Photochemically Induced Dynamic Grating by Means of Side Chain Polymer Liquid Crystals

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Dynamic holographic grating by means of photochemical nematic-to-isotropic phase transition has been studied in a polymer liquid crystal containing an azobenzene moiety with strong donor−acceptor substituents in the side chain. Periodical change in the phase structure was caused reversibly by trans−cis photoisomerization and cis−trans thermal back-isomerization of the azobenzene moiety and led to formation of the dynamic grating following change in refractive index on the order of 10^{-2}. The production and removal of the grating with a narrow fringe spacing of 1.4 μm was achieved within ~150 and ~190 ms, respectively. Moreover, the optical switching behavior of the holographic diffraction was observed repeatedly by turning on and off the writing beams.

Introduction

Holography is a technique to modulate the amplitude and phase of light, in which recording and display of a three-dimensional image are performed by light. In particular, dynamic holography has been attracting much attention because of its potential for optical device applications such as real-time image processing and phase conjugate mirrors as well as the other optical communication and information processing.[1−3] In general, holographic recording can be achieved by combining two coherent lights, which are object and reference lights, in recording media. The variation in intensity in the interference pattern causes periodic modulation of refractive index or surface profile in the media, resulting in the formation of phase grating. The recorded optical information is read out by irradiation of other coherent light. Particularly exciting advances with respect to holographic recording materials were brought about by Natansohn et al. and Tripathy et al., who independently reported a surface relief grating by means of amorphous polymers containing azobenzene moieties.[4−8] On the other hand, in the dynamic holography, recording, reading out, and erasing of the optical information should be performed at real time. The required properties for the materials used in dynamic holography, therefore, are reversibility and a quick change in the refractive index caused by light. A response time of a few tens of milliseconds is necessary for the real-time image processing. Recently, extensive research on the materials for the dynamic holography has been in progress.[9−15]

We have performed so far systematic studies on the nematic-to-isotropic (N−I) phase transition of polymer liquid crystals (PLCs) containing photochromic molecules such as azobenzene and spiropyran derivatives.[16−28] These chromophores can change their molec-

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[1] Prasad, P. N.; Williams, D. J. In *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

[2] Yeh, P.; Chiou, A. E.; Hong, J.; Beckwith, P.; Chang, T.; Khoshnevisan, M. *Opt. Eng.* **1989**, *28*, 328.

[3] Yeh, P. In *Introduction to Photorefractive Nonlinear Optics*; Wiley: New York, 1993.

[4] Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.

[5] Barrett, C. J.; Natansohn, A. L.; Rochon. P. L. *J. Phys. Chem.* **1996**, *100*, 8836.

[6] Kim, D.-Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166.

[7] Kim, D.-Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835.

[8] Kumar, J.; Li, L.; Jiang, X. L.; Kim, D.-Y.; Lee, T. S.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *72*, 2096.

[9] Ducharme, S.; Scott, J. C.; Twieg, R. J.; Moerner, W. E. *Phys. Rev. Lett.* **1991**, *66*, 1846.

[10] Zhao, C.; Park, C.-K.; Prasad, P. N.; Zhang, Y.; Ghosal, S.; Burzynski, R. *Chem. Mater.* **1995**, *7*, 1237.

[11] Wiederrecht, G. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 3231.

[12] Khoo, I. C. *Opt. Lett.* **1995**, *20*, 2137.

[13] Ono, H.; Kawatsuki, N. *Appl. Phys. Lett.* **1997**, *71*, 1162.

[14] Ono, H.; Saito, I.; Kawatsuki, N. *Appl. Phys. Lett.* **1998**, *72*, 1942.

[15] Chen, A. G.; Brady, D. *J. Opt. Lett.* **1992**, *17*, 441.

[16] Tazuke, S.; Kurihara, S.; Ikeda, T. *Chem. Lett.* **1987**, 911.

[17] Kurihara, S.; Ikeda, T.; Sasaki, T.; Kim, H.-B.; Tazuke, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1751.

[18] Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 42.

[19] Kurihara, S.; Ikeda, T.; Tazuke, S.; Seto, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3251.

