Surface Relief Formation with Molecular Orientation in Photoreactive Liquid Crystalline Polymer Film

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Surface relief gratings (SRG) with anisotropic gratings in photo-cross-linkable liquid crystalline (LC) polymethacrylate films comprising 4-(4-methoxycinnamoyloxy)-biphenyl (MCB) side groups were fabricated by irradiating with a linearly polarized ultraviolet (LPUV) light through a grating photomask and subsequent annealing at LC temperature range of the film. A reorientation of the mesogenic groups accompanied the molecular diffusion after the annealing, although the molecular diffusion and the reorientation direction depended on degree of the photoreaction of the mesogenic groups and the polarization (E) of LPUV light. When the degree of the photoreaction was around 7 mol%, molecules moved from illuminated area to non-illuminated area, and the molecular reorientation direction was parallel to the grating line regardless of E of LPUV light. In contrast, the diffusion direction was determined from the non-illuminated area to the illuminated region, and the molecular reorientation direction was always parallel to E of LPUV light when the degree of the photoreaction was around 20 mol%. All the fabricated SRGs showed characteristics of the polarization dependent gratings due to the surface relief formation and the molecular reorientation direction. The diffraction properties of the SRGs were good agreement with theoretical analyses.

Key words: surface relief grating, photoinduced orientation, polymer liquid crystal, diffraction grating, optical anisotropy

1. Introduction

Surface relief (SR) structures are used in microelectronic and microoptical devices such as diffraction gratings. Many techniques to fabricate SR structures have been investigated, including embossing or cast-molding to polymeric materials by the use of a rigid master, photolithographic method using a photoresist with wet-etching, and dry-processes using photoreactive polymeric materials. [1-3] In many cases, Raman-Nath-type SR gratings (SRGs) do not exhibit a polarization-dependency of the incident light beams in their diffraction efficiency when the SR structures exhibit isotropic character in nature.

It is well known that holographic exposure in an azobenzene-containing polymeric film leads the re writable SR formation. [4-6] The anisotropic grating is simultaneously formed when using polarized laser system because a reorientation of the azobenzene molecules occurs. [7,8] The height of the SR and molecular diffusion depends on the type of the azobenzene and exposure condition. Polarization holograms were also fabricated in azobenzene polymer films to generate a periodic molecular orientation. [7-9] The SR formation often occurs when the irradiation is carried out with the intensity modulation, but the polarization-modulated exposure also results in the SR formation in azobenzene systems. [5] The molecular diffusion direction and its orientation direction were investigated in detail by the use of a grating photomask with large periodicity. [10]
Alternatively, a thermally stable holographic recording was investigated in photo-cross-linkable liquid crystalline polymer (PLCP) films, where both the SR and molecular reorientation were observed at the same time. [11,12] We had reported that both polarization and intensity holograms were fabricated in PLCP comprising mesogenic 4-(4-methoxyxycinnamoyloxy)biphenyl (MCB) side groups (P1; Fig. 1). [11] The SR formation and polarization dependency in the diffraction efficiencies were observed only for the intensity holograms. However, the direction of the molecular diffusion and reorientation structure were not clarified. In this paper, to elucidate the molecular motion and reorientation behavior of P1 films upon the SR formation, various kinds of SRGs in P1 films were fabricated using grating photomasks. The SR formation and the reorientation behavior of the mesogenic groups were evaluated by measuring the surface topology and diffraction properties of the resultant gratings.

![Chemical structure of P1](image)

**Fig. 1.** Chemical structure of P1 used in this study

2. Experimental

2.1. Materials

The PLCP P1 was synthesized according to the literature. [13] Weight average of molecular weight of P1 was about 68,000 g/mol and exhibited nematic LC nature around 116 °C and 320 °C.

2.2. Photoirradiation and fabrication of SRG

A thin P1 film was prepared by a spin-coating method on a quartz substrate, resulting in a 0.6 μm-thick film. The film was irradiated with linearly polarized (LP) UV light from a 250W high-pressure Hg-UV lamp (150 mW/cm² at 365 nm) equipped with Glan-Taylor polarization prisms and a cut-off filter below 250 nm.

SR structure of P1 film was fabricated using a grating photomask. Fabrication process is shown in Fig. 2. Two kinds of 30 μm pitch photomasks; 25 μm/5 μm (Line/Space) (A-mask) and 5 μm/25 μm (L/S) (B-mask), were used to determine a direction of the molecular diffusion. To evaluate the relationship between the molecular reorientation direction and the grating lines, polarization (E) direction of LPUV light was adjusted 0°, -45° and 90° with respect to the grating lines. Non-polarized UV (NPUV) light was also used. After the exposure, sample films were annealed at 150 °C for 20 min to generate the SR structure and the molecular reorientation.

