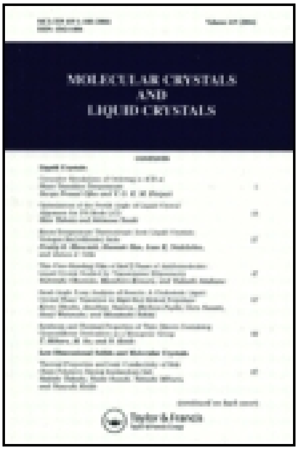

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Formation of Grating by Means of Photoinduced Alignment Change of Polymer Liquid Crystals with Azobenzene Moieties

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Formation of Grating by Means of Photoinduced Alignment Change of Polymer Liquid Crystals with Azobenzene Moieties

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We prepared a polymer liquid crystal (PLC) with *ortho*-substituted azobenzene to explore the effect of the structure of the photochromic unit on the formation of holographic grating. On this behavior, a remarkable difference was observed between two materials. Grating formation of the *ortho*-substituted azobenzene moiety proceeded faster than that of common azobenzene analogs without substituents at the *ortho* position. This result is explained in terms of the stability of the LC phase structure. We investigated the relationship between alignment behavior and change of the diffracted light intensity. The result shows that in the *ortho*-substituted azobenzene sample, the diffraction efficiency showed maximum when orientational relaxation is completed in a bright area of the interference pattern.

Keywords: Holographic Grating; Photoinduced Alignment Change; Azobenzene; Polymer Liquid Crystals

INTRODUCTION

The holographic data storage process has been extensively studied using functionalized polymers with side-chain azobenzene groups [1-5,8-14]. We previously reported formation of holographic grating by means of photochemical phase transition of PLCs containing

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azobenzene moieties [4,5]. Large modulation of refractive index was induced by the photochemical phase transition in LCs based on *trans-cis* photoisomerization of azobenzene molecules [6,7]. The refractive index variation in PLC arises from difference in 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 refractive index in PLC, $|n_e - n_o|$ should be used in place of $|n_e$ (or n_o) $- n|$. The difference $|n_e - n_o|$ corresponds to birefringence of LC molecules. Modulation of the refractive index $|n_e - n_o|$, therefore, can be achieved by change in alignment of LC molecules with linearly polarized light.

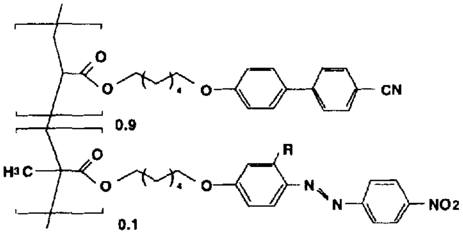
The photoinduced birefringence has been studied by means of azopolymer systems [15-17]. It has been known for more than a decade that linearly polarized light can induce reorientation of azobenzene groups through photochemical *trans-cis-trans* isomerization cycles [18]. Using polarized light, azobenzene moieties attached to the polymer chains are fallen 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 such as optical switching and holographic data storage [1-3,8-14].

In this paper, we studied formation of holographic grating and photoinduced alignment behavior using PLCs with a low content of azobenzene moieties in the side chain. We investigated the effect of the structure of the photochromic unit on the formation of grating. The aim of this work is to explore the detailed mechanism of the grating formation from the viewpoints of alignment behavior of the PLCs.

EXPERIMENTAL

Materials

Figure 1 shows the structure, thermodynamic properties and molecular weight 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 [20,21]. Sample films were prepared by casting a THF solution of the polymer onto a glass substrate which had been coated with poly(vinyl alcohol) and rubbed to align mesogens. Homogeneously aligned films were obtained after annealing. Thickness of the sample film was measured as about 1 μm with a profile measurement microscope. It was clearly observed that the N to I phase transition temperature (T_{NI}) of **CB-ABM** was lower than that of **CB-AB**. In general, the thermal stability in the N phase is reduced by substitution which leads to an increase in molecular breadth. From these results, it appears that the *ortho*-methoxy substituent on the azobenzene destabilized the LC phase structure. Since T_{NI} of the two polymers is different in this study, experiments were performed at the reduced temperature, T (K)/T_{NI} (K) of 0.92, which is useful to compare various physical properties of LCs with different values of T_{NI} on the same orientational ordering.



CB-AB : R = H

G 26 N 99 I Mn = 12,000 Mw/Mn = 1.3

CB-ABM : R = OCH_3

G 33 N 79 I Mn = 13,000 Mw/Mn = 1.4

FIGURE 1 Chemical structure and properties of PLCs used in this study. G, glass; N, nematic; I, isotropic phase; Mn, number-average molecular weight; Mw, weight-average molecular weight.

Formation of Holographic Grating

Formation of grating in the PLCs was performed by a procedure similar to the literature [4,5]. In this study, two s-polarized beams from an Ar^+ laser at 488 nm were used as writing beams. Direction of the electric field vector of the incident light was parallel to that of uniaxial alignment. The incident angle of writing beams was fixed at $\theta = 7°$ (fringe spacing: 2 μm). 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. Photoinduced alignment change of PLCs was investigated by the following procedure. The sample film placed in a thermostated block was irradiated with linearly polarized light from an Ar^+ laser (s-polarized light). 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.

