

# Preparation of Liquid Crystalline Networks Doped with Azobenzene Molecules and Their Photochemical Grating Formation Behavior

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**ABSTRACT:** Liquid crystalline (LC) networks with macroscopically uniaxial molecular orientation were prepared by photopolymerization of mixtures of LC mono- and diacrylates and a donor-acceptor azobenzene compound in a homogeneous glass cell at the nematic phase, and their photoresponsive properties were investigated. The transparency of the LC networks decreased with a decrease in the crosslinking density with LC diacrylate. The LC networks crosslinked with a few mol percent of LC diacrylate showed an enantiotropic phase transition from an anisotropic phase

to an isotropic phase as well as high transparency. Formation and removal of the grating were investigated by irradiating two writing beams with an argon ion laser. Grating less than 1.0  $\mu\text{m}$  could be achieved, and the response time of formation and removal of the grating were in a range of a few tens of microseconds. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 943–951, 2003

**Key words:** azo polymers; crosslinking; liquid-crystalline polymers (LCP); networks, photochemistry

## INTRODUCTION

Photoresponsive polymer systems have been extensively studied on optical applications. In particular, photoresponsive liquid crystalline (LC) polymers have become of interest in recent years, because of their self-organizing properties, responsiveness to external stimuli, and large anisotropy in physical properties.<sup>1–10</sup> Bulk polymerization of LC monomers in a unidirectional orientation is one of methods to prepare LC polymer systems having macroscopically uniaxial molecular orientation. Broer et al. and Hikmet and Lub reported that densely crosslinked uniaxial polymer networks, those were prepared by polymerization of polyfunctional LC monomers in the unidirectional orientation, showed excellent transparency and stable anisotropic molecular orientation.<sup>11–13</sup> However, the densely crosslinked polymer networks removed any molecular reorientation due to extreme restriction of the molecular motion, resulting in no responsiveness to any external stimuli. On the other hand, lightly crosslinked polymer networks were found to show stable macroscopic molecular orientation as well as a responsive ability to external stimuli,<sup>14–17</sup> that is, the lightly crosslinked polymer networks retain liquid crystallinity. We have also re-

ported the preparation and properties of LC networks by polymerization of mono- and difunctional LC monomers with respect to the crosslinking effect<sup>18</sup> and photochemical change in the molecular orientation of the LC networks containing azobenzene molecules using *trans-cis* photoisomerization of the azobenzene molecules.<sup>10</sup> Single-pulse irradiation experiments with a Nd:YAG laser revealed that the crosslinking of the LC networks improved the response behavior, that is, the response time for the change in the birefringence decreased with increase in the crosslinking density.<sup>10</sup>

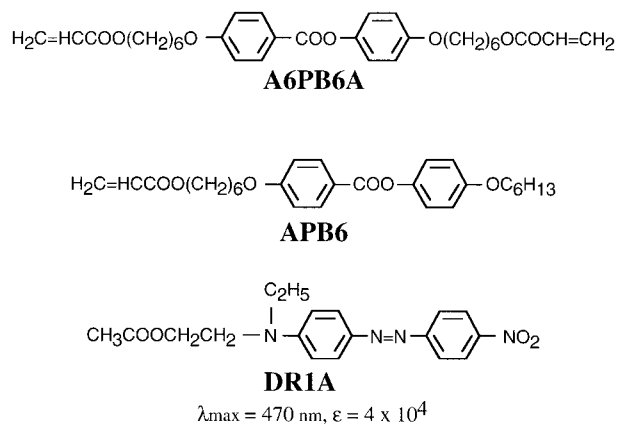
Holography is one of the intriguing applications of photoresponsive polymer systems.<sup>19–24</sup> In particular, dynamic holography offers an attractive potential for optical devices such as real-time image processing. For real-time image processing, the recording, reading, and erasing of the optical information should be performed at real time. Therefore, lightly crosslinked LC networks will be suited for dynamic grating because of their quick responsiveness and repetition reliability. In this study, we describe the preparation of macroscopically uniaxial LC networks containing donor-acceptor azobenzene molecules and discuss the effects of the crosslinking on the formation and removal of grating by turn-on and -off irradiation of two writing beams.

## EXPERIMENTAL

### Synthesis and characterization of uniaxial LC networks containing azobenzene molecules

Two monomers, **APB6** and **A6PB6A**, were synthesized and characterized as described earlier (Fig.

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**Figure 1** Compounds used in this study.

1).<sup>25,26</sup> An acetyl derivative of Disperse Red 1 (**DR1**, Wako Pure Chemical Industries, Ltd.) was prepared by acetylation of **DR1** with acetyl chloride in the presence of triethylamine in tetrahydrofuran (THF). Purification was carried out by recrystallization from ethanol (yield: 80%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  (ppm): 1.3 (t, 3H, methyl), 2.1 (s, 3H, acetyl), 3.5–3.7 (m, 4H, methylene), 4.3 (t, 2H, COOCH<sub>2</sub>), 6.8–8.3 (m, 8H, aromatic). IR (KBr) (cm<sup>-1</sup>): 1740 ( $\nu_{\text{C=O}}$ ).

