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Formation of intensity grating in a polymer liquid crystal with a side-chain azobenzene moiety by photoinduced alignment change of mesogens

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We studied the behavior of photoinduced alignment change of a polymer liquid crystal (PLC) containing an azobenzene moiety in the side chain and formation of a grating by means of the photoinduced alignment of PLCs. The alignment change was evaluated by irradiation with s-polarized light at 488 nm. We investigated the effects of light intensity and incident angles of writing beams (two s-polarized (**s**+**s**) configuration) on grating formation in PLC films, and explored the relation between the alignment change and diffraction efficiency. The diffraction efficiency showed a maximum when the change in photoinduced alignment was almost complete in the bright area of interference patterns. The maximum value obtained for the modulation of the refractive index was 0.04. These results indicate that a PLC with an azobenzene moiety is effective under (**s**+**s**) polarization conditions, compared with other azopolymer systems.

Introduction

The photoinduced birefringence of azopolymer systems has been extensively studied.[1–3] It has been known for more than a decade that linearly polarized light can induce reorientation of azobenzene groups through photochemical *trans–cis–trans* isomerization cycles.[4] Using polarized light, azobenzene moieties attached to the polymer chains are aligned perpendicular to the direction of the electric field vector of the incident light. By using this property, polymers containing azobenzene moieties have been developed as materials for photonic applications. We revealed previously that the two-dimensional alignment behavior of polymer liquid crystals (PLCs) containing azobenzene moieties in the side chain was influenced by the intensity of linearly polarized light,[5] the length of spacer unit,[6] the structure of the azobenzene units,[7] and the azobenzene moiety content.[8]

PLCs are known as high-performance materials for optical storage due to their large optical anisotropy and high stability below the glass transition temperature (T_g).[9–16] In fact, since Wendorff *et al.* demonstrated holographic data storage in PLCs with side-chain azobenzene moieties in 1987,[11] there has been a lot of interest in this area. It was reported that the formation of phase-type gratings based on the difference in the refractive index between *trans*-azobenzene and *cis*-azobenzene could be achieved in PLCs with azobenzene moieties.[12] However, the detailed mechanism of the formation of phase-type gratings is not clear.

The holographic grating process has been extensively studied using functionalized polymers with side-chain azobenzene groups.[9–12,17–27] In most cases, the grating has been formed by the use of polarized light as writing beams. However, the behavior of the grating formation differs according to the polarization configuration of the writing beams. Tripathy *et al.* and Sourisseau *et al.* explained this difference as follows.[23,24] Two p-polarized (**p**+**p**) and two circularly polarized (**co-**+**contra-circ.**) configurations give rise to the greatest magnitude of surface modulation of polymer films (several hundred nm) with diffraction efficiency (η) of up to 30%. Under the orthogonal (**p**+**s**) polarization condition, the efficiency is very low (<1%) with a small surface modulation (<10 nm). Furthermore, the two s-polarized (**s**+**s**) configuration produces a very small surface modulation, nearly negligible, (<few nm) and shows the smallest value of η (<0.1%). Then, the modulation of refractive index is smaller than that under other conditions (<0.01).

We previously reported formation of holographic gratings by means of the photochemical phase transition of PLCs containing azobenzene moieties.[13,14] A large modulation of the refractive index was induced by the photochemical phase transition in LCs based on the *trans–cis* photoisomerization of azobenzene molecules.[15,16] The degree of modulation of the refractive index in PLCs was much larger than that of amorphous polymers containing azobenzene moieties.[14] The modulation of refractive index in PLC arises from the difference in refractive index between a nematic (N) phase and an isotropic (I) phase.

We also studied the formation of holographic gratings by means of photoinduced alignment change of PLCs containing azobenzene moieties.[28] It was found that the grating formation is strongly affected by the stability of the LC phase structure. The mechanism of grating formation can be classified into two mechanisms. In a PLC with low thermal stability in an N phase, η reaches a maximum value when the orientational relaxation (photochemical phase transition) is complete in the bright area. On the other hand, in a PLC with relatively high thermal stability, η shows the maximum value when the photoinduced alignment is almost complete in the bright area.

