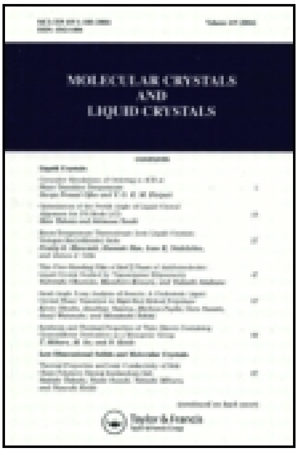

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Refractive-Index Modulation by Means of Photosensitive Liquid Crystals

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Refractive-Index Modulation by Means of Photosensitive Liquid Crystals

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Liquid crystals (LCs) show an anisotropic nature in various aspects of optical and electronic properties. This anisotropy enables LC materials to be used as active media in display devices. Birefringence, an anisotropy in optical properties of LCs, is especially useful from the viewpoint of the change in refractive index induced by light. This is the principle of LC photonics, in which optical signals are processed with the aid of LC materials. In this article, various approaches are described to change the alignment of the LC molecules: 1) photochemically induced phase transition of LCs by photochromic reactions is an order to disorder transition and can be brought about in a time scale of micro- to nanosecond; 2) reorientation of LC molecules by means of linearly polarized light is a change in alignment of LC molecules that occurs within the LC phases and induces a large change in refractive index, but needs more time. Applications of LC systems as holographic materials are discussed.

Keywords Azobenzene; Holographic Grating; Photochemical Phase Transition; Photoinduced Alignment Change; Polymer Liquid Crystals; Refractive-Index Modulation;

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INTRODUCTION

We will soon have an information society where a huge amount of information is exchanged simultaneously all over the world through optical fiber networks. We will need optical elements that have such functions as switching, storage, interconnection, and computing of optical signals transported through the optical fibers. To process optical data, it is most effective to modulate refractive indices of the optical elements. Especially, refractive-index modulation by light as a stimulus is regarded as a final goal for optical elements that can change their refractive index as much and as fast as possible upon photoirradiation.

Liquid crystals (LCs) show unique and excellent properties such as 1) anisotropy in refractive index (birefringence); 2) a cooperative effect; 3) a self-organizing nature in a certain temperature range with fluidity; 4) alignment change by external fields. These properties will lead to a unique feature of LCs: a large change in refractive index can be obtained by changing the alignment of LCs. This property of LCs is very useful for refractive-index modulation, which in turn is quite favorable for optical data processing, because as described above to change the refractive index of materials or devices by external fields is the most effective way to control optical signals.

Two types of photoinduced alignment change of LC molecules would be possible: 1) change in director of LCs in LC phases; 2) change in phases (phase transition) as shown in Fig. 1. In both cases, a large change in the refractive index is obtained; however, the former will be preferable in view of a larger change in the refractive index. In the case where one employs linearly polarized light as probe light and the polarization of the probe light is parallel to the director of LCs, the probe light detects n_e (extraordinary refractive index). If the director of LCs is changed perpendicular to the initial direction by another light as a stimulus, the probe light will then detect n_o (ordinary refractive index). This will lead to a change in the refractive index corresponding to birefringence ($\Delta n = n_e - n_o$). LCs possess large values of Δn ($\Delta n > 0.1$), so we can obtain such large changes in the refractive index by the photoinduced alignment change of LCs (Fig. 1A). If the refractive index of an isotropic phase of LCs is denoted by n, the order of the refractive index is usually $n_o < n < n_e$. Then we can still have a large change in the refractive index by inducing an LC to isotropic (I) phase transition of LC materials by light (Fig. 1B).

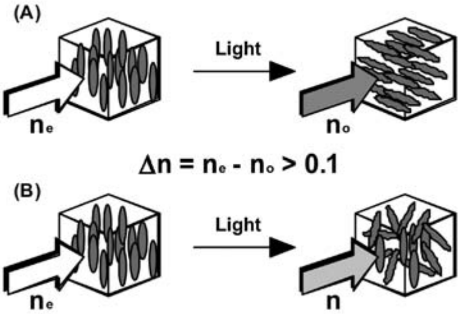

FIGURE 1 Modulation of alignment of liquid crystals. (A) change in director of LCs in LC phases; (B) change in phases (phase transition).

