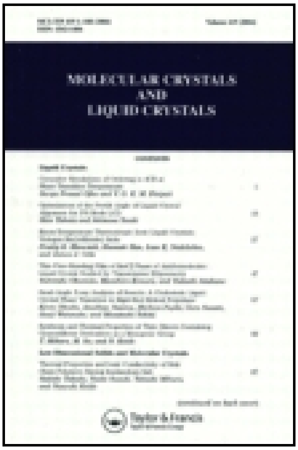

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Holographic Storage in Photoresponsive Crosslinked Polymer-Liquid Crystals Composites

Naoki Yoshimoto [a] , Shin'ya Morino [a] , Aki Kaiho [a] & Kunihiro Ichimura [a]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

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Holographic Storage in Photoresponsive Crosslinked Polymer-Liquid Crystals Composites

NAOKI YOSHIMOTO, SHIN'YA MORINO, AKI KAIHO and KUNIHIRO ICHIMURA

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Holographic gratings were formed by using crosslinked polymer-liquid crystal composites containing azobenzenes. The holographic recording was based on photoinduced alignment of a nematic liquid crystal filled in a cell as a result of the amplification of photoreorientation of azobenzene residues and exhibited volume holographic properties with Bragg diffraction. Spatial frequency of 1 μm was obtained for a cell of 200 μm in thickness, whereas diffraction efficiencies depended on holographic exposure doses and cell thickness. A free-standing film of this composite system was also prepared to perform holographic recording.

Keywords: holographic storage; photoresponsivity; crosslinked polymer; liquid crystal; birefringence

INTRODUCTION

Recently, much attention has been paid on hybrid systems of liquid crystals (LCs) and polymers such as polymer dispersed LCs (PDLCs) and polymer stabilized LCs (PSLCs)[1,2]. These systems exhibit electrically driven light scattering or reflection and applicable for holographic recording[3,4]. Holographic PDLC devices have so far reported multilayer structures consisting of alternate layers of a polymer and small LC droplets formed by photocuring of isotropic mixtures of acrylates and

LCs under irradiation with interference light of two beams. The periodic modulation of the refractive index is caused to give rise to light reflection at a specific wavelength in accordance to Bragg's diffraction. Photorefractive LCs are also holographic materials using electrooptical properties. Materials displaying photorefractive effect have been studied for low-mass LCs[5], PDLCs[6,7], and high- and low-mass LC mixtures[8,9]. Photorefractive effect arises not only from electrooptical properties but also molecular orientation (so-called "orientational enhancement") due to high performances of two-beam coupling[10]. Holographic PDLCs and photorefractive LCs use changes in birefringence induced by electrooptical properties and/or photocuring, and have volume holographic properties.

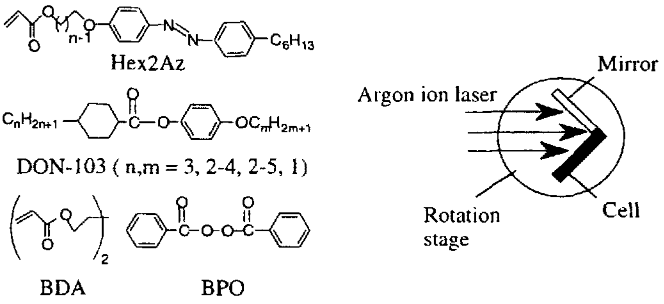
Photogeneration of birefringence induced by photochromic molecules such as azobenzenes has been extensively studied by using various molecular systems[11]. For example, photochromic molecules have been doped into poly(vinyl alcohol) (PVA)[12] or attached covalently to liquid-crystalline polymers[13] and peptides[14] to create holographic gratings as a consequence of the photochromism. Surface relief gratings by using azobenzene side chain polymers have been recently developed[15]. Photoisomerization of azobenzene molecules tethered to a surface layer of a substrate leads to reversible control of LC alignment[16,17] so that homogeneous LC alignment is generated by irradiation with linearly polarized light of axis-selective photoisomerization. LC directors are determined by the electric field vector of the light. This kind of *surface-assisted* photocontrol of LC alignment is regarded as a unique optical hybrid system resulting from the appropriate combination of LCs as large birefringent media with photoresponsive surfaces.

We have demonstrated recently that LC alignment in a hybrid system comprised of a low-mass LC and a crosslinked polymers with azobenzene side chains is controlled by irradiation with linearly polarized[18] and by obloque irradiation with non-polarized light.[19,20] The *matrix-mediated* photocontrol of LC alignment is triggered by the photoreorientation of azobenzene residues studded to crosslinked polymers. Consequently, this composite system provides large photoinduced changes in birefringence originated from LC alignment. One of the practical significances of the system is good transparency to visible light because of low loadings of azobenzene residues even in volume cells. We report here that holographic gratings are formed in the LC / crosslinked polymer composite system, which records a refractive index modulation in thick cells. Volume holograms formed by photogenerated LC alignment in crosslinked polymer matrices are also described.