RESULTS AND DISCUSSION

Grating Formation by Using PLCs

We attempted the formation of grating using PLCs films. Figure 2 (a) shows the change in intensity of diffracted light as a function of irradiation time at 50 °C (**CB-ABM**) and 70 °C (**CB-AB**). Intensity of the writing beams was 120 mW/cm^2. These figures clearly show that intensity of the diffracted light increased first with an increase of irradiation time, but it then decreased with irradiation time. This behavior may be due to an increase at first, followed by a decrease, of difference in the refractive index between bright and dark areas of the interference patterns. In **CB-ABM**, after 4 min, η showed a maximum: it reached up to 2 %. This value is largest and 20 times as large as those reported previously under the two s-polarization condition [12,13]. In contrast, in **CB-AB**, the value of η increased slowly, and the time necessary to reach a maximum value of η (4.5 %) was 10 min. These differences mainly depend on photoinduced alignment behavior based on *trans-cis-trans* isomerization cycles of the azobenzene moiety.

As shown in Figure 2 (b), the transmittance of the probe light decayed on irradiation of linearly polarized light and gradually increased and finally became saturated. This consequence shows that photoinduced alignment change of the PLCs is induced by *trans-cis-trans* isomerization cycles of the azobenzene moieties [19]. When photoirradiation was ceased, transmittance of the probe light slightly increased. This process is due to the thermal *cis-trans* back-isomerization of the azobenzene moieties and consecutive thermal self-organization of the LCs. The difference of a degree of alignment change between two materials seems to be due to differences in the rate of *trans-cis-trans* isomerization cycles of the azobenzene moieties. In the **CB-ABM** film, it is possible that photoisomerization cycles of azobenzene moieties proceed more effectively than those in the **CB-AB** film because of low thermal stability of the LC phase [22].

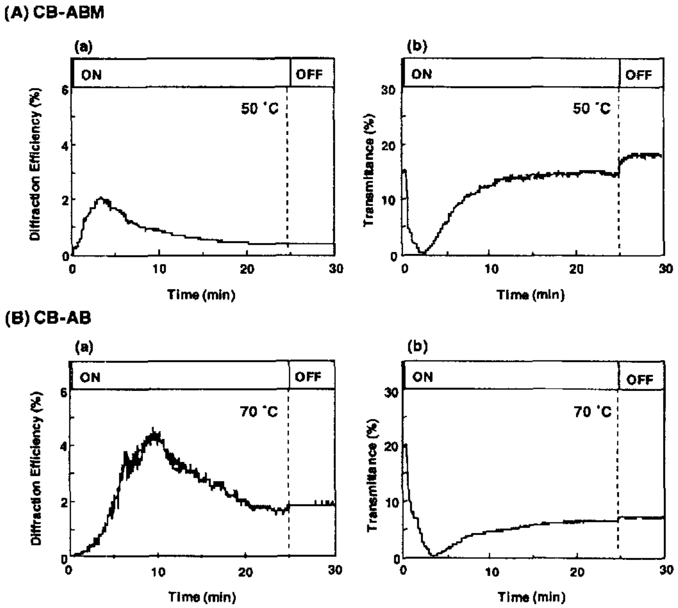


FIGURE 2 Change in intensity of diffracted light (a) and photoinduced alignment change (b) in **CB-ABM** (A) and **CB-AB** (B) by linearly polarized light at the reduced temperature of 0.92 Photoirradiation was carried out at 488 nm with light intensity of 120 mW/cm^2.

Relationship between Grating Formation and Alignment Behavior

To clarify the mechanism of the grating formation in detail, we explored the relationship between the change in the diffracted light intensity and the photoinduced alignment behavior. Figure 3 shows the dynamics of the change in transmittance by alignment change and the diffraction intensity of the **CB-ABM** (A) and **CB-AB** (B) films. Total intensity of the linearly polarized light was adjusted at 120 mW/cm^2 in these experiments. In **CB-ABM**, as is apparent from the change in diffracted light intensity and the transmittance, η showed maximum when the transmittance of probe light was zero. This means that the refractive index variation (Δn) in grating arises from difference in refractive index between an N phase and an I phase ($|n_e - n_I|$). On the other hand, in **CB-AB**, η showed maximum when the transmittance of probe light was almost saturated. This result suggests that the photoinduced alignment change is completed in the bright areas of the interference pattern and the refractive index variation becomes maximum, resulting from the value of $|n_e - n_o|$.

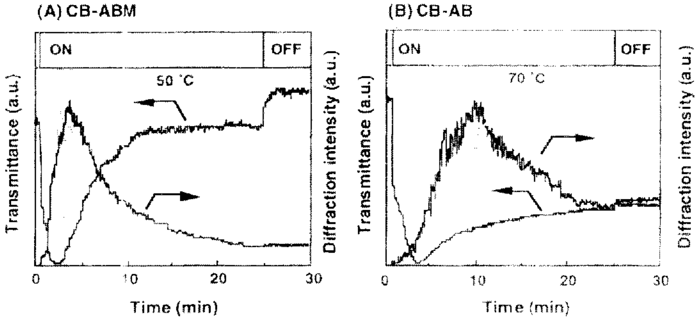


FIGURE 3 Dynamics of the diffraction intensity and transmittance of the **CB-ABM** (A) and **CB-AB** (B) films. Photoirradiation was carried out at 488 nm at an incident angle of θ = 7°.

