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Pure Polarization Gratings from Photocrosslinkable Polymer Liquid Crystals

Nobuhiro Kawatsuki, Masaomi Kuwabawa, Yasumasa Matsuura, Akira Emoto[1] and Hiroshi Ono[1]
Department of Materials Science and Chemistry, Himeji Institute of Technology, Japan,
FAX: 81-792-67-4886, kawatuki@chem.eng.himeji-tech.ac.jp,
[1]Department of Electrical Engineering, Nagaoka University of Technology, Japan,
onoh@nagaokaut.ac.jp

The pure polarization gratings were fabricated from photocrosslinkable polymer liquid crystals (PPLCs) by both holographic technique and photomask process. In case of the holographic method, polarization holography using orthogonal linearly polarized beams and orthogonal circular polarized light beams were applied to create polarization gratings with narrow periodic structures. For the photomask method, PPLC in which the reorientation direction can be controlled both parallel and perpendicular to the polarization of the exposing linearly polarized light were used, and the resultant grating contained relatively large spacing. Thermally enhanced photoinduced molecular reorientation formed polarization gratings according to the polarization of the irradiating light beams without surface topology. For both cases, conversion of the polarization of the diffracted beams was observed according to the polarization of the incident beam and these phenomena are in fair agreement with the theoretical investigations. These pure polarization gratings exhibited thermal stability up to 150°C and it is anticipated that they will be applicable in various kinds of new diffraction optical devices.
Key words: polymer liquid crystals, photocrosslinking, photoinduced reorientation, polarization grating, holography

1. INTRODUCTION

Polarization grating research has received much attention due to its potential applications for new optical devices such as spectral polarimeters, holographic information storage and diffractive optical elements. A particular feature of polarization gratings is derived from their periodic structure of their molecular orientation without topological modulation, which elicits variation of the polarization states of the diffraction beams. [1-9] The diffraction properties of holographic polarization gratings have been theoretically analyzed, [10,11] and several types of photoreactive materials, including azobenzene-containing polymers [3-9,12,13] and photo-crosslinkable polymer liquid crystals [14,15], have been reported for polarization gratings.

Among the materials that have been studied for generating polarization gratings, azobenzene-containing polymers have been widely investigated because an azobenzene molecule reorients perpendicular to the polarization **E** when a film containing azobenzene groups is exposed to linearly polarized (LP) light. [16-18] Therefore, irradiating azobenzene-containing polymers with a light whose polarization direction is periodically modulated creates polarization gratings. However, two problems exist with this method: (1) a simultaneous surface relief formation which changes the properties of the polarization grating often observed, [4,5,19-21] and (2) the thermal stability is poor. A permanent pure polarization grating can be created in the azobenzene system using Langmuir-Blodgett films of amphiphilic azo-dye molecules. [8,9] In addition, we recently reported thermally stable holographic pure polarization gratings using a polymethacrylate liquid crystal with 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups (PMCB6M). [14,15] Irradiating this material with LP ultraviolet (LPUV) light and subsequent annealing leads to uniaxial molecular reorientation parallel to **E**. [22,23] Thermally enhanced photoinduced molecular reorientation formed polarization gratings in relation to the polarization state of the light beams without surface topology. [14]

In order to achieve periodic molecular orientation in polarization gratings as mentioned above, a holographic method using orthogonal polarization beams with uniform exposure intensity is usually performed. If adjusting the light exposure results in molecular reorientation both parallel and perpendicular to the polarization of LP light, periodic molecular alignment can be created by intensity-modulated light exposure. As a result, polarization gratings can be fabricated by irradiating with LP light through a photomask with a variety of grating patterns.

In this paper, we describe two types of thermally stable polarization grating elements based on the molecular reorientation according to the polarization direction of the exposing method; holographic approach and new fabrication technique using a grating photomask. Photocrosslinkable copolymer liquid crystals, which can control molecular reorientation both parallel and perpendicular to **E** of the LPUV light, were synthesized and applied to a fabrication using a photomask. Adjusting the exposure of LPUV light generated a periodic molecular orientation structure on the film. The mechanism of grating formation coincided with the thermally enhanced molecular reorientation in relation to the reorientation direction and order of the mesogenic groups. The conversion of the polarization of the diffraction beams was observed to be similar to polarization gratings fabricated by the holographic technique.