EXPERIMENTAL

Chemical structures of materials used here are shown in Figure 1 (a). A cell filled with LC / photoresponsive polymer networks was fabricated according to our previous report.[18] A homogeneous solution of benzoyl peroxide (BPO), an azobenzene derivative (Hex2Az) and a nematic LC, DON-103 (T_{NI} = 73 °C), in dichloromethane was evaporated *in vacuo* at room temperature, followed by mixing with 1,4-butanediol diacrylate (BDA) as a crosslinker. A mixture consisting of 5 wt% of BPO, 30 wt% of BDA, 5 wt% of an azobenzene derivative and 60 wt% of DON-103 was sandwiched between two cleaned glass plates. The cell gap was adjusted from 25 μm to 300 μm by using film spacers. Orthoscopic observation revealed that the mixture is in an isotropic phase. The cell was heated at 80 °C for 10 min to achieve the radical polymerization.

Holographic recordings were carried out by using the setup illustrated in Figure 1 (b). Linearly polarized beams at the wavelength of 488 or 514 nm from an argon ion laser were used as a writing beam. The intensity of the writing beams were *ca.* 45 mW cm^{-2}. The writing beams were expanded and collimated. The angle between the two beams was 14 ° or 28 °. Diffraction efficiencies were evaluated here as intensity



(a) (b)

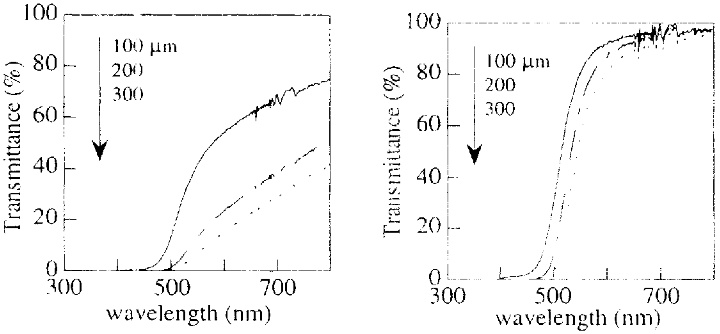
FIGURE 1 (a) Chemical sturactures of compounds used in this study and (b) optical setup for holography experiments.

rations of the +1 order diffracted beam to the beam transmitted through a sample cell by using a He-Ne laser beam. Writing and reading experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Photoinduced refractive index modulations

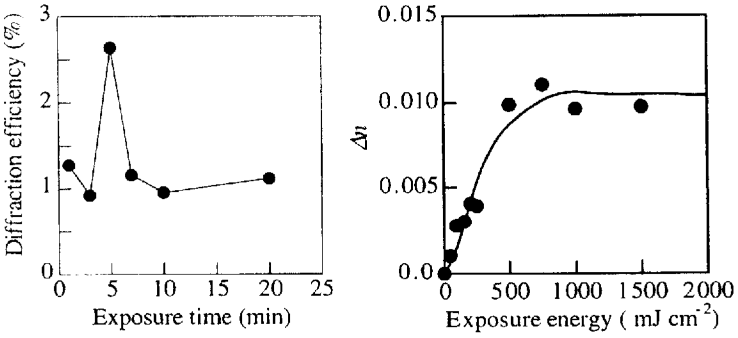
The polymerized cell showed weak light scattering at room temperature, indicating the occurrence of phase separation as a result of the polymerization. A clearing point as a transition temperature between nematic and isotropic phase (T_{NI}) was checked by orthoscopic observation and determined to be 47.5 °C. The T_{NI} was much lower than that of the pure DON-103 (T_{NI} = 73 °C), reflecting the contamination with various components. Figure 2 shows the transmission spectra of the sample at room temperature and at $T > T_{NI}$. The transparency at room temperature was preserved at writing wavelength, 488 nm and 514 nm. Cells heated above T_{NI} displayed significantly low light scattering at the writing wavelengths. Despite loss of transparency at the room temperature, the transmittance of the 100 μm thick sample shows *ca.* 7 % at the writing wavelength (488 nm).



(a) room temperature (b) isotropic phase

FIGURE 2 Transmission spectra measurement at room temperature (a) and isotropic phase temperature (b). Sample thickness is indicated in the figure.