[20] Ikeda, T.; Sasaki, T.; Kim, H.-B. *J. Phys. Chem.* **1991**, *95*, 509.

[21] Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1992**, *25*, 3807.

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

[23] Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.

[24] Tsutsumi, O.; Shiono, T.; Ikeda, T.; Galli, G. *J. Phys. Chem. B* **1997**, *101*, 1332.

[25] Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *119*, 7791.

[26] Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **1997**, *101*, 2806.

[27] Tsutsumi, O.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 355.

[28] Tsutsumi, O.; Demachi, Y.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Nagase, Y. *J. Phys. Chem. B* **1998**, *102*, 2869.

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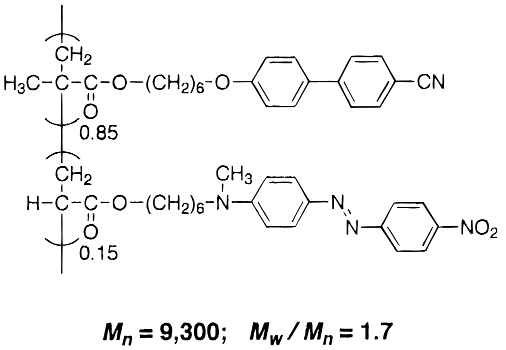

G 35 N 104 I

Figure 1. Structure and composition of the polymer liquid crystal, **PLC 1** , used in this study. Abbreviations: G, glass; N, nematic; I, isotropic; M_n, number-average molecular weight; M_w, weight-average molecular weight.

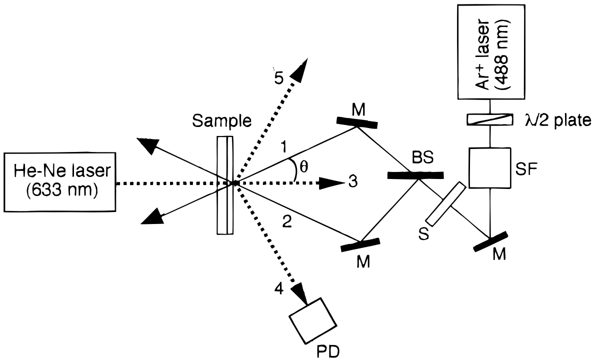

Figure 2. Schematic illustration of the experimental setup: M, mirror; SF, spatial filter; S, shutter; BS, beam splitter; PD, photodiode; beam 1 and 2, writing beam; beam 3−5, diffraction beam of 0- and ±1-order, respectively. θ is the incident angle of the writing beams. Polarized direction of the writing beam was perpendicular to the rubbing direction, i.e., *p*-polarization, and that of the reading beam was parallel to the rubbing direction, i.e., *s*-polarization.

ular shape upon photoirradiation, which leads to the isothermal N−I phase transition (photochemical phase transition). For example, the trans forms of azobenzene derivatives can stabilize the N phase due to their rodlike shape, while the cis forms destabilize the N phase because their shape is bent. Therefore, the trans−cis photoisomerization of the azobenzene in the N phase can induce disorganization of the LC phase structure. Furthermore, the N phase can be recovered by the thermal cis−trans back-isomerization. If the photochemical phase transition could be periodically induced by interference of the two coherent lights in the identical PLC films, they will act as materials for the dynamic grating. Since there is a large difference in the refractive index between N and I phases (~0.1), it is expected that the grating produced shows a high diffraction efficiency.[25] In addition, PLCs with azobenzene moieties show a rapid change between N and I phases by photoirradiation, which results in reversible and quick change in the refractive index. In fact, photochemical phase transition occurred in ~200 μs upon pulse irradiation.[23,24] In this paper, we attempted all-optical control of the dynamic gratings with the photoresponsive PLCs showing large and rapid change in the refractive index. We used the donor−acceptor azobenzene derivatives as photosensitive moiety. They show a fast thermal I−N phase transition on the basis of the fast cis−trans thermal back-isomerization compared to that of the nondonor−acceptor azobenzene derivatives.[27−29] The mechanism and the effect of the writing beam on the dynamic grating are investigated and discussed.