ANAL. Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.7%; H, 5.6%; N, 15.7%. Found: C, 60.5%; H, 5.6%; N, 15.6%.

Polymerizable monomer mixtures were prepared by adding 3 mol % of 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator to mixtures of **APB6**, **A6PB6A**, and **DR1A** (Table I). The mixtures were injected into two glass plates. Photopolymerization was carried out at a nematic phase by irradiation of ultraviolet light (366 nm) with a 500-W high-pressure Hg lamp (intensity, 11 mW/cm<sup>2</sup>) for 3 min. After polymerization, the samples were removed from the glass plates and were subjected to gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-80M; eluent, THF; standard, polystyrene) and infrared spectroscopy.

The mixtures of **APB6**, **A6PB6A**, and **DR1A** containing 3 mol % of the photoinitiator were injected into the homogeneous glass cell with a 5- $\mu\text{m}$  cell gap at the isotropic phase. Photopolymerization of the mixtures was carried out by the same method described above.

### Optical properties

As a measure of the degree of uniaxial molecular orientation, transmittance of the LC networks between two crossed polarizers was measured as a function of the rotation angle. The transmittance was measured using samples polymerized in the homogeneous glass cell with a 5- $\mu\text{m}$  cell gap with a probe light from a laser diode (Suruga Seiki Co.; 670 nm; 5 mW). The

homogeneous glass cell was purchased from the EHC Co., and it consisted of two glass plates coated with polyimide and rubbed to obtain a homogeneous alignment. The rotation angle was defined as the angle between the direction of rubbing treatment (orientation axis of the glass cell) and the direction of the polarization of the probe light from the laser diode. The measure of the degree of uniaxial molecular orientation ( $P$ ) was defined as follows<sup>27</sup>:

$$P = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \times 100 (\%) \quad (1)$$

where  $I_{\max}$  and  $I_{\min}$  are the maximum and the minimum transmitted light intensities, respectively.

### Optical switching behavior

The sample polymerized in the homogeneous glass cell with a 5- $\mu\text{m}$  cell gap was thermostated and placed between two crossed polarizers. The polarizing direction of the two crossed polarizers was set at an angle of 45° with respect to the orientation axis of the cell. The photochemical change in the birefringence of the uniaxial LC networks was examined using an argon ion laser (Ar<sup>+</sup> laser, Graphics series 165) at 488 nm to cause *trans-cis* photoisomerization of **DR1A**. The laser diode was used as a probe light source. The change in the transmitted light intensity of the probe light from the laser diode was monitored with a laser power meter (Neo Ark, PM-221).

Holographic experiments were performed by a similar setup described earlier.<sup>19</sup> A setup for the holographic experiments is shown in Figure 2. The Ar<sup>+</sup> laser was used as the source. The beam passed through a pinhole and was divided into two using a

**TABLE I**  
Phase-transition Temperatures of Monomer Mixtures and LC Networks

APB6	A6PB6A (mol %)	DR1A	Phase-transition temperature <sup>a</sup> (°C)	
			Before polymerization	After polymerization*
95	0	5	S 46, N 55 I	—
94	1	5	S 45, N 54 I	LC 108 I
92	3	5	S 44, N 54 I	LC 117 I
90	5	5	S 41, N 51 I	LC 119 I
88	7	5	S 45, N 55 I	LC 129 I
94	5	1	S 48, N 60 I	LC 131 I
93	5	2	S 46, N 56 I	LC 127 I
92	5	3	S 48 N 58 I	LC 125 I

S, smectic; N, nematic; I, isotropic; LC, liquid crystalline phases.

<sup>a</sup> Phase-transition temperature was defined as the temperature to reduce the transmittance intensity through crossed polarizers to 10% of the maximum value.

beam splitter. Two writing beams with an equal intensity were overlapped in the film through adjustments of the mirrors. A grating spacing ( $d$ ) was varied by control of an incident angle ( $\theta$ ) of the two writing beams. The grating spacing is

$$d = \lambda / (2 \sin \theta) \quad (2)$$

where  $\lambda$  is the wavelength of the writing beam. A linearly polarized He-Ne laser light (633 nm) was used to monitor the first-order diffraction efficiency. The beam from the He-Ne laser was incident at normal to the surface of the sample. The first-order diffraction efficiency ( $\eta$ ) was determined by the ratio of intensities between the impinging probe beam ( $I_0$ ) from the He-Ne laser and the first-order diffracted beam ( $I_1$ ):

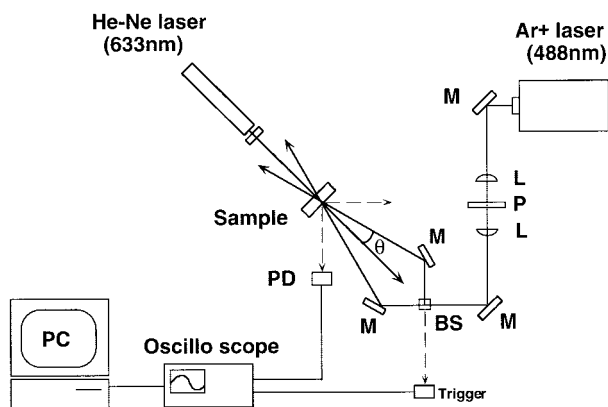
$$\eta = I_1 / I_0 \quad (3)$$

To study the formation and removal of the dynamic grating, the diffracted beam was detected with the laser power meter and recorded on a Tektronix TDS210 digital oscilloscope.