Photochemically induced phase transition is one of the approaches to realize an effective modulation of the alignment of LCs with azobenzene derivatives. For instance, azobenzene in *trans*-form is inclined to stabilize the LC phase because of its rod-like molecular shape. On the other hand, *cis*-form is bent and has an opposite function to the stability of the phase structure. As a result, *cis*-azobenzene lowers LC-I phase transition temperature of LCs. If the phase transition temperature becomes lower than the irradiation temperature, an isothermal LC-I phase transition is induced (***photochemical phase transition***) in these guest/host systems.

The important feature of azobenzene LCs, in which the azobenzene moiety plays both roles as a mesogens and a photosensitive moiety, is that they show an LC phase only when the azobenzene moiety is in the *trans*-form while they never show any LC phase at any temperature when the azobenzene moiety is in the *cis*-form. This enables the azobenzene LCs to undergo the LC-I phase transition instantaneously when the photoisomerization is induced with a short laser pulse [1]. Our recent research has revealed that the photochemical phase transition of polymer azobenzene LCs occurs in nanosecond timescale (~ 200 ns) by irradiation with a single shot of a laser pulse (25 ps, fwhm).

As described above, LC materials have large optical anisotropy resulting from self-assembly characteristics and provide additional features such as an ability to respond to applied external fields. These features are quite favorable from the viewpoint of formation of rewritable phase-type holograms as well as realization of dynamic holography. In the past decade, with the aim of 2-D or 3-D image recording, many studies have been performed on the refractive-index-modulated holographic grating using LC materials [2-7]. However, it is often difficult to obtain a holographic grating showing a narrow fringe spacing (i.e., high resolution) and high stability because of the high mobility of LC molecules. It is easy to imagine that side-chain polymer LCs (PLCs) may be one of the most promising materials in holography, because they possess not only high viscosity due to polymer structure but also superior LC properties in which flexible side-chain spacers play a crucial role to decouple the motion of the polymer backbone from that of the aligned mesogens. Wendorff et al. have shown for the first time that a holographic recording can be built into PLCs containing azobenzene moieties in the side-chain. It was reported that the formation of phase-type gratings based on difference in the refractive index between *trans*-azobenzene and *cis*-azobenzene could be achieved in PLCs with an azobenzene moiety [8].

In this paper, we report the formation of holographic gratings by means of two types of refractive-index modulation of PLCs with an azobenzene moiety. It was expected that additional properties, which could not be observed in the conventional surface-relief gratings would emerge in this study: Refractive-index modulation (**Δn**) in the formation of gratings might become an important factor.

EXPERIMENTAL

Materials

Figure 2 shows the structure, molecular weight and thermodynamic property of PLCs with azobenzene moieties as well as their abbreviation used in this study. These polymers were prepared using a procedure similar to the literature [9,10]. The molecular weight of the polymer was determined by gel permeation chromatography calibrated with standard polystyrenes. The thermal properties of PLCs were examined on a polarizing optical microscope equipped with Mettler hot-stage. Thermotropic property was determined with a differential scanning calorimeter at a heating rate of 10 C/min.

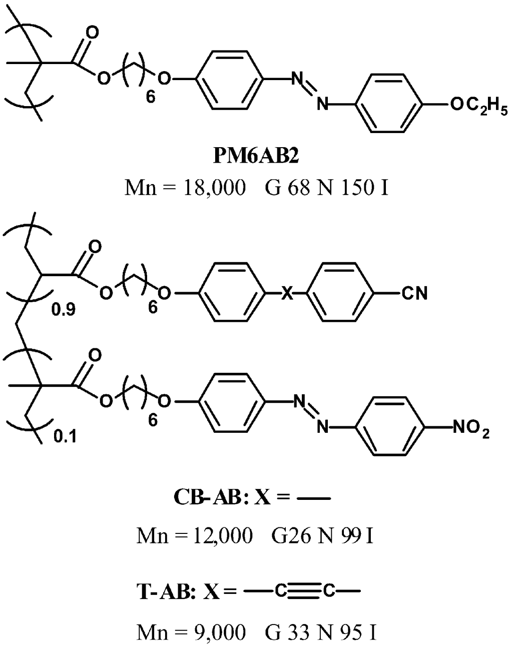

FIGURE 2 Chemical structures and properties of PLCs used in this study. Mn, number-average molecular weight; G, glass; N, nematic; I, isotropic phase.