Experimental Section

Materials. The structure of the PLC (**PLC 1**) used in this study is shown in Figure 1. **PLC 1**, which contains an azobenzene moiety with a tertiary amine as an electron donor and a nitro group as an acceptor, was synthesized as reported by Robello.[30] More recently, the thermodynamic property of **PLC 1** was evaluated in detail and it was found that **PLC 1** shows an N phase between 35 and 104 °C.[28]

Film Preparation. PLC 1 was dissolved in THF at a low concentration (~10^{-3} mol/L) and then a small portion of the resultant solution was cast on a glass substrate which had been coated with poly(vinyl alcohol) and rubbed to align mesogens. After the solvent was removed completely under the reduced pressure at room temperature, the PLC film was annealed for 12 h at a temperature just below the N-to-I phase transition temperature to yield a monodomain of a well-aligned N phase. Thickness of the LC films was estimated as 100−350 nm by absorption spectroscopy on the basis of molar extinction coefficients of the azobenzene moiety.

Holographic Experimental Setup. Figure 2 shows the holographic experimental setup. The grating was written by two linearly polarized Ar$^+$ laser beams operating at 488 nm (beam 1 and 2 in Figure 2). Turning on and off the two writing beams were controlled with a mechanical shutter with a response time of <0.5 ms. Two writing beams with an equal intensity were crossed in the sample film and produced the interference pattern with the fringe spacing (Λ) which was estimated by the following equation

$$\Lambda = \frac{\lambda}{2 \sin \theta} \tag{1}$$

where λ is the wavelength of writing beam, and θ represents an incident angle of the writing beam. Under this condition, the resulting grating was in the Raman−Nath (thin) grating regime, which is known to generate multiple-order diffraction.[31] A linearly polarized He−Ne laser light (633 nm) with weak intensity was used as a reading beam (beam 3 in Figure 2), which was incident at normal to the surface of the polymer film. The phase grating formation was monitored by measuring the power of the first-order diffraction beam (beam 4 in Figure 2) with a photodiode. The diffraction efficiency, η, was determined by the ratio of intensities between the reading and the diffraction beams.

Results and Discussion

Dynamic Grating by Photochemical Phase Transition. The absorption maximum in UV−vis absorption spectrum of **PLC 1** is located at around 500 nm due to a π−π* transition of the *trans*-azobenzene moiety.[28,29,32] When the PLC film was exposed to an Ar$^+$ laser of 488 nm at 100 °C, the absorbance at 500 nm decreased with trans−cis isomerization. After irradiation, it was confirmed that the PLC film showed the same spectrum as that before irradiation in 2 ms due to thermal cis−trans back-isomerization.[28] The obtained lifetime of the

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(29) Xie, S.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1993**, *5*, 403.

(30) Robello, D. R. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1.

(31) Eichler, H. J.; Günther, P.; Pohl, D. W. In *Laser Induced Dynamic Grating*; Springer-Verlag: Berlin, 1986.

(32) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004.

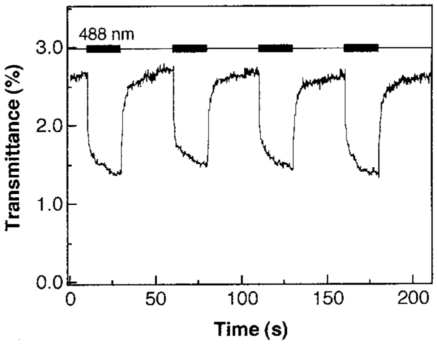

Figure 3. Photochemical N–I and thermal I–N phase transition of **PLC 1**. Photoirradiation at 488 nm (1.3 W/cm^2) was performed at 100 °C.