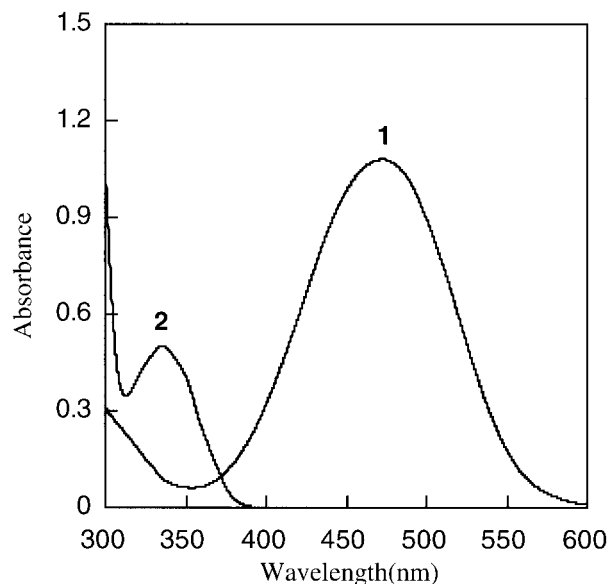
## RESULTS AND DISCUSSION

### Properties of LC polymer networks

Figure 3 shows absorption spectra of DR1A and the photoradical initiator used in methanol. It is clearly shown that the absorption maximum of the radical initiator and the absorption minimum of DR1A are overlapped around 350 nm. Thus, the polymerization of mixtures consisting of APB6, A6PB6A, and DR1A was performed by ultraviolet (UV) irradiation with a high-pressure Hg lamp at 366 nm. Infrared spectra of the mixture of APB6/A6PB6A/DR1A (90:5:5 mol %) containing 3 mol % of the photoradical initiator before and after photopolymerization are given in Figure 4.



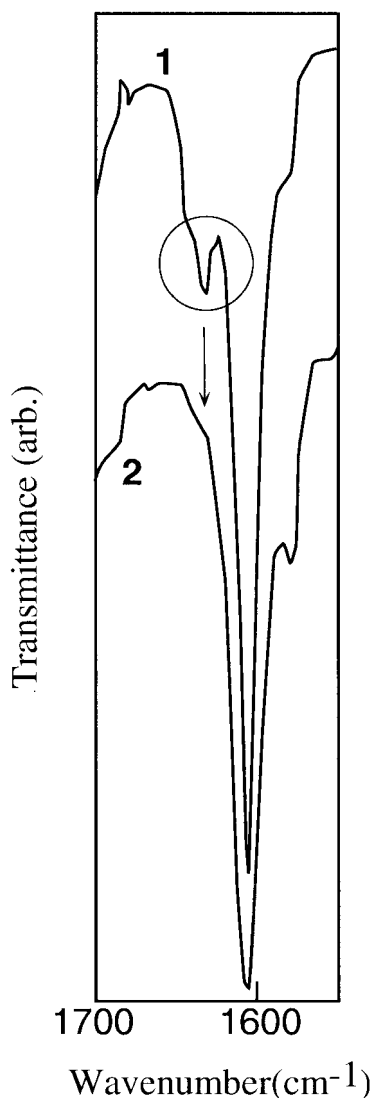
**Figure 2** Experimental setup for dynamic grating; M, mirror; L, lens; P, pinhole; BS, beam splitter; PD, photodiode.



**Figure 3** Absorption spectra of (1) DR1A and (2) 2,2-dimethoxy-2-phenylacetophenone in MeOH.

The mixture exhibited a nematic phase between 41 and 51°C. The photopolymerization was carried out by UV irradiation at 47°C for 3 min on the two glass plates. The peak at  $1630 \text{ cm}^{-1}$  corresponding to vinyl stretching disappeared after the UV irradiation, indicating the proceeding of the photopolymerization of the mixture. In addition, the conversion of the mixture was determined by measuring the residual amount of the monomers in the sample after polymerization using GPC because of the insolubility of the sample due to the crosslinking with A6PB6A. The conversion was found to become higher than 80% by the UV irradiation for 3 min.

To explore the stability of macroscopic molecular orientation of the samples polymerized, the transmittance through the sample without a polarizer was measured as a function of the temperature. Figure 5 shows the temperature dependence of the transmittance of three poly(APB6/A6PB6A/DR1A) networks containing different amounts of A6PB6A. The LC networks were prepared by photopolymerization of the monomer mixtures containing 1, 3, and 5 mol % of A6PB6A in the homogeneous glass cell at the nematic phase to hold the uniaxial molecular orientation. The transmittance of the samples in the cell was higher than 80% at the nematic phase before polymerization because of the uniaxial molecular orientation. A significant decrease in the transmittance was caused by photopolymerization of the monomer mixtures containing 1 and 3 mol % of A6PB6A. The transmittance of both polymerized samples became higher than 80% by heating above 120°C due to the phase transition to the isotropic phase. By subsequent cooling, the transmittance was decreased and restored to the initial



**Figure 4** IR spectra of APB6/A6PB6A/DR1A (90:5:5 mol %) mixture (1) before polymerization and (2) after polymerization by UV irradiation at 47°C for 3 min.