In this paper, we studied the formation of holographic gratings and photoinduced alignment behavior using a PLC with a low content of azobenzene moieties in the side chain. We investigated in detail the effects of light intensity and incident angles of writing beams on intensity grating in a PLC under

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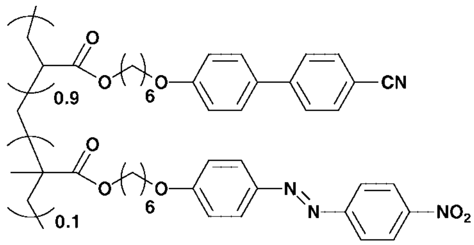

CB-AB

$M_n = 12000$; $M_w/M_n = 1.3$

G 26 N 99 I

Fig. 1 Chemical structure and properties of **CB-AB** used in this study. M_n, number-average molecular weight; M_w, weight-average molecular weight; G, glass; N, nematic; I, isotropic phase.

(**s**+**s**) polarization conditions. The aims of this work are to explore the detailed mechanism of grating formation and to enhance the diffraction efficiency and the modulation of refractive index from the viewpoints of alignment behavior of the PLCs.

Experimental

Material

The structure of a PLC with an azobenzene moiety as well as its abbreviation used in this study is represented in Fig. 1. This polymer was prepared using a procedure similar to the literature.[29] The mole fraction of the azobenzene monomer in the copolymer was 10 mol% as determined by absorption spectroscopy. The thermodynamic properties and molecular weight of PLC are shown in Fig. 1. Absorption spectra were recorded with a UV–vis absorption spectrometer (Japan Spectroscopic Co., V-550). Sample films were prepared by casting a THF solution (2×10^{-3} M) of the polymer on to a glass substrate which had been coated with poly(vinyl alcohol) and rubbed to align mesogens. Homogeneously aligned films were obtained after annealing. The thickness of the sample film was measured as about 1 μm with a profile measurement microscope (Keyence Co., VF-7500).

Photoinduced alignment change

The photoinduced alignment change of PLC was investigated by the following procedure. The polymer film placed in a thermostated block was irradiated with linearly polarized light from an Ar^+ laser (National Laser Co., H61WBLd0AW for a laser head; Laser Drive Inc., 9600 for a laser power supply). The wavelength was chosen at 488 nm. The direction of polarization of the pumping light was parallel to that of alignment of mesogens, *i.e.*, s-polarization. The intensity of the probe light at 633 nm from a He–Ne laser (NEC, GLC5370, 1 mW) transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode. The order parameter (S) of the PLC containing an azobenzene moiety was evaluated as reported previously.[5] We measured the absorbance with the polarized beam parallel ($A_{//}$) and perpendicular ($A_{\perp}$) to the polarization direction of the irradiation light. The order parameter was obtained by means of eqn. (1).

$$S = (A_{//} - A_{\perp})/(A_{//} + 2A_{\perp}) \quad (1)$$

Formation of holographic grating

The formation of a grating in the PLC was performed by a procedure similar to the literature.[13,14] In this study, two s-polarized beams from the Ar^+ laser at 488 nm were used as writing beams. The direction of the electric field vector of the incident light was parallel to that of uniaxial alignment. The incident angle of the writing beams was fixed at $\theta = 7°$ except for evaluation of the effect of fringe spacing. Diffraction efficiency (η) was defined as the ratio of the intensity of the first-order diffraction beam to that of the transmitted beam through the film in the absence of the writing beams.

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 80 °C) for 10 min. After grating was recorded at 80 °C, the films were cooled to room temperature, and then observation of the films was carried out at room temperature.

Results and discussion

Change in alignment of PLC

The photoinduced alignment behavior has been studied in azopolymer systems. 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 another direction using a uniaxially aligned PLC film. As shown in Fig. 2, 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 the PLC due to *trans–cis* photoisomerization of the azobenzene moieties.[13–15] 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.[6] 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.[7] To discuss the alignment change behavior quantitatively, the order parameter of the PLC was evaluated. The concept of the order parameter is used for describing the degree of orientational order of mesogens in PLCs. Fig. 3 shows polarized absorption spectra of the **CB-AB** film measured before and after irradiation with linearly polarized light at 488 nm at 80 °C. The absorption at 380 nm is due to the *trans*-azobenzene moiety, and we used this peak for the