Formation of Holographic Gratings

In order to obtain uniaxially aligned films, PLCs were dissolved in tetrahydrofuran (2 mg/ml) and then the polymer solution was cast on the glass substrate, which had been rubbed unidirectionally. An optically transparent and homogeneously aligned film was obtained after annealing the film at a temperature just below the nematic (N) to I phase transition temperature of PLCs. Thickness of the films was measured with a profile measurement microscope (Keyence, Model VF-7500). Formation of gratings in the PLCs was performed by the following procedure similar to the literatures [11,12]. In this study, two beams from an Ar^+ laser at 488 nm were used as writing beams. The incident angle between the writing beams was fixed at $\theta = 14$ (fringe spacing (Λ): 2 μm). Diffraction efficiency (η) was defined as the ratio of the intensity of the first-order diffraction beam (He-Ne laser at 633 nm) to that of the transmitted beam through the film in the absence of the writing beams. Photoinduced refractive-index modulation of PLCs was investigated as follows. The sample film placed in a thermostated block was irradiated with light from an Ar^+ laser. Intensity of the probe light from a He-Ne laser transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

RESULTS AND DISCUSSION

Formation of Phase-Type Grating Based on Photochemical Phase Transition

Figure 3(A) and (B) show dynamics in the first-order diffraction efficiency as a function of exposure energy at 80 C and room temperature, respectively. Multiple diffraction beams were immediately observed on exposure to unpolarized 488-nm writing beams at each temperature, since the grating formation was conducted in the Raman-Nath regime in this study. During exposure at 80 C, the η increased and reached to its maximum value (~ 20 %), and then gradually decreased. On the other hand, no decay was observed when the film was exposed to the writing beams at room temperature. The η was close to a saturated value (~ 25 %). Dashed line in each figure indicates an exposure energy at which the gratings exhibited the same value of η (= 20 %). The exposure energy needed for η = 20 % was approximately 13 J/cm^2 in the N phase and 300 J/cm^2 in the glassy state. It is clear that effective formation of the grating was achieved in the N phase. In other words, the sensitivity of material was improved by 23 times in the LC phase. In PLCs, mobility of mesogens in the LC phase is extremely high compared with that in the glassy state.

Previously, we reported that the grating formation in polymer azobenzene LCs is associated with photochemical phase transition: the photochemical phase transition of polymer azobenzene LCs proceeds even at room temperature, but it is induced readily in the LC phases [1]. It is, therefore, reasonable to consider that this improvement in the sensitivity is attributed to an effective induction of the photochemical phase transition, which occurred in bright areas of the interference pattern.