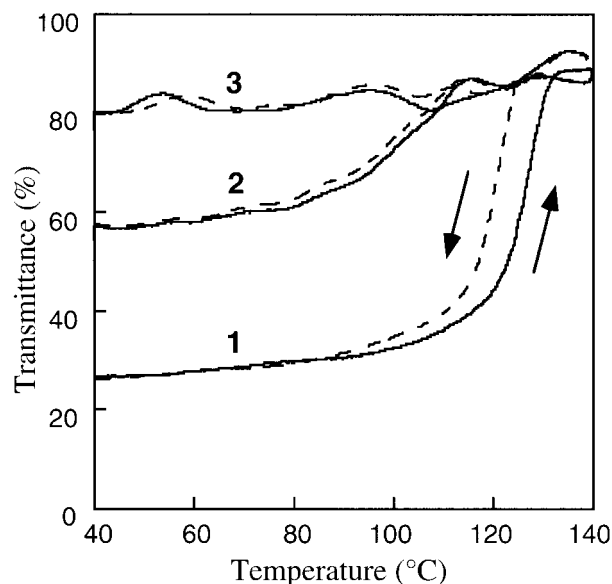
level (solid and broken lines). We reported that LC networks with an extremely low crosslinking density and without crosslinking could not sustain the uniaxial molecular orientation and, consequently, came to scatter light due to a polydomain structure.<sup>10,18</sup> Actually, the polydomain structure was observed for the network crosslinked with 1 mol % of A6PB6A. On the contrary to both networks, the LC network crosslinked with 5 mol % of A6PB6A shows little change in the transmittance by heating and cooling. The degree of uniaxial molecular orientation ( $P$ ) which was based on eq. (1) was 8 and 57% for the networks crosslinked with 1 and 5 mol % of A6PB6A, respectively.

#### Photochemical switching behavior

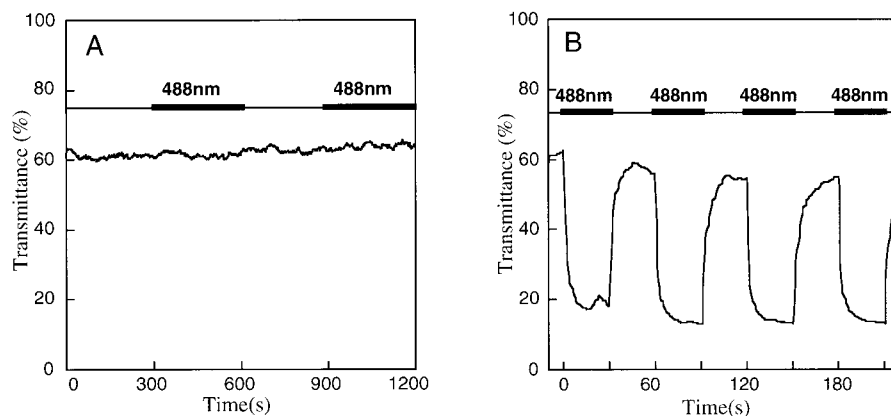
Prior to the study of the formation and removal of the grating, the effect of the direction of the light polar-

ization was clarified by the effect of the photoisomerization of DR1A on the molecular orientation of the LC networks. Figure 6 shows the photochemical change in the transmittance through the poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) network between two crossed polarizers by irradiation of the Ar<sup>+</sup> beam at 488 nm at a Tred of 0.98. Tred is defined as  $T/T_i$ , where  $T$  is the irradiation temperature and  $T_i$  is the isotropization temperature given in Table I. No change in the transmittance was observed when the direction of the polarization of light was normal to the rubbing direction, namely, no change in the birefringence. The  $P$  value of the poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) network is 57%, so that, qualitatively, most of the mesogenic molecules and DR1A molecules align parallel to the rubbing direction. Therefore, the result implies that the quantity of the photoisomerized DR1 is insufficient to cause the transmittance change by the irradiation of the light with polarization normal to the long axis of the DR1A molecule. On the other hand, the reversible change in the transmittance is brought about by turn-on and -off the irradiation of the Ar<sup>+</sup> beam at 488 nm with parallel polarization to the rubbing direction. The increase in the transmittance by turn-off of the irradiation takes place rapidly. The reversible change in the transmittance is explained as a result of the disorganization and the reorientation of the uniaxial molecular orientation of the LC networks by the *trans-cis* photoisomerization and rapid thermal *cis-trans* back-isomerization of DR1A.<sup>19,28,29</sup>

Figure 7 shows the formation and removal of a first-order diffraction signal of the poly(APB6/