cis-azobenzene is much shorter than that of nondonor–acceptor azobenzenes. It is well-known that the thermal cis–trans back-isomerization of azobenzene derivatives proceeds by two processes: an inversion mechanism and a rotation mechanism.[33,34] In the nondonor–acceptor azobenzenes, the thermal isomerization occurs mainly through the inversion mechanism because of a low activation energy compared to that for the rotation mechanism.[33–41] On the other hand, in such donor–acceptor azobenzenes used in this study, the activation energies for the two mechanisms are close to each other; therefore, the thermal cis–trans back-isomerization of the donor–acceptor azobenzenes involves both the inversion and the rotation processes, resulting in a short lifetime of *cis*-azobenzenes.[33–41]

Before investigation of the formation of the grating, we explored the photochemical phase transition behavior of **PLC 1** by the conventional transmission-mode measurement.[18] Figure 3 shows the photochemical N–I phase transition and the thermal I–N phase transition at 100 °C. Before irradiation of a linearly polarized Ar$^+$ laser beam (488 nm), a probe beam at 633 nm from a He–Ne laser could transmit through a pair of crossed polarizers with the PLC film (thickness, ~200 nm) sandwiched between them, because of the birefringence of **PLC 1**. The transmittance of the probe beam decayed on irradiation at 488 nm in the N phase. This change in the transmittance indicates reduction of the birefringence of the PLC film, resulting from production of domains in which the N–I phase transition was induced by trans–cis photoisomerization of the azobenzene moiety. The transmittance of the probe beam recovered when photoirradiation was ceased. This result indicates that the thermal I–N phase transition is induced by the thermal cis–trans back-isomerization of the azobenzene moiety. Furthermore, the photochemical N–I phase transition and the thermal I–N phase transition could be induced repeatedly in **PLC 1**. It is well-known that such control of birefringence of LCs can also be achieved by optical-field-induced reorientation and Freedericksz transition.[41–51] If the observed change in transmittance is due to these effects, an analogous phenomenon is to be observed even in optically isotropic states of the LCs. However, no change in transmittance was observed in the I state in our system. Therefore, the result shown in Figure 3 is owing to the photochemical N–I phase transition and the thermal I–N phase transition.

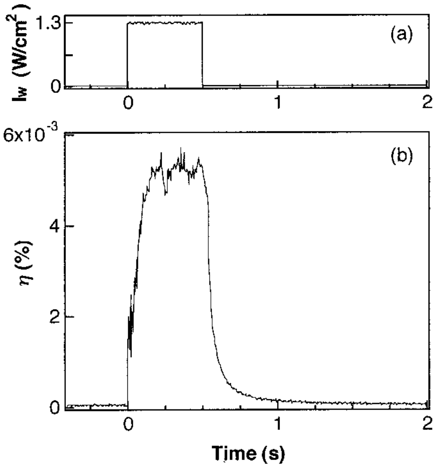

Figure 4. Typical formation and removal of the dynamic grating with a fringe spacing of 1.4 μm by turning on and off two writing beams. The total intensity of the writing beams was 1.3 W/cm^2 (0.65 W/cm^2 in each beam). (a) Intensity of the writing beam (I_w). (b) The time dependence of the diffraction efficiency (η).

Next we evaluated the formation of the dynamic grating with **PLC 1**. The incident angle (θ) of the writing beams was 10°, resulting in the interference pattern with a fringe spacing of 1.4 μm. As shown in Figure 4, irradiation of the sample film (thickness, ~200 nm) with two writing beams at 100 °C generated immediately the diffraction beam, which was observed during irradiation of the writing beams. This phenomenon demonstrates the formation of the phase grating in the PLC film. The obtained grating could be removed rapidly by turning off the writing beams. We evaluated the response time in the production and removal of the grating, which was defined as the time necessary to increase or decrease the intensity of the diffraction beam to 90 or 10% of the saturated value, respectively. It was found that each response time could be estimated as ~150 and ~190 ms. Moreover, the switching of the diffraction beam was investigated under the same condition as for Figure 4. The diffraction signal could be observed repeatedly by turning on and off the writing beams without the decrease in the intensity of the diffraction beam (Figure 5). There are some reports