2. EXPERIMENTAL

2.1. Matrials

The PPLCs **P1** (Mn=42000, Mw/Mn=2.2) and **P2** (Mn=52700, Mw/Mn=1.9) used in this study are shown in Figure 1.[14] These PPLCs were synthesized according to the literature, and exhibited nematic liquid crystalline phase between 116°C and 315 °C for **P1** and 85°C and 227°C for **P2**. Thin films of the PPLC were prepared by spin-coating method from a methylene chloride solution on to a quartz substrate. The film was transparent and showed amorphous in nature after the spin-coating.

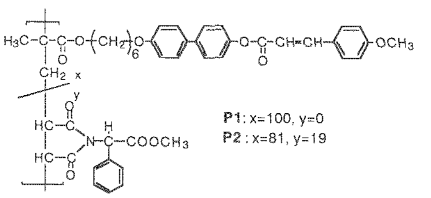

Fig. 1. PPLCs used in this study

2.2. Holographic gratings

Holographic gratings of 300 nm-thick **P1** film were written using two linearly or circular polarized, mutually coherent He-Cd laser beams, which emits cw 325 nm light, with an intensity of 190 mW/cm^2, incident on the sample from the polymer film side. The crossing angle between two writing beams was 9.8 degree, which forms a grating spacing of about 2 μm. The polarization of the laser beams was adjusted to orthogonal polarizations by a half-wave plate. After irradiating, the film was annealed at 150°C for 15 min to induce the reorientation of the mesogenic groups.

2.3. Gratings using a photomask

The **P2** was used. The photoreaction was performed using an ultrahigh pressure Hg lamp equipped with Glan-Taylor polarizing prisms and a cut-off filter under 290 nm wavelength light to obtain LPUV light. The intensity was 11 mWcm^{-2} at 313 nm. The grating was written using a photomask to adjust the exposure doses, which comprises line and space of 30 μm and 30 μm, respectively. After exposure, the film was annealed at 150°C for 15 min.

2.3. Evaluation

The diffraction efficiency and the polarization properties of the diffracted beam from the recorded gratings in the transmission mode was probed with a linearly or circular polarized He-Ne laser at 632.8 nm which normally incidents on the sample film. The diffraction efficiency in the first order was expressed as, $\eta_{+1} = I_{+1}/I_0$, where I_{+1} and I_0 are the intensity of the first-order diffraction beam and incident probe beam, respectively.

3. RESULTS AND DISCUSSION

3.1. Holographic gratings

For the irradiating with two orthogonal linearly (OL) polarized 325 nm lights to a **P1** film, the diffraction from the prove light beam right after the irradiation was almost invisible at any azimuth angle because of negligible birefringent characteristics of the film. On the other hand, when the exposed film was annealed, the diffraction spots appeared, suggesting the organization of the polarization grating.

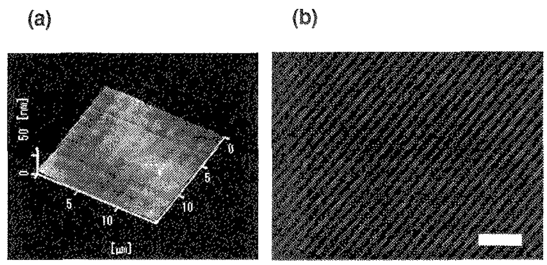

Fig. 2 (a) Surface topology (AFM) of the fabricated grating with OL light beams. (b) Polarization optical microscope observation of the grating. Bar exhibits 5μm length.