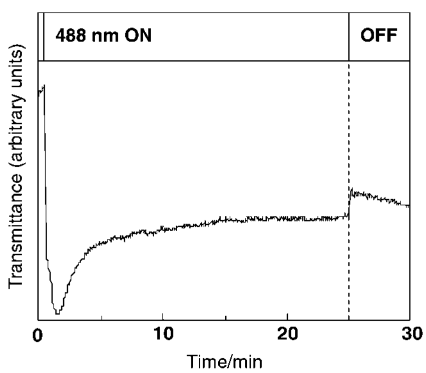

Fig. 2 Photoinduced alignment change in the **CB-AB** film by linearly polarized light at 80 °C. Photoirradiation was carried out at 488 nm with light intensity of 120 mW cm^{-2}.

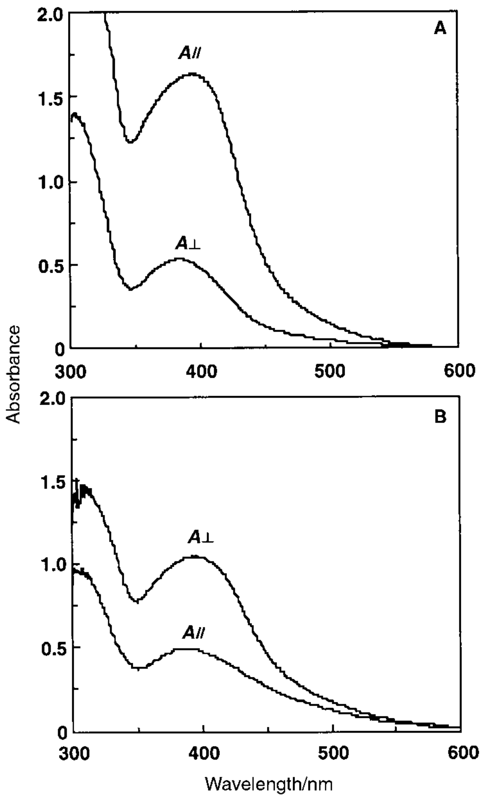

Fig. 3 Polarized absorption spectra of the **CB-AB** film: (A), before irradiation; (B), after irradiation with linearly polarized light at 488 nm at 80 °C. $A_{//}$ and $A_{\perp}$ are absorbances measured with a polarized beam parallel and perpendicular to the polarization direction of writing beams, respectively.

determination of the order parameter (S) of **CB-AB**. Before irradiation, the value of S was 0.40, which indicates a typical aligned NLC phase. After irradiation, the value of S changed to −0.23, indicating that alignment of mesogens in PLC is perpendicular to the electric vector of the irradiation light. Reduction of the total absorbance after irradiation could be due to the out-of-plane alignment of mesogens. Stumpe *et al.* reported the out-of-plane alignment of PLCs by linearly polarized light.[30] Upon irradiation with linearly polarized light a photoorientation process occurs in PLC films, which results in an optical in-plane anisotropy. The annealing of the films above T_g leads to a homeotropic alignment of PLC in the center of the irradiated area. Ichimura *et al.* also reported that prolonged irradiation with linearly polarized light brings about the photochemically induced out-of-plane reorientation of the azobenzene molecules, which is determined by the propagation direction of the actinic light, leading to the formation of H-aggregates.[31] In this study, photoirradiation was carried out above T_g, 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.

Grating formation in PLC

We attempted the formation of grating using the photoinduced alignment change of PLC. Fig. 4 shows the change in intensity of diffracted light as a function of irradiation time at various temperatures. The intensity of the writing beams was 120 mW cm^{-2}. This figure clearly shows that diffraction beams were generated when the writing beams were irradiated. The intensity of the diffracted light increased at first, but it decreased with irradiation time. When photoirradiation was carried out at 80 °C, we observed maximum diffraction

