol. 105, pp. 2308-2313, 2001.
- [3] S. Yoneyama, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, "Formation of Grating by Means of Photoinduced Alignment Change of Polymer Liquid Crystals with Azobenzene Moieties," *Mol. Cryst. Liq. Cryst.*, in press.
- [4] H. Takatsu, K. Takeuchi, Y. Tanaka and M. Sasaki, "Physical Properties of Nematic Tolans," *Mol. Cryst. Liq. Cryst.*, vol. 141, pp. 279-287, 1986.

- [ 5 ] (a) P. L. Rochon, C. J. Barrett and A. L. Natansohn, *Appl. Phys. Lett.*, vol. 66, pp. 136-138. (b) C. J. Barrett, A. L. Natansohn, and P. L. Rochon, "Mechanism of Optically Induced High-Efficiency Diffraction Gratings in Azo Polymer Films," *J. Phys. Chem.*, vol. 100, pp. 8836-8842, 1996.
- [ 6 ] (a) D. Y. Kim, S. K. Tripathy, L. Li, L and J. Kumar. "Laser-Induced Holographic Surface Relief Gratings on Nonlinear Optical Polymer Films," *Appl. Phys. Lett.*, vol. 66, pp. 1166-1168. (b) D. Y. Kim, L. Li, L. X. L. Jiang, V. Shivshankar, J. Kumar and S. K. Tripathy, "Polarized Laser Induced Holographic Surface Relief Gratings on Polymer Films," *Macromolecules*, vol. 28, pp. 8835-8839, 1995.
- [ 7 ] (a) S. Hvilsted, F. Andruzzi and P. S. Ramanujam, "Side-Chain Liquid-Crystalline Polyesters for Optical Information Storage," *Opt. Lett.*, vol. 17, pp. 1234-1236, 1992. (b) S. Hvilsted, F. Andruzzi, C. Kulinna H. W. Siesler and P. S. Ramanujam, "Novel Side-Chain Liquid Crystalline Polyesters Architecture for Reversible Optical Storage," *Macromolecules*, vol. 28, pp. 2172-2183, 1995.
- [ 8 ] (a) Y. Wu, Y. Demachi, O. Tsutsumi, K. Kanazawa, T. Shiono and T. Ikeda, "Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 1. Effect of Light Intensity on Alignment Behavior," *Macromolecules*, vol. 31, pp. 349-354, 1998. (b) Y. Wu, Y. Demachi, O. Tsutsumi, K. Kanazawa, T. Shiono and T. Ikeda, "Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 2. Effect of Spacer Length of the Azobenzene Unit on Alignment Behavior," *Macromolecules*, vol. 31, pp. 1104-1108, 1998. (c) Y. Wu, Y. Demachi, O. Tsutsumi, K. Kanazawa, T. Shiono and T. Ikeda, "Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 3. Effect of Structure of the Photochromic Moieties on Alignment Behavior," *Macromolecules*, vol. 31, pp. 4457-4463, 1998. (d) Y. Wu, Q. Zhang, K. Kanazawa, T. Shiono, T. Ikeda and Y. Nagase "Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 5. Effect of the Azo Contents on Alignment Behavior and Enhanced Response." *Macromolecules*, vol. 32, pp. 3951-3956, 1999.
- [ 9 ] W. J. Gambogi, A. M. Weber and D. J. Trout "Advances and Applications of Dupont Holographic Photopolymers." *Proc. SPIE*, vol. 2043, pp. 2-13, 1993.