Diffraction efficiency (η) of a cell depended on holographic exposure doses, as shown in Figure 3 (a). The maximum value of η of a 25 μm-thick cell was 2.6 % at an exposure dose when irradiated time was carried out for 5 min to give an exposure dose 9.0 J cm^{-2}. As shown in Figure 3 (b), birefringence was generated by irradiation of a cell of the same thickness with 436 nm linearly polarized light from a high pressure Hg-lamp. Note here that the photoinduced birefringence is leveled off at exposure doses of about 500 mJ cm^{-2}, indicating that the photogeneration of birefringence is completed far before holographic gratings exhibit the maximum η value. Diffraction efficiency is also influenced by formation of interference fringe in addition to photoinduced birefringence.



(a) (b)

FIGURE 3 (a) Exposure time dependence of the diffraction efficiency with a 25 μm-thick cell. The incidence angle between two writing beams was 14 °. (b) photoinduced birefringence change of a 25 μm-thick sample with linearly polarized 436 nm light.

Thick Hologram Properties

The dependence of the diffraction efficiency on cell thickness is shown in Figure 4. The diffraction efficiency is 20 % for the 100 μm-thick cell, which has reasonable transparency at the writing wavelength. A 100 μm-thick volume hologram showed the angular selectivity at the Bragg angle. A quantitative estimation of volume hologram is made using the Q parameter, which is defined

$$Q = 2\pi\lambda d/(n\Lambda^2) \qquad (1)$$

where λ and d are the wavelength of a writing laser (488 nm) and a cell thickness, respectively. n is the average refractive index, which is estimated to be 1.55. Λ is the spatial period of the grating followed by the equation:

$$\Lambda = \lambda/\sin\theta \qquad (2)$$

where θ is the incidence angle between writing beams. When the incident angle is 14 °, Q is calculated to be 12.8 for $d = 25$ μm, and 51 for $d = 100$ μm, respectively. Q values of thick holograms are larger than 40 ~ 60[21] so that the property of thick hologram is obviously obtained for 100 μm-thick cells.

Diffraction efficiencies were very small when exposure was made at 514 nm. The absorption coefficient of azobenzene side chains at 514 nm is smaller than that of 488 nm so that photoinduced reorientation of the azobenzene does not significantly occur at this wavelength.

A spatial period of 1 μm was generated by holographic irradiation at at 488 nm . In this case, a diffraction efficiency of a 200 μm-thick cell

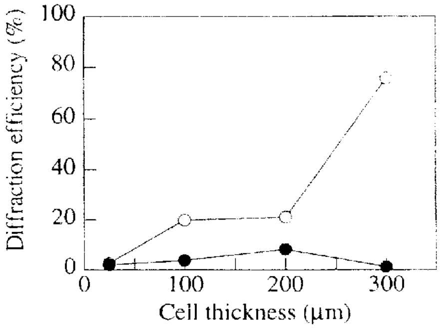
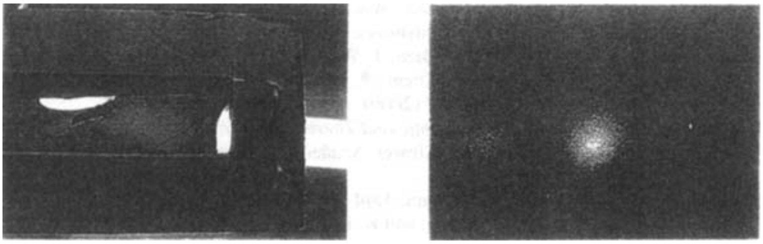


FIGURE 4 Dependence of diffraction efficiency on cell thickness after irradiation with light beams from a Ar$^+$ laser at 488 nm (opened circles), and 514 nm (filled circles), respectively, for 5 min at an incidence angle of 14 °.

was 5.6 % after the irradiation for 10 min. This value is comparable with a photorefractive material using high- and low-mass LC mixture.[8] Crosslinked polymers stabilize the photoinduced LC alignment to give rise to the narrow spatial period.

A 300 μm-thick free-standing film of this composite system was also prepared to perform holographic recording. Figure 5 shows photographs of a free-standing film showing spots of diffracted and transmitted beams. This film has rough surfaces so that the writing two beams are out of focus. Nevertheless, a diffracted spot was observed even in a free-standing film which contains 60 % of nematic LCs.



(a) (b)

FIGURE 5 Photographs of a free-standing film (a) before and (b) after holographic exposure for 5 min at an incident angle of 14 °, exhibiting spots of transmitted (center) and diffracted (left side) beams. See Color Plate XII at the back of this issue.

CONCLUSIONS

A novel holographic material has been developed by using composites containing of LC and crosslinked polymers with azobenzene side chains. Fabricated cells still maintained reasonable transparency for writing beams in spite of light absorption the azobenzene because of its low loading. Diffraction efficiency depended on holographic exposure doses and cell thickness. The composites showed volume-type holograms with the Bragg diffraction. A free-standing film was also fabricated to perform holographic recording.

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