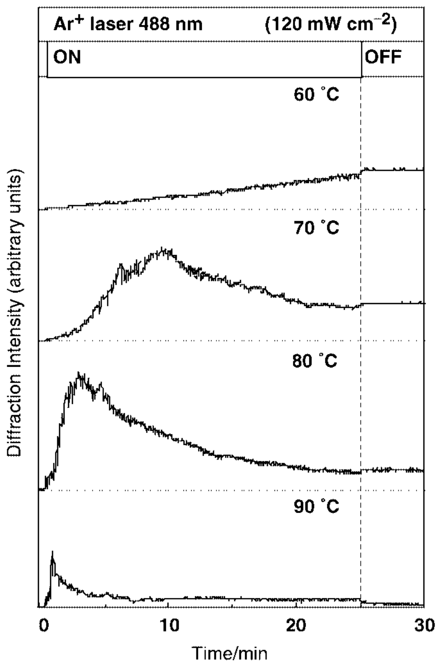

Fig. 4 Change in intensity of diffracted light in the **CB-AB** film at various temperatures. Light intensity was 120 mW cm^{-2}.

efficiency (η_{max}) of about 6%. This value is largest among the (**s**+**s**) polarization configuration systems.[23,24] The mobility of mesogens as well as the *cis–trans* isomerization rate of the azobenzene moiety increase with an increase in temperature, which results in a faster response with increased intensity of the diffraction beam. Actually, the alignment change based on the *trans–cis–trans* isomerization cycles was affected by temperature. Fig. 5 shows the temperature dependence on the alignment change of **CB-AB**. It was clearly observed that the response time for the alignment change decreased as temperature increased. Furthermore, the efficiency of alignment change increased with temperature. At the same time, however, the thermal N–I phase transition can take place more easily due to low thermal stability of an LC phase with an increase in temperature. These two conflicting factors may produce the profiles shown in Fig. 4. Diffraction intensity decreased with a further increase in temperature owing to a decrease in

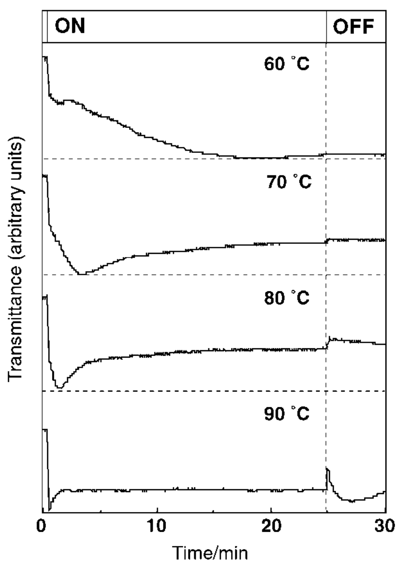

Fig. 5 Change in transmittance of probe light at various temperatures. Photoirradiation was performed at light intensity of 120 mW cm^{-2}.

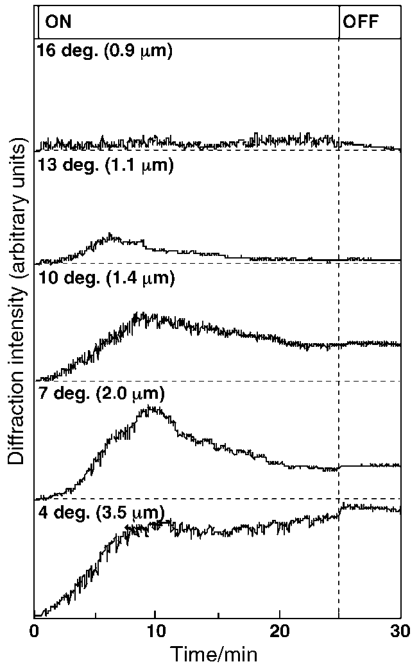

Fig. 6 Effect of incident angle on the formation of grating in the **CB-AB** film. Photoirradiation was carried out at 70 °C. Numbers in the figure are incident angles with calculated values of Λ in parentheses.

difference of the refractive index between bright and dark areas of the interference patterns.

Effect of fringe spacing on grating formation

In practical applications, storage capacity and resolution of materials are very important factors. So the effect of fringe spacing (Λ) on the formation of grating was explored. By changing the incident angle of the writing beams from 4° to 16°, Λ was varied from 3.5 to 0.9 μm. We performed all experiments in the Raman–Nath regime and observed multiple diffraction beams. Fig. 6 shows the dependence of the fringe spacing on the diffraction intensity of the **CB-AB** film. Photoirradiation was performed at 70 °C. It was found that η was very small when the fringe spacing was 0.9 μm. On the other hand, when the fringe spacing was larger than 2.0 μm, the η_{max} reached more than 5%. In addition, when the fringe spacing was 3.5 μm, a stable grating could be formed.