![Fabrication process of SRG of P1 film](image)

**Fig. 2.** Fabrication process of SRG of P1 film

2.3. Characterization

The degree of the photoreaction, which was exposed without a photomask, was estimated by monitoring the change in absorbance at 315 nm of UV-vis spectroscopy.

An atomic force microscope (AFM) apparatus using a dumping mode and a polarization optical microscope (POM) were used for the observation of the SR structure and the molecular reorientation. Diffraction efficiency of the fabricated SRG was measured with LP 633 nm He-Ne laser with changing the polarization direction of the incident light beam.

3. Results and discussion

We previously reported that irradiating a thin P1 film with LPUV light generated a small negative photoinduced optical anisotropy and a subsequent annealing procedure at LC temperature range of the film enhanced the optical anisotropy when degree of the photoreaction was around 7 mol%. But the thermal amplification of the optical anisotropy reversely occurred when degree of the photoreaction was around 20 mol%. [13b,14] Namely, adjusting the exposure energy controls the thermally enhanced molecular reorientation direction both perpendicular and parallel to E of LPUV light. Additionally, since the intensity holography makes the SRGs in P1 film, polish photoreaction using a photomask will also generate SR structures. In this context, molecular diffusion and reorientation behavior were evaluated by adjusting the degree of the photoreaction to be 7
mol% and 20 mol%.

3.1. SR formation

The thermally induced molecular motion is generated in photoactive polymeric materials when the mobility of the molecules is changed after the photoreaction. [2,3] Bastiaansen et al. reported that a molecular diffusion from the non-illuminated area to illuminated area was observed to form a SR using a polymer/monomer mixture doped with photoinitiator. [3] Since both photoisomerization and photo-cross-linking reactions occur upon the photoreaction of P1 film, the thermal property may become different according to the amount of the type of the photoreaction. This will affect the molecular diffusion direction.

Figs. 3a – 3d display AFM photographs of generated SRG of P1 film when exposed to LPUV light through a grating photomask with different L/S, and subsequently annealed. The E of LPUV light was parallel to the grating lines. For all cases, SR appeared after the annealing, although there was not any change in the film surface after the exposure. Similar SR structure was formed when E of LPUV light was changed. It exhibits that molecules move from the illuminated area to the non-illuminated area for films with 7 mol% of the photoreaction, since the unexposed area is swelled after the annealing (Figs. 3a and 3b). On the other hand, opposite molecular diffusion was observed for films with 20 mol% of photoreaction (Figs. 3c and 3d), where the exposed region became swelled up after the annealing. These results suggest that the molecular motion is thermally generated and the diffusion direction depends on the degree of the photoreaction.

Since the photoisomerization reaction mainly occurs at the early stage of the photoreaction of P1 film, [11] glass transition temperature in the illuminated area decreases and the mobility becomes higher than the non-illuminated area. In this context, thermally initiated diffusion from the softer region to harder one is generated similar to the case of the polymer/monomer system. [3] The generated SR form is close to the sinusoidal shape when A-mask was used as shown in Fig. 4a. This is because that the thermal treatment makes a stable form during the molecular diffusion.

In contrast, since the illuminated area becomes hard due to higher amount of the photo-cross-linking reaction for the film with 20 mol% of the photoreaction, molecular diffusion from the non-illuminated area cannot form a sinusoidal SR shape as shown in Fig. 4b. Such SR structure is often observed in the development of the photoresists. Additionally, the height of the SR is approximately 130 nm, which is lower than that formed with 7 mol% of the photoreaction, where the SR height is approximately 220 nm. The mobility of the molecules will be restricted due to the higher photo-cross-linked structure.

3.2. Optical property of SRG and direction of the
molecular reorientation

POM observation of the SRG films revealed optical anisotropy. This implies that the molecular reorientation accompanies the SR formation. Diffraction properties of such gratings should reveal polarization dependency of the incident beam. In this section, the SRG films fabricated using A-mask for the film with 7 mol% (SRG shape similar to Fig. 4a), and B-mask for the films with 20 mol% (SRG shape similar to Fig. 4b) of the photoreactions were evaluated, respectively.

Figs. 5a – 5f plot 1st order diffraction efficiencies of SRGs. For SRGs with 7 mol% of the photoreaction (G1 – G3), diffraction efficiency is the largest when polarization of the incident beam is parallel to the grating line regardless of E of the exposed UV light as shown in Figs. 5a – 5c. This implies that the SRG involves an anisotropic grating in which refractive index of the parallel direction to the grating line is larger than that perpendicular. The same polarization dependency was observed even though the non-polarized UV light was used. These results suggest that MCB mesogenic groups thermally reoriented upon the molecular diffusion, and self-organization along the SR structure (grating line) was generated due to the LC nature as illustrated in Fig. 6a.

(a)
(b)

Fig. 6. Schematic image of the molecular diffusion accompanied by molecular orientation. (a) 7 mol% of photoreaction, and (b) 20 mol% of photoreaction.