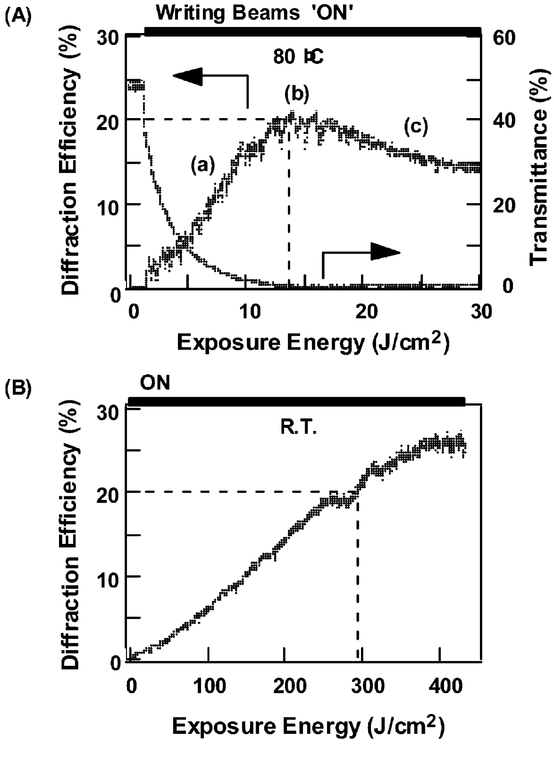

FIGURE 3 First-order diffraction efficiency (η) as a function of exposure energy at 80 C (A) and at room temperature (B). Dashed line in each figure indicates an exposure energy needed for η = 20 %. Figure 3(A) also shows the change in transmittance by photochemical phase transition of **PM6AB2**.

Mechanism for Grating Formation Based on Photochemical Phase Transition

Figure 3(A) also shows the change in transmittance due to photochemical phase transition of **PM6AB2**. An unpolarized 488-nm beam from the Ar^+ laser was employed as the pumping beam. The transmittance of the probe beam gradually decreased on irradiation of the pumping beam, which caused *trans-cis* photoisomerization of azobenzene moieties. From dynamics both of the grating formation and of the photochemical phase transition, we can speculate that the formation of grating in the film consists of three processes ((a), (b) and (c) as shown in Figure 3(A)). Mechanism of the formation of surface relief grating (SRG) on polymer films was extensively discussed by Natansohn et al. [13,14]. In this study, we only discuss the mechanism for grating formation in the film, which is schematically illustrated in Figure 4 where processes (a), (b) and (c) in Figure 3(A) are supposed to correspond to (a), (b) and (c) in Figure 4, respectively. In process (a), *trans-cis* photoisomerization generates I domains in bright areas of the pattern, which grow on further irradiation. Assuming that refractive indices of the N and I phases are denoted as n and n', respectively, difference in the refractive index (**Δn**) between n (the dark areas) and n' (the bright areas) becomes larger during exposure because the photochemical phase transition proceeds. Hence, the η increases. In the process (b), the η reaches to a maximum value, indicating that the photochemical phase transition is completed in the bright areas and **Δn** becomes maximum. Change in the transmittance supports our consideration. Further irradiation of the writing beams brings about the decay of the η (process (c)). This means that **Δn** becomes smaller. In other words, the orientational order of the azobenzene moieties decreases in the dark areas of the pattern. Two factors may be responsible for the decrease. One is induction of the photochemical phase transition in the dark areas. Since distribution of light intensity on the film is expressed as a sinusoidal curve, photochemical reaction may occur even in the dark areas, so that the photochemical phase transition can take place gradually from the boundary between the dark and the bright areas of the pattern. The other is propagation of perturbation of the phase transition to the dark areas [11,12]. This also induces the orientational relaxation of mesogens in the dark areas.

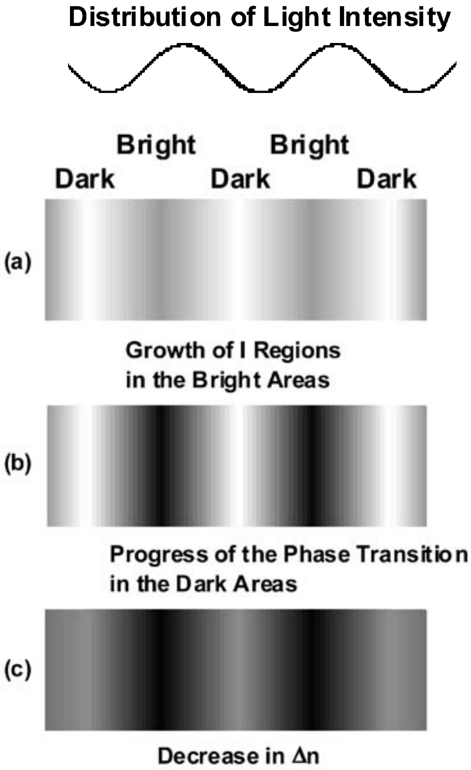

FIGURE 4 Plausible mechanism for the formation of grating in the **PM6AB2** film. States (a), (b) and (c) correspond to the processes shown in Figure 3(A). (a): Growth of the isotropic domains in bright areas of the interference pattern; (b): complete induction of the photochemical phase transition in bright areas; (c): induction of the photochemical phase transition even in the dark areas.