Effect of light intensity on grating formation

After exposure to writing beams at different intensity, the η_{max} of the **CB-AB** film was evaluated as shown in Fig. 7. When the

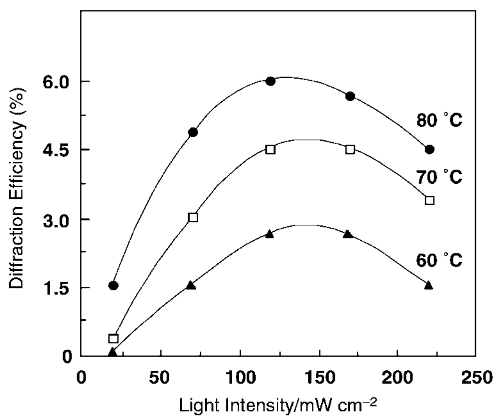

Fig. 7 Effect of light intensity of the writing beams on the diffraction efficiency in the **CB-AB** film: (▲), 60 °C; (□), 70 °C; (●), 80 °C. The writing beams intersected in the film at an incident angle of $\theta = 7°$.

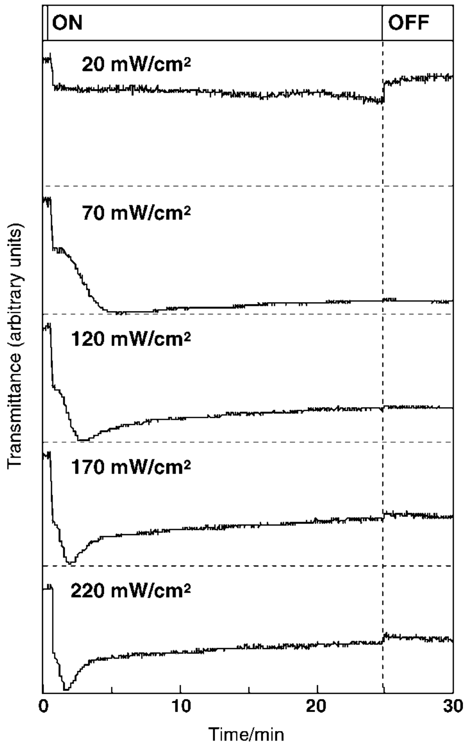

Fig. 8 Effect of light intensity of the pumping light on the alignment behavior. Photoirradiation was carried out at 70 °C.

intensity was 20 mW cm^{-2}, η_{max} was very small; the polarized light at 20 mW cm^{-2} could not induce homogeneous alignment in the PLC film as shown in Fig. 8. With an increase in the light intensity, η_{max} also increased, showing a maximum value at around 120 mW cm^{-2} at every temperature, and then decreased. These bell-shaped profiles of η_{max} may be interpreted in terms of intensity-dependent alignment behavior of PLCs containing azobenzene moieties.[5] When the PLC is exposed to high-intensity polarized light, the azobenzene moieties and other mesogens are likely to change their alignment perpendicular to the direction of the electric vector of the irradiation light; however, when it is exposed to low-intensity polarized light, alignment change is incomplete and ceases before they change their alignment perpendicular to the actinic light. This gives an explanation for the increase of η_{max} with light intensity. On the other hand, when the light intensity of the writing beams is very high, 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_{max}.

Relation between grating formation and alignment behavior

To clarify the mechanism of grating formation in detail, we explored the relation between the diffracted light intensity and the photoinduced alignment behavior. Fig. 9 shows dynamics of the change in transmittance by alignment change and diffraction intensity of the **CB-AB** film. Photoirradiation was carried out at 70 °C (A) and 80 °C (B). Total intensity of the linearly polarized light was adjusted at 120 mW cm^{-2} in these experiments. 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 complete in the bright areas of the interference patterns, the η_{max} is obtained since the difference in the refractive index between the bright and the dark areas reaches a maximum.