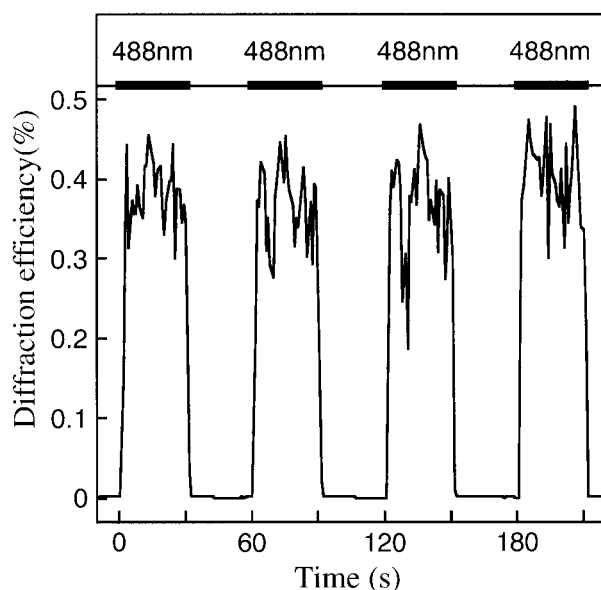


**Figure 5** Changes in the transmittance of the poly(APB6/A6PB6A/DR1A) network as a function of temperature on (—) heating and (---) cooling. (1) APB6:A6PB6A:DR1A = 94:1:5 mol %; (2) APB6:A6PB6A:DR1A = 92:3:5 mol %; (3) APB6:A6PB6A:DR1A = 90:5:5 mol %.



**Figure 6** Changes in transmittance of the poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) network between two crossed polarizers by irradiation of Ar<sup>+</sup> laser at 488 nm (0.8 W/cm<sup>2</sup>) with polarization (A) normal and (B) parallel to the direction of the rubbing direction of the cell at T<sub>red</sub> of 0.98 (111°C).

A6PB6A/DR1A) (90:5:5 mol %) network by turn-on and -off of two Ar<sup>+</sup> beams at a T<sub>red</sub> of 0.98 (111°C). The grating spacing was 2.0 μm according to eq. (2) by control of the incident angle ( $\theta$ ) at 7°. The polarization of the writing beams were parallel to the rubbing direction of the glass cell, and an intensity of each writing beam was adjusted to 0.4 W/cm<sup>2</sup>. The diffraction efficiency is determined by monitoring the intensities of the impinging probe beam ( $I_0$ ) and of the first-order diffracted beam ( $I_1$ ). The diffraction signal was induced by turn-on of the writing beams and disappeared rapidly by turn-off of the beams. As shown in Figure 6, the irradiation leads to disorganization of the uniaxial molecular orientation of the LC

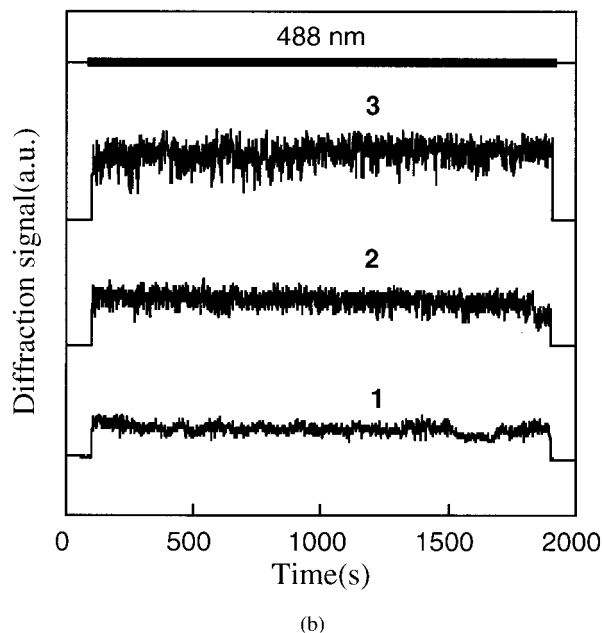
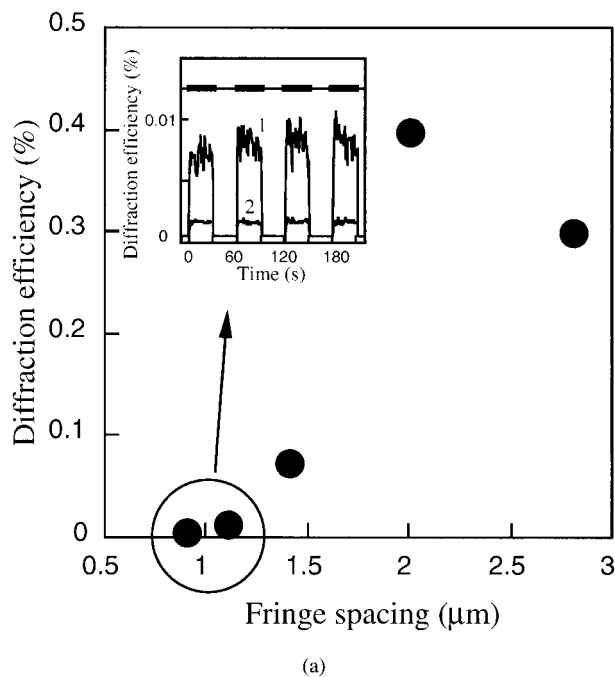


**Figure 7** Change in the diffraction efficiency of the poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) network induced by turning on and off two writing beams (each beam intensity, 0.4 W/cm<sup>2</sup>) at T<sub>red</sub> of 0.98 (111°C). Fringe spacing of 2.0 μm at T<sub>red</sub> of 0.98 (111°C).

networks, resulting in a decrease in the birefringence. Therefore, the reversible change in the first-order diffraction signal is interpreted in terms of disorganization and reorientation of the uniaxial molecular orientation by the reversible photoisomerization of DR1A.