Formation of Phase-Type Grating Based on Photoinduced Alignment Change

The photoinduced alignment behavior has been studied in azopolymer systems [15-18]. In most cases, the photoinduced alignment change is induced from a polydomain state to a monodomain state, whose alignment direction is perpendicular to that of the electric field vector of the polarized light. In this study, on the other hand, the photoinduced alignment change was brought about in the monodomain state: the direction of alignment of mesogens in the PLC was changed to other direction using a uniaxially aligned PLC film. As shown in Fig. 5, in the initial state, probe light was observed through a pair of crossed polarizers, with the sample film between them, owing to birefringence of the PLC. Transmittance of the probe light decayed on irradiation of linearly polarized light at 488 nm in the N phase. This was caused by the photochemical N-I phase transition of PLC due to *trans-cis* photoisomerization of the azobenzene moieties. On further irradiation, the transmittance gradually increased and finally became saturated. This result indicates that photoinduced alignment change of mesogens was induced by *trans-cis-trans* isomerization cycles of the azobenzene moieties. When photoirradiation was ceased, transmittance of the probe light slightly increased. This process is due to thermal *cis-trans* back-isomerization of the azobenzene moieties and subsequent thermal self-organization of the LC.

We attempted the formation of gratings using photoinduced alignment change of PLCs. Fig. 5 shows the change in intensity of diffracted light as a function of irradiation time. Intensity of the linearly polarized light was 120 mW/cm^2. When photoirradiation was carried out at 70 C, we observed η of 4.5 %. Intensity of the diffracted light increased first, then decreased with irradiation time. The efficiency of alignment change in the bright areas of the interference patterns increased with irradiation time. At the same time, however, the orientational relaxation of mesogens may occur in the dark areas of the interference patterns due to the cooperative effects of mesogens. This is likely to reduce the difference in refractive index between the dark and the bright areas and leads to a decrease in η. To clarify the mechanism of grating formation in detail, we explored the relation between the diffracted light intensity and the photoinduced alignment behavior. Fig. 5 (A) also shows dynamics of the change in transmittance by alignment change and diffraction intensity of the **CB-AB** film. As is apparent from the change in the diffracted light intensity and the transmittance, η showed a maximum when the transmittance of probe light was nearly saturated. This result indicates that when the photoinduced alignment change is almost completed in the bright areas of the interference patterns, the maximum η is obtained since the difference in the refractive index between the bright and the dark areas becomes maximum.