On the other hand, diffraction properties for SRGs with 20 mol% of the photoreaction (G4 – G6) exhibit different polarization dependency when E of LPUV light is different as shown in Figs. 5d – 5f. The maximum diffraction efficiency is observed when the polarization angles of the incident beam are 0° (180°), 90° (270°) and 135° (315°) for SRGs fabricated with E of LPUV light perpendicular, parallel and -45° to the grating line, respectively. These results suggest that the molecular reorientation direction is parallel to E of LPUV light. The reorientation caused by the photo-cross-linked anchors, which reorient mesogenic groups parallel to E, has a priority over the molecular diffusion-initiated reorientation along the grating line, as illustrated in Fig. 6b.

2.3. Theoretical calculation

Theoretical consideration was performed using a grating model containing both SR structure and refractive index modulation. The electric field amplitude of the light through the SRG, \( E_{\text{out}} \), is obtained using the electric field amplitude of the incident beam, \( E_{\text{in}} \), and Jones matrices for the SR structure, \( T_{\text{rel}} \), and the anisotropic gratings, \( T_{\text{gr}} \), as expressed in Eq. 1, [15]
\[ E_{\text{out}} = R(-\alpha) \cdot T_{\text{ini}} \cdot R(\alpha) \cdot T_{\text{rel}} \cdot E_{\text{in}} \cdot T_{\text{out}} \]  

(1),

where \( R \) is the axis conversion matrix to adjust the optical axis and photoinduced anisotropy. The electric field of the diffraction beams, \( E_{\text{diff}} \), is obtained by means of Fourier transformation of \( E_{\text{out}} \) (Eq. 2), and the intensity of the diffraction beam \( I(x') \) is expressed in Eq. 3. Detailed method for the theoretical calculation will be describe elsewhere.

\[ E_{\text{diff}}(x') = F \cdot F^{-1} \cdot E_{\text{out}}(x) \]  

(2)

\[ I(x') = \left| E_{\text{diff}}(x') \right|^2 \]  

(3)

![Fig. 7. SR structure used for the calculation of G4 - G6 gratings.](image)

Using these equations to obtain the calculated \( \Delta n \) and \( \Delta d \) values, theoretical curves were fitted to the experimental results plotted in Fig. 5. For G1 – G3 films, sinusoidal SR structure and the molecular reorientation direction parallel to the grating lines were applied for the calculation. For G4 – G6 films, SR structure illustrated in Fig. 7, and the molecular reorientation direction perpendicular for G4, parallel for G5 and -45° for G6 were used, respectively. The summary of the SR structure and the reorientation direction and its modulation are displayed in Fig. 8. The theoretically-obtained \( \Delta d \) and \( \Delta n \) values are summarized in Table 1. The calculated values are good agreement with the experimental data.

![Fig. 8. SR structure and refractive index modulation of SRGs fabricated in this study. SRGs (a) - (f) correspond to G1 - G6.](image)

4. Conclusion

Molecular motion direction and the reorientation behavior on the SR formation in PLCP PI film irradiating with LPUV light and subsequent annealing were clarified by evaluating the surface topology and the diffraction efficiency of the fabricated SRG films. The degree of the photoreaction controls the molecular diffusion and reorientation direction. When degree of the photoreaction was 7 mol%, molecular diffusion from illuminated area to non-illuminated area occurred with the molecular reorientation parallel to the grating line. Molecular reorientation according to the direction of the photo-cross-linked anchors took precedence although molecular diffusion from the non-illuminated area to the illuminated area was generated when degree of the photoreaction was 20 mol%.

The diffraction efficiency of the fabricated SRG films exhibited the polarization dependency due to an anisotropic grating character, which coincided with the theoretical consideration. We anticipate that the polarization dependent gratings are applicable to the optical pick-up head to improve the efficiency of laser light, and to the polarization detective optical elements.

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Table 1. Experimental and theoretical values used for the characterization of SRGs

<table>
<thead>
<tr>
<th>SRG film</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>LPUV</td>
<td>( \Delta d ) (nm) (^a)</td>
</tr>
<tr>
<td>G1</td>
<td>perpendicular</td>
<td>202</td>
</tr>
<tr>
<td>G2</td>
<td>parallel</td>
<td>222</td>
</tr>
<tr>
<td>G3</td>
<td>Non-LP</td>
<td>213</td>
</tr>
<tr>
<td>G4</td>
<td>perpendicular</td>
<td>83</td>
</tr>
<tr>
<td>G5</td>
<td>parallel</td>
<td>150</td>
</tr>
<tr>
<td>G6</td>
<td>45°</td>
<td>13°</td>
</tr>
</tbody>
</table>

\(^a\) Measured with AFM. \(^b\) Reorientation direction

References

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