Effect of Light Intensity on Grating Formation

After exposure to writing beams at different intensity, the η_{max} of the **CB-ABM** and **CB-AB** films was evaluated as shown in Figure 4 (A). In **CB-ABM**, the value of η was almost constant (< 2.0 %) regardless of the light intensity. This result shows that the value of Δn arises from difference in refractive index between an N phase and an I phase. The photochemical phase transition was induced even with low-intensity light in the **CB-ABM** film due to low thermal stability of the LC phase. On the other hand, in **CB-AB**, when the intensity was 20 mW/cm^2, η was very small; the polarized light at 20 mW/cm^2 could not induce homogeneous alignment in the **CB-AB** film. However, when the intensity of the writing beams was higher than 120 mW/cm^2,

η decreased as the intensity of the writing beams increased. From this observation, it is shown that the orientational relaxation of mesogens occurs in the dark areas of the interference pattern. It may be due to the cooperative effects of LCs arising from the alignment change in the bright areas. Actually, when the light intensity was 120, 170 and 220 mW/cm^2, the rate of photoinduced alignment increased with increasing light intensity. Concerning the response time, it is defined as the time necessary to reach the η_{max} (Figure 4 (B)). The response time decreased with an increase of the light intensity in **CB-ABM**. This behavior is probably due to an increase of the concentration of *cis*-azobenzene required to induce the photochemical phase transition. In the **CB-AB** film, the response time was almost constant (< 600 s) irrespective of light intensity. This observation seems to be because the alignment change proceeds almost in the same time scale regardless of the light intensity, but the degree of the alignment change depends on each experimental condition.

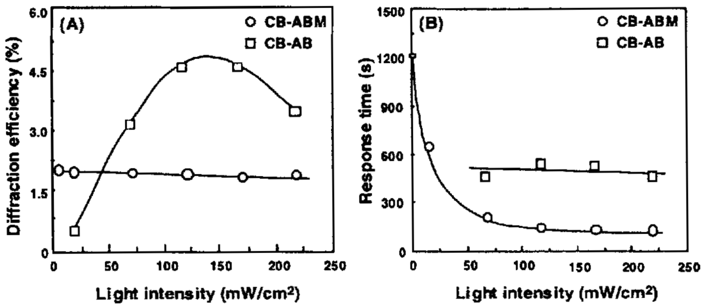


FIGURE 4 Effect of the light intensity on the diffraction efficiency (A) and on the response time (B): (□), CB-AB at 70 °C; (O), CB-ABM at 50 °C. The writing beams intersected in the film at an incident angle of $\theta = 7°$.

Mechanism for Formation of Grating

We can assume that the grating formation in the PLCs film is due to two mechanisms, each of which consists of three processes. In **CB-ABM**, which shows low thermal stability in an N phase, just after irradiation, alignment change is induced by *trans-cis* photoisomerization of azobenzene groups in bright areas of the interference pattern. This orientational relaxation of PLCs results in generation of diffracted beams with periodic change in the refractive index (first process). During exposure, Δn increases as the orientational relaxation proceeds. Hence, η becomes large. When η shows a maximum value, it is probable that the orientational relaxation is completed in the bright areas (second process). The result of the dynamics of the transmittance and diffraction intensity (Figure 3 (A)) supports this view. Further irradiation of the writing beams causes a gradual decrease of η. This phenomenon is explained as follows. The orientational relaxation of molecules in the dark areas occurs by the cooperative effects based on the alignment change of PLCs in the bright areas (third process). In **CB-AB**, which possesses high thermal stability compared to **CB-ABM**, the first process is the same as the case of **CB-ABM**. However, in the second process, the η reaches to a maximum value, indicating that the photoinduced alignment is almost completed in the bright areas. This view is supported experimentally (Figure 3 (B)). The third process is almost the same as that of **CB-ABM**. Consequently, the mechanism of grating formation by means of PLCs depends on the stability of the LC phase structure.

CONCLUSION

In summary, we explored the formation of holographic grating by means of photoinduced alignment change of PLCs containing azobenzene moieties. It was found that the grating formation was strongly affected by the stability of the LC phase structure. A study on the effect of light intensity of writing beams on the formation of grating indicates that the mechanism of grating formation can be classified into two mechanisms. In the PLC with low thermal stability in an N phase, when the orientational relaxation is completed in the bright area, η reaches to a maximum value. On the other hand, in the PLC, which shows relatively high thermal stability, when the photoinduced alignment is almost completed in the bright area, η shows the maximum value. Further experiments are currently in progress to obtain detailed understanding of the effects of the structure of the mesogenic units on the grating formation.

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