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(33) Asano, T.; Okada, T. *J. Org. Chem.* **1984**, *49*, 4387.
(34) Asano, T.; Okada, T. *J. Org. Chem.* **1986**, *51*, 4454.
(35) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004.
(36) Asano, T. *J. Am. Chem. Soc.* **1980**, *102*, 1205.
(37) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161.
(38) Asano, T.; Yano, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900.
(39) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. *J. Am. Chem. Soc.* **1982**, *104*, 1733.
(40) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. *J. Org. Chem.* **1983**, *48*, 2808.
(41) Shin, D.-M.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 5206.
(42) Khoo, I. C.; Zhuang, S.-L. *Appl. Phys. Lett.* **1980**, *37*, 3.
(43) Khoo, I. C. *Phys. Rev. A* **1981**, *23*, 2077.
(44) Durbin, S. D.; Arakelian, S. M.; Shen, Y. R. *Phys. Rev. Lett.* **1981**, *47*, 1411.
(45) Herman, R. M.; Serinko, R. J. *Phys. Rev. A* **1979**, *19*, 1757.
(46) Wong, G. K. L.; Shen, Y. R. *Phys. Rev. Lett.* **1973**, *30*, 895.
(47) Wong, G. K. L.; Shen, Y. R. *Phys. Rev. A* **1974**, *10*, 1277.
(48) Prost, J.; Lalanne, J. R. *Phys. Rev. A* **1973**, *8*, 2090.
(49) Shelton, J. W.; Shen, Y. R. *Phys. Rev. Lett.* **1970**, *25*, 23.
(50) Shelton, J. W.; Shen, Y. R. *Phys. Rev. A* **1972**, *5*, 1867.
(51) Herman, R. M.; Serinko, R. J. *Phys. Rev. A* **1979**, *19*, 1757.

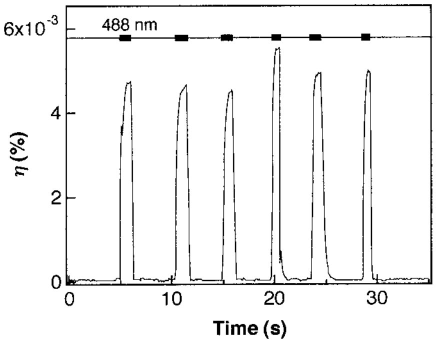

Figure 5. Switching behavior of the diffraction beam by turning on and off the writing beams. The writing beams intersected in the sample film at an incident angle of $\theta = 10°$, leading to the formation of the grating with the fringe spacing of 1.4 μm.

relating to the optical and electrical switching of the diffraction beam by low molecular weight liquid crystals (LMWLCs)[12-15] and polymer-dispersed liquid crystals.[52-55] Although several studies on holographic recording were reported by Wendorff et al.,[56-58] very little study has been performed so far on the all optically controlled dynamic grating using PLCs.

The formation of the dynamic grating was observed only in the sample film showing birefringence, eliminating the possibility of the thermal and population grating. Therefore, it can be assumed that the grating is formed due to the periodic induction of the photochemical N−I phase transition by interference of the two coherent beams. To confirm that the observed grating is certainly owing to the photochemical phase transition in origin, we attempted polarizing microscopic observation of the recorded grating in the PLC film. The recording of the grating was performed by the following procedure. The grating was written first in the PLC film at 100 °C, and then the film was cooled to room temperature during irradiation of the writing beams. Figure 6 displays a polarization micrograph of the grating observed through crossed polarizers. It was found that dark lines were periodically created in the PLC film, which were optically isotropic regions because no angular dependence was observed. As shown in Figure 3, irradiation of **PLC 1** with the pumping light at 488 nm caused the N−I phase transition due to the trans−cis photoisomerization of the azobenzene moiety. Consequently, appearance of the I regions is attributable to the photochemical N−I phase transition, leading to the formation of the grating based on the difference in the refractive index between the I phase and the N phase (Figure 7). Induction of the photochemical phase transition at room temperature has been already achieved in our homopolymer system.[23] If irradiation of the sample film prepared from the homopolymer with the interference light is performed below its glass transition temperature, such a system will act as a material for the real-time holographic recording.