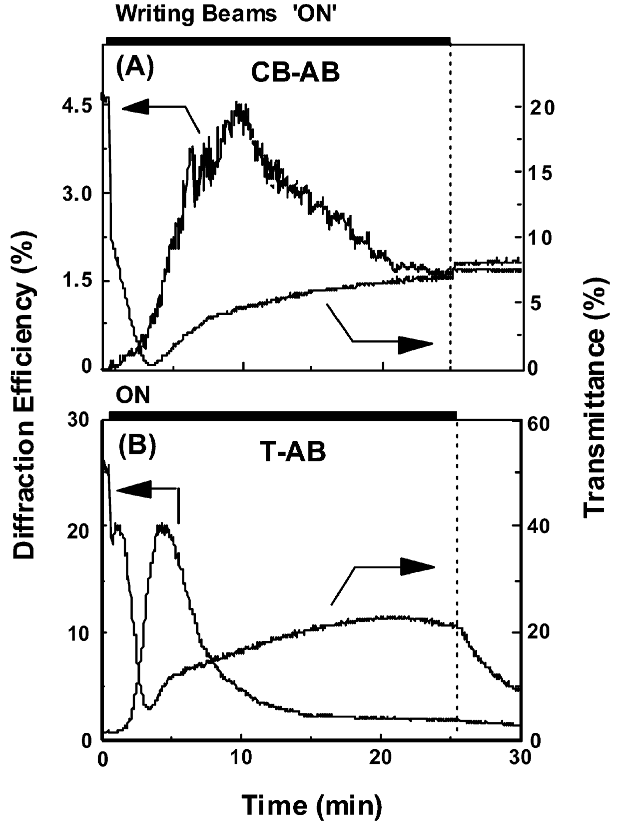

FIGURE 5 Change in the diffraction efficiency and transmittance of the **CB-AB** film at 70 C (A) and the **T-AB** film at 60 C (B). Photoirradiation was performed at 488 nm at an incident angle of θ = 14 . Film thickness, 1,200 nm; light intensity, 120 mW/cm^2.

The η and the modulation of the refractive index (**Δn**) were not very high (5 % and 0.04, respectively) on the grating formation in **CB-AB**. However, introduction of the tolane moiety with high birefringence at the side chain enabled to achieve the value of η about 20% and the maximum value for **Δn** of about 0.08 (Fig 5 (B)). It was revealed that η and **Δn** are dependent on the structure of the mesogenic unit.

Novel Approach to Fast Response of Grating Formation

Wendorff et al. recently reported that thermal amplification of η in a low molecular weight azobenzene LC [19]. They demonstrated the enhancement of photoinduced alignment of LC molecules and a significant amplification of the amplitude of SRG during the thermal development. In this study, we investigated the mechanism of large enhancement of η in the PLCs films.

Materials and optical setup used in this study were the same as those of the preceding sections (Fig. 5). After grating formation, the surface structure of the PLC films was investigated with an AFM. Photoirradiation was performed at 85 C for 500 ms. After a grating was recorded, the films were cooled to room temperature, and their surface profiles were observed at room temperature.

Figure 6 shows change in the diffraction beam at 85 C (light intensity, 900 mW/cm^2; the exposure time, 500 ms). In the **T-AB** film, on irradiation of the writing beams, the η increased and decreased within 500 ms. However, when the writing beams were turned off, the η rapidly increased and attained a maximum value (< 20 %) within 1 s. This value was larger than those previously reported under similar experimental conditions [20]. Furthermore, it is worth mentioning that η of 20 % was acquired with a extremely low dose (< 450 mJ/cm^2) compared to that of a recent report (< 15 J/cm^2). When the η showed a maximum, the sample film was rapidly quenched by a metal plate. One can see the stable grating without significant change in η at room temperature. The surface structure of the **T-AB** film was investigated with an AFM. Periodic structure of the SRG was about 2 μm wide and its height was about 15 ~ 20 nm. Tripathy et al. reported that when a small surface modulation (about 10 nm) is produced, η shows a small value (< 1 %). Therefore, the mechanism of grating formation in this study cannot be explained on the basis of SRG. We explored the detail mechanism from the viewpoint of modulation of refractive index of PLCs. **Δn** was evaluated using the values of η and film thickness with an assumption that the grating formation is entirely due to refractive-index modulation of LCs and the contribution of surface modulation is negligible. The calculated value of **Δn** was about 0.07. Transmittance (T) of probe light passed through a pair of crossed polarizers, with a uniaxially aligned film between them, is defined by the following equation,

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

where d is film thickness (1,200 nm), Δn is birefringence of sample film and λ is the wavelength of the probe light (633 nm), respectively. Before irradiation, the calculated birefringence of the **T-AB** film was 0.08. This result indicates that periodic refractive-index modulation based on the birefringence of PLCs may be induced in the interference pattern. The plausible mechanism of enhancement of η is schematically illustrated in Fig. 7.

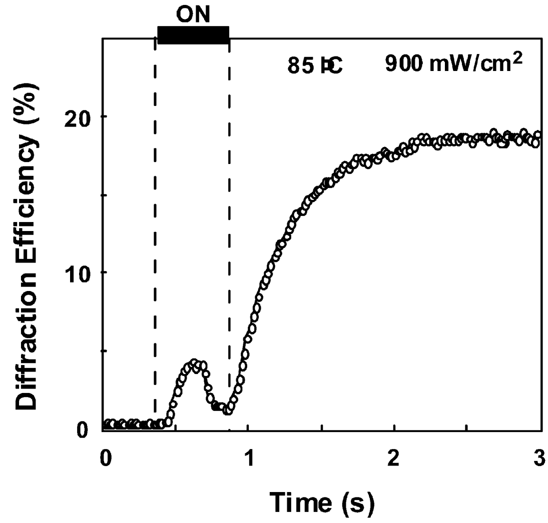

FIGURE 6 Enhancement of diffraction efficiency on grating formation in the **T-AB** film.