The diffraction signal as a function of the incident angle  $\theta$  gives important information on the maximum achievable spatial resolution. Dependence of the grating spacing on the diffraction efficiency and diffraction signal profile is shown in Figure 8. The maximum efficiency of about 0.4% is attained at 2.0 μm of the grating spacing. Although the intensity is very small, the diffracted beam is observed even at the grating spacing of 0.9 μm, as can be seen in Figure 8(A). It is known that the molecular orientation of liquid crystals can be easily controlled by alignment treatment such as rubbing of the polymeric surface on the glass cell. As described above, the LC networks used were prepared by polymerization of LC monomers in the uniaxial molecular orientation, and the networks, consequently, hold the uniaxial molecular orientation. The mesogenic groups aligned uniaxially in the networks can be expected to force an anchoring effect on the groups in the networks to each other. The formation of grating is based on the disorganization or reorientation by means of *trans-cis* photoisomerization of the azobenzene molecules. The anchoring effect due to the mesogenic groups aligned influences negatively the formation of grating. In addition, the negative anchoring effect on the formation of grating may be enlarged by decreasing the grating spacing. Although the dependence of the diffraction efficiency on the grating spacing is not clear at the present time, the anchoring effect is considered to affect more or less the diffraction efficiency as a function of grating spacing.

On the other hand, it has been reported that LC polymers having the donor-acceptor azobenzene moiety exhibited a decay of the diffraction signal by prolonged irradiation when the grating spacing was less



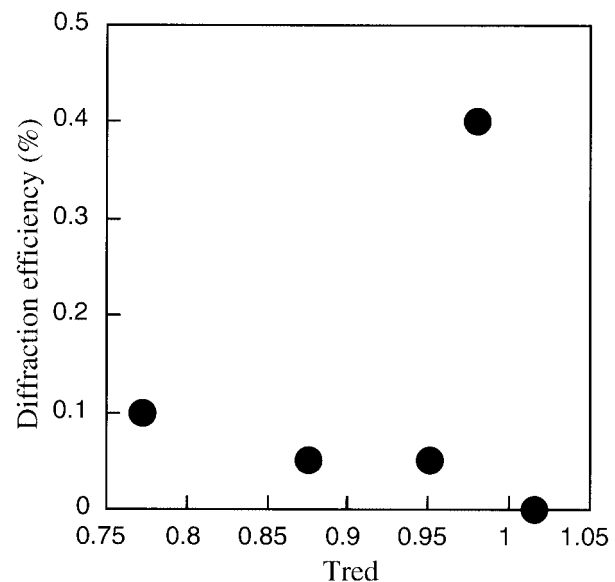
**Figure 8** (A) Effect of grating spacing on diffraction efficiency of poly(APB/A6PB6A/DR1A) (90:5:5 mol %) network by irradiating two Ar<sup>+</sup> beams. Inset: Change in the diffraction signal at (1) 1.1  $\mu\text{m}$  and (2) 0.9  $\mu\text{m}$  of fringe spacing. (B) Effect of prolonged irradiation of Ar<sup>+</sup> beams on the diffraction signal: (1) 0.9  $\mu\text{m}$ ; (2) 1.4  $\mu\text{m}$ ; (3) 2.0  $\mu\text{m}$ . Each beam intensity was 0.4 W/cm<sup>2</sup> and was irradiated at Tred of 0.98.

than 1  $\mu\text{m}$ .<sup>19</sup> Contrary to the LC polymer systems without crosslinking, the lightly crosslinked LC network maintains a stable diffraction signal even after prolonged irradiation, as can be seen in Figure 8(B). The restriction of the molecules with the light

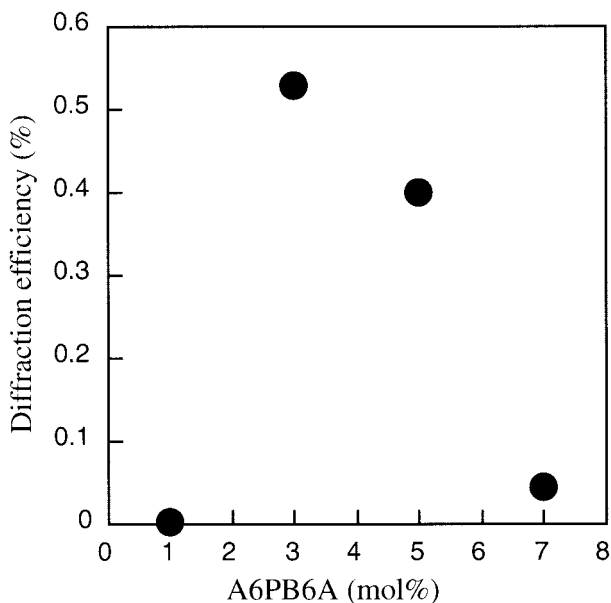
crosslinking may contribute to the stability of the diffraction signal.