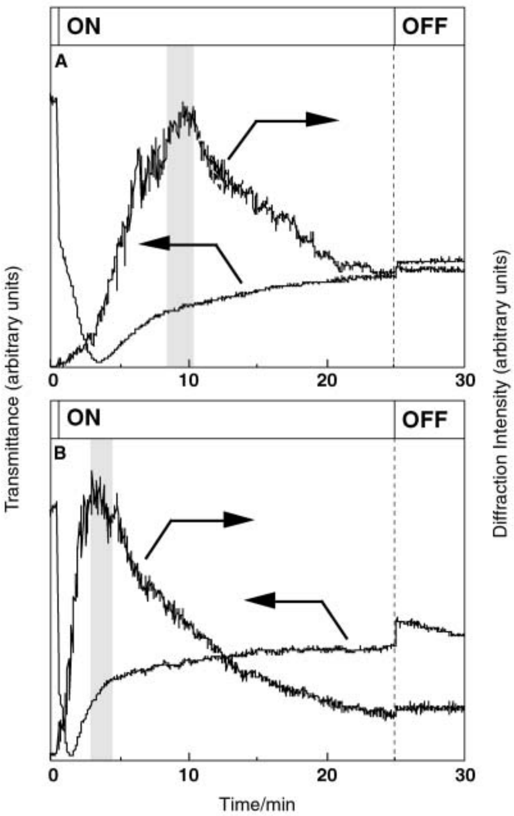

Fig. 9 Diffraction intensity and transmittance of the **CB-AB** film as a function of irradiation time at different temperature: (A) 70 °C, (B) 80 °C. Photoirradiation was performed at 488 nm at an incident angle of $\theta = 7°$.

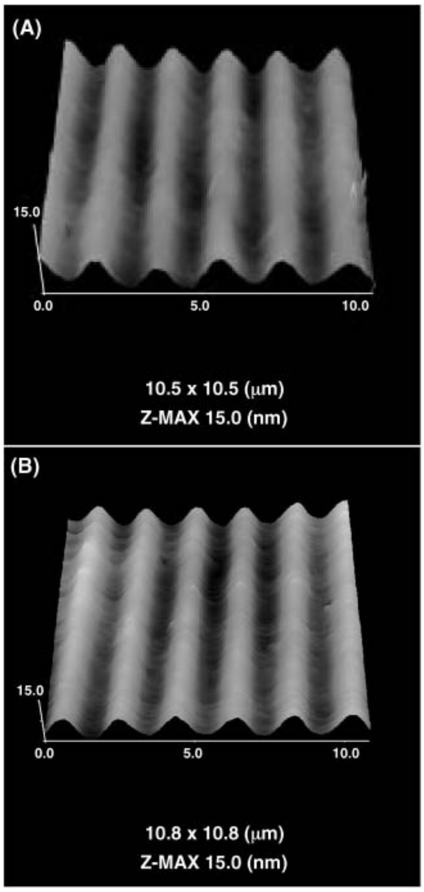

Fig. 10 AFM 3-D views of the gratings recorded in a nematic phase (A) and a glassy state (B). AFM observation was carried out at room temperature. Photoirradiation was performed at an incident angle of $\theta = 7°$ ($\Lambda = 2.0$ μm).

Modulation of surface structure in PLC films

We previously reported a novel type of phase-type grating in PLC films.[14] The grating consisted both of spatial modulations of surface structure (surface relief grating) and of periodic arrangement of N and I phases. The spatial modulation of the refractive index resulted from the photochemical N–I phase transition based on the *trans–cis* photoisomerization of azobenzene moieties. In this study, we explored the surface structure of grating based on photoinduced alignment change of PLCs with AFM. Natansohn *et al.* and Tripathy *et al.* explored the mechanism of surface relief grating on azopolymer films.[20,24] Grating formation was performed under different conditions: PLC films in an N phase (80 °C) and those in a glassy state (20 °C). Photoirradiation was performed at a light intensity of 70 mW cm^{-2} for 10 min. The surface modulation is shown in detail in Fig. 10. The periodic structure of the surface relief was about 2.0 μm wide in each case while its height was in the range of 7 to 10 nm. In an N phase, the value of η was 5.0% while it was 0.8% in a glassy state. This difference results from the degree of alignment change of mesogens based on *trans–cis–trans* isomerization cycles of the azobenzene moieties. Tripathy *et al.* and Sourisseau *et al.* explained the surface relief grating as follows. The (**s**+**s**) configuration produces a very small modulation (<few nm) and shows the smallest value of η (<0.1%). In fact, the ratio of the height of relief to the film thickness was very small (about 1.0%), and contribution of the surface modulation to the spatial modulation of the refractive index is almost negligible in this study. From these results, the modulation of the refractive index (Δn) could be evaluated by means of eqn. (2):[32]

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

where d and λ are the film thickness and the wavelength of the reading beams, respectively. The maximum value of Δn was estimated as 0.04.