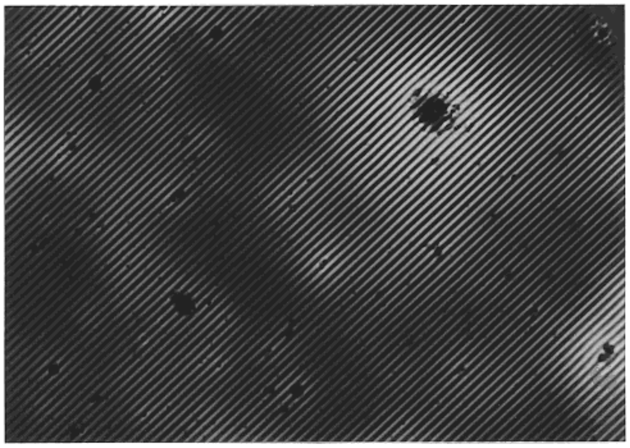

Figure 6. Polarization micrographs of recorded grating with a fringe spacing of ∼2 μm in the PLC film.

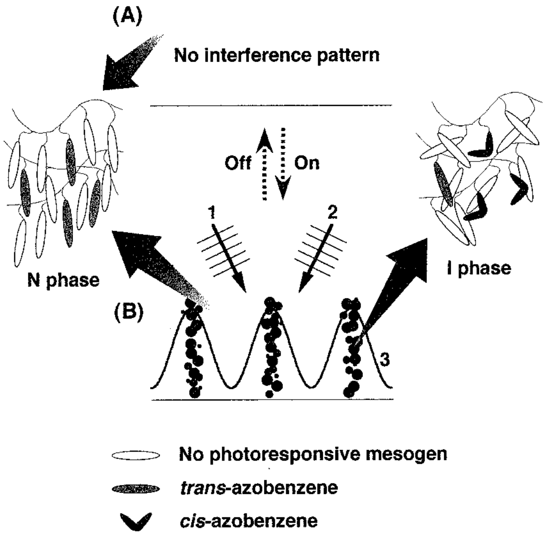

Figure 7. Schematic illustration of formation and removal of grating: 1 and 2, writing beams; 3, interference fringe; (A) an initial N phase before irradiation of writing beams; (B) induction of the N−I phase transition at bright regions of the interference pattern.

Effect of Thickness of the PLC Film on the Diffraction Efficiency. The molar extinction coefficient of **PLC 1** at ∼500 nm is so large (∼10^4) that the writing beam may be absorbed only in the surface of the sample film. Then, the trans−cis photoisomerization may also be induced near the surface and the N−I phase transition occurs only in the surface. In general, the diffraction efficiency (η) of index-of-refraction gratings is represented by the following equation[31]

$$\eta = \left(\frac{\pi d \Delta n}{\lambda}\right)^2 \qquad (2)$$

where d is a film thickness, Δn represents the degree of the change in the refractive index, and λ is the wavelength of the reading beam. If the grating is created even in the bulk region and both Δn and λ are constant, the diffraction efficiency will be proportional to the square of the film thickness. To confirm the formation of the grating in the whole of the bulk of the PLC film,

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(52) Sutherland, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Bunning, T. J. *Chem. Mater.* **1993**, *5*, 1533.
(53) Sutherland, R. L.; Tondiglia, V. P.; Natarajan, L. V.; Bunning, T. J.; Adams, W. W. *Appl. Phys. Lett.* **1994**, *64*, 1074.
(54) Zhang, J.; Sponsler, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 1506.
(55) Doane, J. W.; Vas, N. A.; Wu, B.-G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269.
(56) Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 59.
(57) Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 467.
(58) Eich, M.; Wendorff, J. H. *J. Opt. Soc. Am. B* **1990**, *7*, 1428.