Figure 9 shows the irradiation temperature dependence on the diffraction efficiency of the poly(APB6/A6PB6A/DR1) (90:5:5 mol %) network. The polymer network exhibited no diffraction at higher than a Tred of unity. The maximum efficiency was attained at a Tred of 0.98, and a little diffraction was observed over the whole temperature range studied. The results also imply that the diffraction of light arises from the disorganization and reorientation of the uniaxial molecular orientation by the reversible photoisomerization of DR1A, and the disorganization effect depends strongly on the temperature. Therefore, the molecular motion is thought to be one of the important factors influencing the diffraction efficiency. The motion of mesogenic molecules in the LC networks is closely related to the crosslinking density.<sup>18,30</sup> In regard to the preparation of the LC networks, the polymerization conversion was higher than 80%, explored by GPC measurements. Therefore, the amounts of A6PB6A fed in the monomer mixtures corresponded roughly to the crosslinking density of the LC networks, although the crosslinking density of the LC networks could not be determined experimentally.

The effect of the crosslinking density on the diffraction efficiency of the LC networks is shown in Figure 10. Except for the poly(APB6/A6PB6A/DR1) (94:1:5 mol %) network, the diffraction efficiency increased with a decrease in the amount of the A6PB6A fed. We reported the crosslinking effect on the stability of the



**Figure 9** Irradiation temperature dependence of diffraction efficiency of poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) by irradiating Ar<sup>+</sup> beams (each beam intensity, 0.4 W/cm<sup>2</sup>). Irradiation temperature was expressed as Tred [=  $T/T_i$ , where  $T$  (K) is the irradiation temperature, and  $T_i$  is the isotropization temperature].



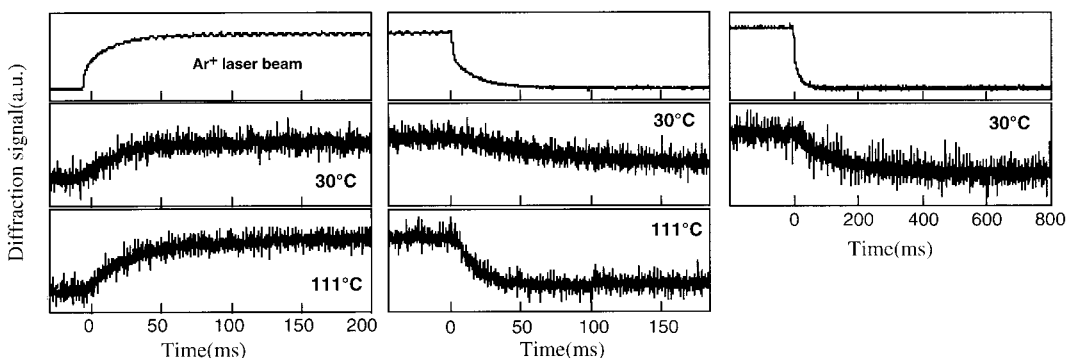
**Figure 10** Effect of crosslinking density on diffraction efficiency of poly(APB6/A6PB6A/DR1A) networks by irradiating Ar<sup>+</sup> beams (each beam intensity, 0.4 W/cm<sup>2</sup>) with a grating spacing of 2 μm at Tred of 0.98.

LC networks and the changes in the birefringence by steady or pulse irradiation on the LC networks containing azobenzene molecules.<sup>10,18</sup> The results showed clearly that the stability of the molecular orientation of the LC networks is enhanced by the crosslinking. In other words, the crosslinking restricts the molecular motion of the mesogenic molecules in the networks. Therefore, the diffraction efficiency decreased by the increase in the crosslinking density. On the other hand, the optical properties of the LC networks such as transparency were also dependent on the crosslinking density, as shown in Figure 5. Less diffraction efficiency of the poly(APB6/A6PB6A/DR1) (94:1:5 mol %) network may be related to its lower transparency.