Mechanism for formation of grating

We can presume that the grating formation in the **CB-AB** film consists of four processes. The mechanism of formation of a grating in **CB-AB** is schematically illustrated in Fig. 11. Just after irradiation, an alignment change is induced by *trans–cis* photoisomerization of the azobenzene moieties in bright areas of the interference patterns. This photoinduced alignment behavior results in generation of diffracted beams with a periodic change in the refractive index (A). During exposure, the difference in the refractive index between the bright and dark areas (Δn) increases because the alignment change proceeds, and η becomes large. η reaches a maximum value when the photoinduced alignment change is complete in the bright areas (B). The result of the dynamics of the transmittance and diffraction intensity (Fig. 9) supports this view. When the writing beams are turned off and the film is cooled to room temperature, the recorded grating remains unchanged because the mesogens in side-chain PLCs are frozen below T_g (C).[15] However, further irradiation of the writing beams causes a gradual decrease in η. This phenomenon is explained as follows. The orientational relaxation of mesogens in the dark areas occurs owing to the cooperative effects based on the alignment change of PLCs in the bright areas (D). Consequently, Δn gradually decreases with exposure of the writing beams. As previously described, when the fringe spacing was large (3.5 μm), η did not decrease even on further irradiation of the writing beams. This is probably because the influence of the orientational relaxation of mesogens is nearly negligible when the fringe spacing is large.

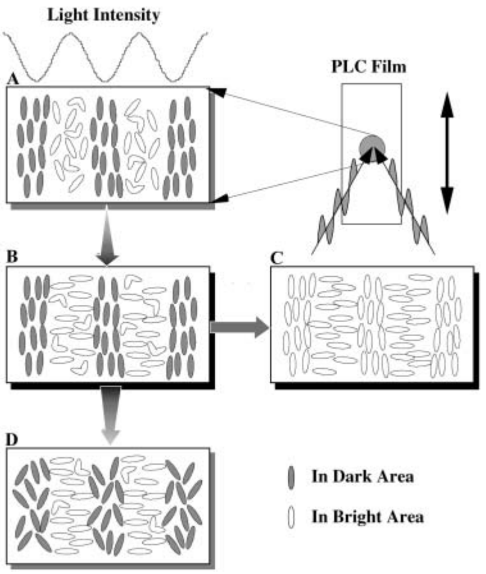

Fig. 11 Plausible mechanism of formation of grating in the **CB-AB** film by linearly polarized light: (A), induction of the alignment change in the bright areas by laser irradiation; (B), completion of the alignment change in the bright areas; (C), retention of the grating after irradiation below T_g; (D), induction of the alignment change in the dark areas. The arrow indicates the direction of the electric field vector of the writing beams.

Conclusion

In summary, we explored the formation of holographic gratings by means of a photoinduced alignment change of a PLC containing an azobenzene moiety. It was found that the grating formation was strongly affected by the process of alignment change. A study on the effect of light intensity of writing beams on the formation of grating indicated that η increased with an increase in light intensity. However, when the light intensity of the writing beams was very high, orientational relaxation of mesogens based on the cooperative effect might occur in the dark areas of the interference patterns due to the alignment change in bright areas. This is likely to reduce Δn between the dark and bright areas and leads to a decrease in η. This is also explained by the results of the experiment on the effect of fringe spacing. In this case, η increased with increasing the fringe spacing. At a narrow spacing, Δn was very small because the distortion of alignment might occur owing to the cooperative effects with the alignment change of PLC. Furthermore, η and Δn showed the largest values of 6% and 0.04, respectively, in the (**s**+**s**) polarization configuration. At present, these values are smaller than those under other polarization conditions. However, it is expected that further enhancement of these values can be achieved by molecular design of PLCs.

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