Stumpe et al. reported the out-of-plane alignment of PLCs by linearly polarized light [21]. Upon irradiation with linearly polarized light a photo-orientation process occurs in PLC films, which results in an optical in-plane anisotropy. The annealing of the films above *Tg* leads to a homeotropic alignment of PLC in the center of the irradiated area. In this study, photoirradiation was carried out above *Tg*, and a similar result may have been obtained on the photoinduced alignment change. Further experiments are currently in progress to obtain detailed understanding of the out-of-plane alignment behavior on the photoinduced alignment of PLC molecules.

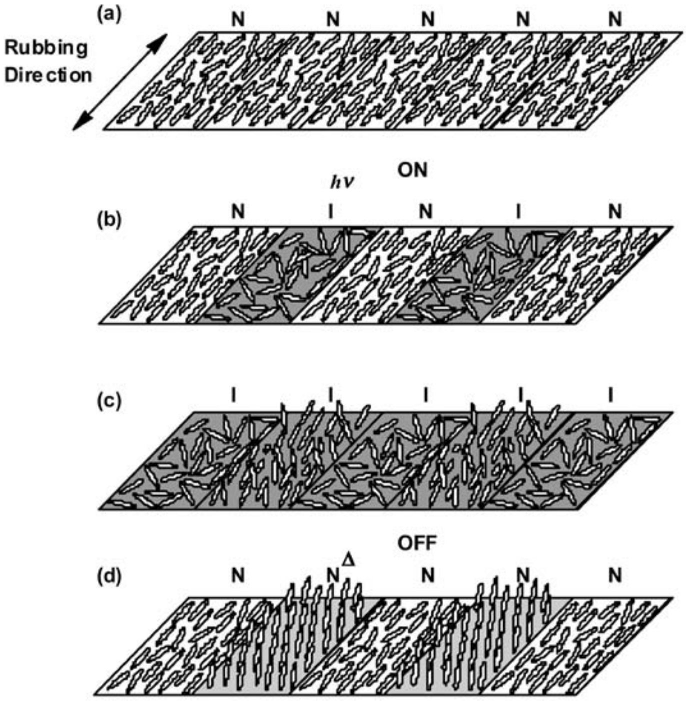

FIGURE 7 Plausible mechanism of enhancement of diffraction efficiency on grating formation in the **T-AB** film.

CONCLUSION

We explored the formation of holographic gratings by means of two types of modulation of refractive index of PLCs with an azobenzene moiety. When the grating formation was carried out in the N phase, a large enhancement of η and a faster response were observed under appropriate conditions. These results indicate that the spatial modulation of the refractive index, which results from the periodic induction of the photochemical phase transition, would mainly contribute to the grating formation. It was also proved that the grating formation based on alignment change of mesogens is strongly affected by the structure of the mesogenic unit. The effect of birefringence of PLCs indicates that a considerable enhancement of η can be achieved by using PLC with a tolane moiety, but more time is need. We investigated a novel approach to the fast response of grating formation based on photoinduced alignment change of PLCs. On irradiation of the high-intensity writing beams, the intensity of the diffraction beam increased and decreased within 500 ms. However, when the writing beams were turned off, the η rapidly increased and attained a maximum value (< 20 %) within 1 s. Furthermore, it is worth mentioning that η of 20 % was acquired with an extremely low dose. We explored the detail mechanism from the viewpoint of modulation of refractive index of PLCs. It was found that periodic refractive-index modulation based on the birefringence of PLCs may be induced in the interference pattern. We believe that these results will contribute to development of various holographic applications such as optical switching and optical data storage.

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