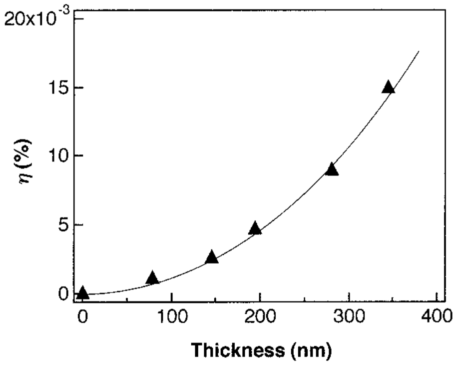

Figure 8. Effect of film thickness on the diffraction efficiency at 100 °C: total intensity of writing beam, 0.92 W/cm^2; fringe spacing, ~2.0 μm.

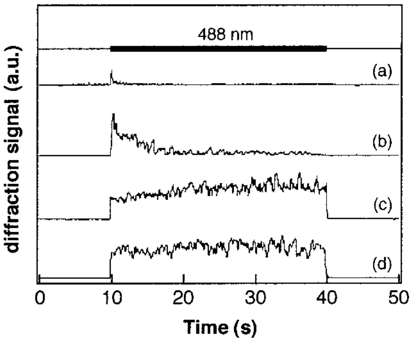

Figure 9. Effect of fringe spacing (Λ) on diffraction beam profiles: (a) 0.71 μm, (b) 0.94 μm, (c) 1.4 μm, and (d) 2.3 μm. Irradiation of PLC film with writing beams (total intensity, 1.3 W/cm^2) was performed at 100 °C.

the thickness dependence of the diffraction efficiency was investigated (Figure 8). It was found that the diffraction efficiency increased upon increasing the film thickness, and the experimental data could be fitted by the quadratic function. This result indicates that the writing beams can penetrate deeply into the sample and the grating can be created not only in the surface but also in the bulk region.

Effect of the Incident Angle of the Writing Beam on the Dynamic Grating. The effect of the incident angle of the writing beams on the formation of the dynamic grating was investigated. The incident angle (θ) of each writing beam was varied from 20° to 6°, leading to the change in the fringe spacing from 0.71 to 2.3 μm. As shown in Figure 9, when the fringe spacing was smaller than 0.94 μm, only transient signals of the diffraction beam were observed. Such a decay of the diffraction signals may be due to disappearance of the difference in the refractive index between the bright and dark regions, which results from decrease in the orientational order of the mesogens at the dark regions by propagation of perturbation of the N−I phase transition. The stable grating could be created at the fringe spacing of >1.4 μm, which is narrower than that of the conventional dynamic grating using LMWLCs.$^{12-15}$ In the LMWLC systems containing photochromic molecules, the formation of the stable dynamic grating with the fringe spacing of <2 μm may be very difficult due to diffusion of the mesogens and the photochromic molecules.$^{59-61}$ On the other hand, in polymeric systems, the mobility of the mesogens would be suppressed because they are covalently bonded to the main chain. Therefore, the formation of the grating with high resolution would be attributable to the low mobility of the mesogen.

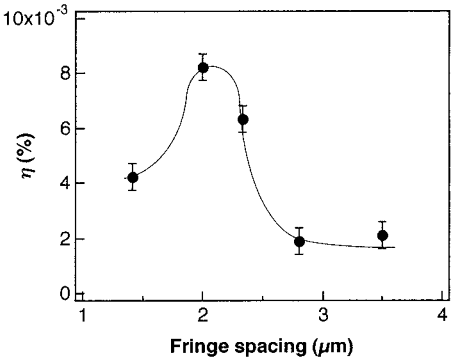

Figure 10. Effect of fringe spacing on diffraction efficiency in **PLC 1** at the intensity of the writing beams of 1.3 W/cm^2 at 100 °C.

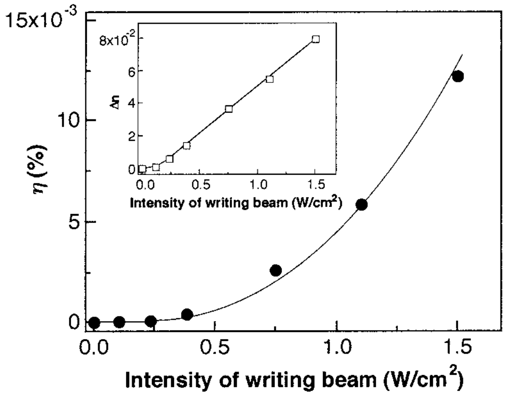

Figure 11. Effect of the intensity of the writing beams on the diffraction efficiency at 100 °C. Inset: relation between Δn and the intensity of the writing beams.