Figure 2 shows the AFM and polarization optical microscope (POM) observations of the fabricated grating, which was exposed to 190 mJ/cm^2 doses. It revealed that surface relief gratings were barely observed and other films with different exposure doses revealed similar surface topologies less than 4 nm, which indicates that constant exposure intensity suppresses the polymer migration. Furthermore, the POM photograph showed the bright area appears every 0.95 μm, which corresponds to the half pitch of the phase grating. [14,15] The bright area implies that the uniaxial molecular orientation and the orientation direction are orthogonal to each other. Additionally, gratings by the orthogonal circular (OC) interference beams exhibited the similar surface topologies. [14]

It is well known that the polarization conversion of the diffracted beams is observed for the polarization gratings. [3-9] For example, Figure 3 represents the polarization analysis when the probe beam is linearly *p* polarized. Both polarizations of the 1st-order diffraction beams were converted to linearly *s* polarization. The 0th-order polarization state did not change. Table 1 summarizes characteristics of the holographic polarization gratings, showing the conversion of the various types of polarization states. These experimental

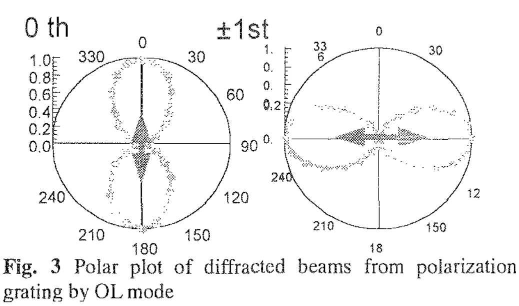

Fig. 3 Polar plot of diffracted beams from polarization grating by OL mode

Table 1 Summary of polarization conversion and diffraction efficiency of the polarization gratings written by OL and OC modes.

Writing	Probe (0th)	+1-order	-1-order
↕ ↔ (OL)	↕	↔ (2.2%)	↔ (2.1%)
	↻	↺ (2.3%)	↺ (2.1%)
	↕	↻ (4.3%)	↺ (4.2%)
↻ ↺ (OC)	↻	↺ (8.1%)	Invisible
	↺	Invisible	↻ (7.9%)

results were completely consistent with the theoretical expectation. [15]

3.2. Polarization gratings using a photomask

When the exposure doses up on **P1** film was insufficient for the parallel reorientation, thermal treatment resulted in the molecular aggregation followed by the perpendicular reorientation. [23] To obtain perpendicular orientation without the molecular aggregation, copolymer **P2** that comprised a monomer with non-mesogenic groups was used. For **P2**, the reorientation direction was controlled both perpendicular (low exposure doses) and parallel (high exposure doses) to the polarization of LPUV light. Therefore, phase gratings with molecular orientation periodically modulated in orthogonal directions were created using one grating photomask. The fabrication process is shown in Figure 4a. First, the film was irradiated with LPUV light, subsequently exposed through a grating photomask, and then annealed to induce the molecular reorientation. The periodicity of the grating is controlled by the photomask. In this study, we fabricated polarization gratings with spatial periodicity of 60 μm as illustrated in Figure 4b, which formed two kinds of lines with molecular orientations of 0° and 90° with respect to the grating vector. Exposures were adjusted to 50 $mJcm^{-2}$ and 150 $mJcm^{-2}$ for each region in order to generate similar molecular orientations with orthogonal direction. Thus, the polarization direction of the LPUV light controls the orthogonal molecular orientation direction. The phase gratings were also created only after the annealing similarly to the case of holographic gratings.

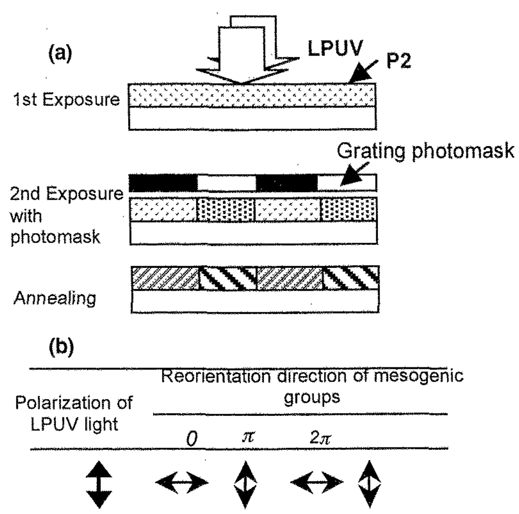

Fig. 4 (a) Fabrication process of the polarization grating using a photomask. (b) Schematic illustration of the polarization modulation of the grating. Arrows exhibit the direction of the molecular orientation.