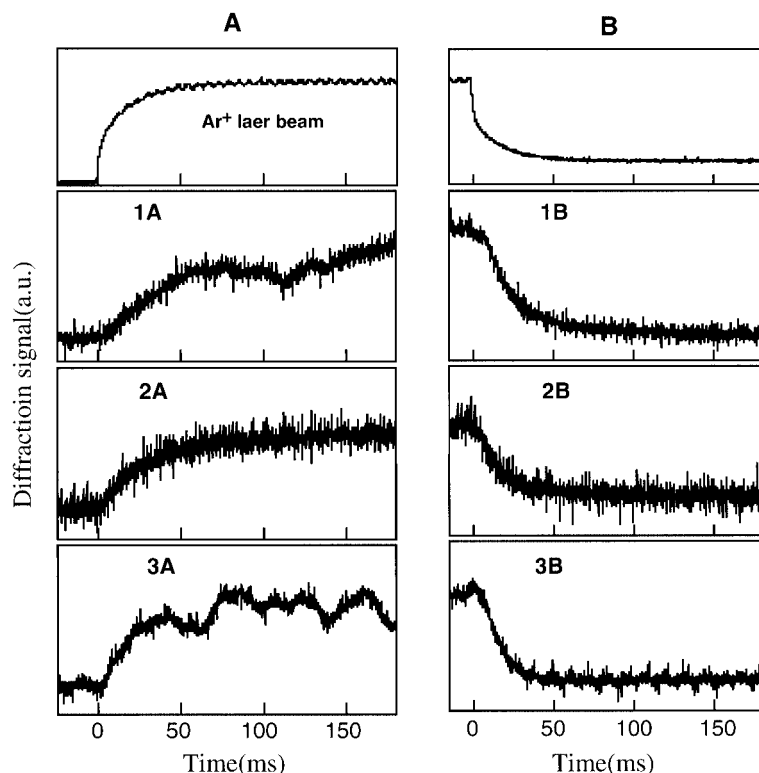
It is noteworthy here to explore the formation and removal behavior of the grating of the LC networks.

Figure 11 shows the time dependence of the diffraction efficiency of the poly(APB6/A6PB6A/DR1) (90:5:5 mol %) network at 30°C (Tred of 0.77) and 111°C (Tred of 0.98). The time-dependence measurements were performed by turning on and off the two Ar<sup>+</sup> beams with a mechanical shutter with a response time of about a few milliseconds. The grating spacing was adjusted at 2.0 μm. It is clearly shown that the intensity of the diffraction signal increases synchronously by the irradiation of the writing beams at both temperatures. The grating was produced in 50 ms at both temperatures, whereas the removal of the grating by turn-off of the writing beams at 30°C required a longer time than that at 110°C: about 50 ms at 111°C and longer than 200 ms at 30°C. The temperature effect may be related to both the rate of the thermal *cis-trans* back reaction and the motion of the network chains.

The formation and the removal of the grating of LC networks with different crosslinking densities are shown in Figure 12. Three LC networks showed almost similar behavior on the formation and the removal of the grating. The formation and removal of the grating were in the range of a few tens of milliseconds, although the poly(APB6/A6PB6A/DR1)(92:3:5 and 87:7:5 mol %) networks gave an unstable diffraction signal. In addition, it is likely that the time required for both formation and removal is influenced by the crosslinking density. Both times were slightly decreased by the increase in the crosslinking density: For example, the removal time was about 30 ms for the network crosslinked with 7 mol % of A6PB6A [poly(APB6/A6PB6A/DR1A) (88:7:5 mol %)] and about 60 ms for the network crosslinked with 3 mol % of A6PB6A [poly(APB6/A6PB6A/DR1A) (92:3:5 mol %)]. The diffraction efficiencies for both networks were different: 0.5 and 0.05% for the networks crosslinked with 3 and 7 mol % of A6PB6A, respectively. Thus, it is difficult to compare the switching rate quantitatively. However, we explored previously the photochemical change in birefringence ( $\Delta n$ ) of similar LC networks crosslinked with 2 and 5 mol % of A6PB6A



**Figure 11** Time dependence of diffraction efficiency of the poly(APB6/A6PB6A/DR1A) (90:5:5 mol %) network by turning on and off Ar<sup>+</sup> beams with a grating spacing of 2.0 μm at Tred of 0.77 (30°C) and 0.98 (111°C).



**Figure 12** Effect of crosslinking density on (A) formation and (B) removal of grating of the poly(APB6/A6PB6A/DR1A) (95- $x$ : $x$ :5 mol %) networks by turning on and off Ar<sup>+</sup> beams (each beam intensity, 0.4 W/cm<sup>2</sup>) with a grating spacing of 2.0  $\mu$ m at Tred of 0.98. (1A and 1B)  $x$  = 3; (2A and 2B)  $x$  = 5; (3A and 3B)  $x$  = 7.

by irradiation with a pulsed laser (full-width at half-maximum, 10 ns).<sup>10</sup> The magnitude of the change in  $\Delta n$  was increased by decreasing the crosslinking density, while the switching rate was increased by increasing the crosslinking density. Based on the results obtained in the present and previous studies, therefore, the crosslinking effect on the time for the formation and removal of the grating is also attributed to the facility of the molecular motion of mesogenic groups in the networks by the *trans*-*cis* photoisomerization of the azobenzene molecules.

## CONCLUSIONS

We prepared slightly crosslinked LC networks containing a donor-acceptor azobenzene compound, poly(APB6/A6PB6A/DR1A), and investigated the formation and the removal of the grating by irradiation of the two writing beams at 488 nm. The diffraction efficiency was found to depend on the irradiation temperature, the grating spacing, and the crosslinking density. A stable diffraction signal was observed even at a grating spacing of less than 1  $\mu$ m. The response time of the formation and the removal of the grating were in the range of a few tens of microseconds. The facility of the molecular motion and the anchoring effect are significant factors on the formation and the removal of the grating of LC networks.

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