Figure 10 shows the influence of the incident angle of the writing beams on the diffraction efficiency. The diffraction efficiency was affected by the fringe spacing, and the optimal spacing was 2 μm. The decrease in the diffraction efficiency in the narrow spacing region can be explained in the same way as in Figure 9. Namely, the alignment of the mesogens at the dark regions is distorted by the perturbation of the N−I phase transition, leading to disappearance of the difference in the refractive index between the bright and the dark regions. On the other hand, the decrease in the diffraction efficiency in the wider spacing region at >2 μm is not clear at the present stage of research.

Effect of the Intensity of the Writing Beam on the Dynamic Grating. The diffraction efficiency as a function of the intensity of the writing beams is illustrated in Figure 11. It is clear that the diffraction efficiency depended upon the beam intensity. As mentioned above, the efficiency is governed by three parameters: Δn, λ, and d. In this case, λ and d were 633 and 200 nm, respectively. Consequently, such intensity dependence of the diffraction efficiency would be related only to Δn and can be explained in terms of Δn as a function of the intensity of the writing beams. The inset

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(59) Hara, M.; Takezoe, H.; Fukuda, A, *Jpn. J. Appl. Phys.* **1986**, *25*, 1756.

(60) Terazima, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1881.

(61) Jin, D.; Kim, H.; Kim, S. H.; Kim, S. K. *J. Phys. Chem. B* **1997**, *101*, 10757.

of Figure 11 shows the effect of the intensity on Δn of **PLC 1**, where the value of Δn was determined by eq 2 and the experimental data of Figure 11. The refractive index was modulated on the order of 10^{-2}, which is large compared to previously reported values.[4−10] Moreover, Δn was affected by the beam intensity. In the present system, the modulation of the refractive index is ascribed to the N−I phase transition, which is caused by the photochemical reaction of the azobenzene moiety. The amount of *cis*-azobenzene produced upon photoirradiation depends on the intensity of light, so the number or the size of the I domains produced by the N−I phase transition, i.e., the degree of the N−I phase transition, would be also influenced by the intensity of the irradiation light.[22] Thus the N−I phase transition would be caused effectively at high intensity because of the large amount of *cis*-azobenzene. On the contrary, a small amount of *cis*-azobenzene was produced at low intensity, so the degree of the N−I phase transition decreases. The intensity dependence of Δn would be due to the difference in the degree of the N−I phase transition. Furthermore, it should be noted that the diffraction signals could be little observed at the intensity of ≤ 0.23 W/cm^2. This result indicates that the obtained grating has a threshold value relating to the intensity of the writing beam. In general, there is no threshold value in the photochemical reaction, so the *cis*-azobenzenes would be produced even upon photoirradiation with lower intensity. Then the *cis*-azobenzenes may induce only a small size of the I domains around them. However, the probe beam detects a macroscopic phenomenon, and we can observe an averaged state of the sample. Therefore, the presence of the threshold value would be due to the lack of the size of the I domains which the probe beam can recognize.

Conclusion

All-optical switching of a diffraction beam based on photochemical phase transition has been studied in the PLC containing an azobenzene moiety in the side chain. It was found that the periodical change in the phase structure could be caused reversibly by the photochemical reaction of azobenzene moiety and led to formation of the dynamic grating following Δn of the order of 10^{-2}. This system showed response times of ∼150 and ∼190 ms on production and removal of the grating, respectively, and a narrow fringe spacing of 1.4 μm was achieved. Furthermore, the optical switching behavior of the holographic diffraction was observed repeatedly by turning on and off the writing beams. In the future work, improvement of the diffraction efficiency is very important because the diffraction efficiency obtained in this study is relatively low. One of the essential approaches is to get larger values of Δn, which will be achieved by introduction of side chain mesogens showing birefringence larger than that used in this study.

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