Surface topology and the POM observation of the fabricated grating are shown in Figure 5. The surface topology from the AFM image exhibited an uneven line along the interface of the grating lines. The unevenness was less than 8 nm. The POM observation showed that the film was bright when the direction of the polarizers in the POM was placed at ±45° with respect to the grating, and became dark when the film was rotated by 45°. Such surface topologies are derived from a small amount of molecular migration caused by the difference in the degree of photoreaction between two exposed areas. These results demonstrate that the reorientational order of each region is almost the same and the orientational directions are at right angles to each other.

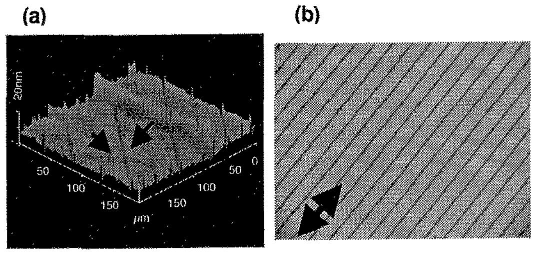

Fig. 5 (a) AFM surface image for the grating. (b) POM photographs of phase gratings of **P2** film.

Figure 6 shows the polar plots of the 0th and ±1st order diffraction beams for a grating film when the polarization azimuth of the monitoring light was +45° with respect to the grating vector. The polarization directions of the first order diffraction beams were converted to −45°, while no polarization change was observed in the non-diffracted beam. Additionally, when the incident beam was left-handed circular polarized, the polarization of the ±1st order diffracted beams converted to right-handed circular polarization. In this case, the non-diffracted beam did not change its polarization. These phenomena are similar to observations made using polarization gratings fabricated with the polarization holography technique using two orthogonal linearly polarized beams. [14,15] Namely, the grating corresponds to holographic polarization gratings fabricated using two writing beams with orthogonal linear polarizations was fabricated. To the best of our knowledge, this is the first report of pure polarization gratings fabricated by means of the photomask method using one LPUV light. In these phase gratings, the conversion of the polarization angle of the diffraction beam can be estimated on the basis of Kirchhoff's diffraction integral including the rectangular phase modulation. Further theoretical and experimental investigations to elucidate detailed optical properties of these polarization gratings are in progress.

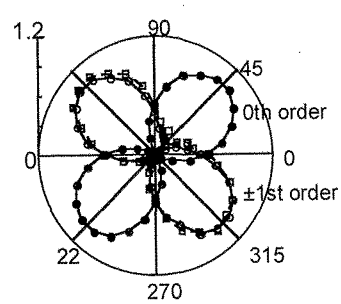

Fig. 6 Polar plot of diffracted beams from polarization grating fabricated by photomask method

4. CONCLUSION

The new types of pure polarization gratings were fabricated from the photocrosslinkable PLC **P1** and **P2** by both holographic technique and photomask process. Since **P1** exhibited thermally enhanced molecular reorientation parallel to the polarization of the UV light, the periodic molecular orientation pattern according to the polarization holography using orthogonal linearly polarized beams and orthogonal circularly polarized light beams of He-Cd laser was successfully achieved. For **P2**, since the material exhibits thermally enhanced molecular reorientation both perpendicular and parallel to **E** of LPUV light, adjusting the exposure doses using a grating photomask created polarization gratings with orthogonal molecular orientation. The resultant gratings exhibited changes in the polarization of diffraction beams similar to the polarization gratings fabricated by the holographic technique using two orthogonal linearly polarized light beams. These phase gratings showed thermal stability up to 150°C. We anticipate that these polarization gratings will be applicable to new optical diffraction devices.

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