Fabrication of Diffractive Waveplates by Scanning Wave Photopolymerization with Digital Light Processor

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Liquid-crystalline materials with precise molecular orientation patterns have attracted much attention due to their potential application to diffractive waveplates by utilizing their optical anisotropy. However, even by the most sophisticated photoalignment processes, the control of large-area molecular orientation patterns remains a challenge due to the need of a fine spatial control of polarization state of incident light or light interference. Recently, we have developed a photoalignment method based on a novel concept of scanning wave photopolymerization (SWaP) that enables us to control arbitrary two-dimensional orientation patterns without polarized light. Here, we demonstrate the fabrication of LC polymer films with a cycloidal molecular orientation over a large area by SWaP with a digital light processor, and investigate their unique optical property of the resultant film as a cycloidal diffractive waveplate. SWaP could be an excellent method to provide a new pathway for designing high-performance optical devices.

Keywords: Photopolymerization, Molecular orientation, Liquid crystal

1. Introduction
Manipulation of polarization, intensity, and shape of a laser beam is key for functionalizing various optical devices. So far, large and complex optical components are required to fabricate optical systems to manipulate laser beams. Diffractive waveplates (DWs) with both functions of diffraction and polarization conversion are promising to replace such complicated optical systems. DWs are thin films composed of liquid-crystalline (LC) materials [1]. Since the diffraction behavior of DWs is governed by the birefringence of aligned LCs with patterned molecular orientation, fine and precise control of molecular orientation is essential to achieve desired optical performance. As the simplest example of such an optical modulation, one-dimensionally aligned LCs can rotate the polarization direction of a linearly polarized incident beam as a half-wave plate when the retardation matches half wavelength of the incident light. Furthermore, two-dimensional (2D) control of molecular patterns allows us to develop optical elements having various functions [2–4]. In particular, the LC films with cycloidal molecular pattern act as cycloidal diffractive waveplates (CDWs), which selectively diffract the circularly polarized incident light depending on its cycloidal pattern [5–7]. Due to these properties, CDWs have the potential to open windows for applications, i.e. next-generation projection displays.

The CDWs are generally fabricated by the polarization holographic technique based on photoalignment processes. In this technique, the interference of two coherent writing beams with orthogonal polarizations induces highly precise complex 2D orientation patterns [8–11]. However,
there remain fundamental challenges in the existing methods including low processability, necessity of polarized laser beams, and difficulty of large-area patterning. In photoalignment methods, inducing molecular orientation requires axis selective photoresponsive dye molecules [12–15]. In addition to the need of specific molecules, the irradiation area to generate polarization patterns in the holographic technique based on interfering beams is limited to the size of a few millimeters [16]. Thus, the conventional method takes much time to generate cycloidal molecular orientation patterns over a large area owing to the necessity of the extremely precise control of the polarization direction.

Recently, we have developed a single-step and dye-free photoalignment process based on a novel concept of scanning wave photopolymerization (SWaP), which enable to easily induce macroscopic and complicated molecular orientation without polarized light [17–23]. Spatiotemporal photopolymerization generates chemical potential gradient between irradiated and unirradiated regions, resulting in a molecular diffusion. The diffusion triggers molecular flow that allows one to align molecules along the flow direction. Thus, SWaP can induce a large-area and complicated orientation pattern in a single step without dyes nor polarized light. We have successfully controlled 2D molecular orientation and fabricated CDWs with a size of 4.4 mm × 2.5 mm by SWaP in the previous work [24]. In this paper, we demonstrate that the fabrication of LC films with cycloidal molecular orientation with a size of 10 mm × 5.6 mm is achieved. Furthermore, we investigate the optical properties of the obtained CDWs.

2. Experimental

Figure 1 shows chemical structures of the materials used in this study. The photopolymerizable monomer, 4’-[6-(acryloyloxy)hexyloxy]-4-cyanobiphenyl (A6CB), was employed as previously reported [15]. The crosslinker, 1,6-bis(methacryloyloxy)hexane (HDDMA), was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. The product was washed with a 5-wt% aqueous sodium hydroxide solution, dried over anhydrous magnesium sulfate, and then obtained by filtration. The photoinitiator, Irgacure 651, was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, and used without further purification.

The glass cell was prepared by adhering ultrasonically cleaned two glass substrates (25 mm × 15 mm) with glue including 2-µm-thick silica spacers (Thermo Scientific, 9000 series). The thickness of the obtained cell was approximately 3 µm according to the evaluation by UV-vis spectroscopy. The photopolymerizable mixture of A6CB, HDDMA, and Irgacure 651 with a molar
ratio of 97:3:1. The mixture was injected into the glass cell at its isotropic temperature (150 °C), and then cooled down to photopolymerization temperature (100 °C), at which the resultant polymer exhibits a nematic phase. Photopolymerization was conducted with UV-DLP (digital light processor, MiLSS irradiator, ASKA COMPANY, MLS-DIR-LC65365) composed of a UV light source (λmax, 369 nm) equipped with a digital micromirror device (DMD; number of pixels, 1920 × 1080; size of each pixel, 7.56 µm) (Fig. 2a). The size of the irradiated area was 10 mm × 5.6 mm according to the measurements by a beam profiler (OPHIR-SPIRICON, SP620). The glass cell was irradiated with the UV light by scanning the periodic rod-shape patterns with a rod width of 20.9 µm (Fig. 2b). The light intensity was optimized to be 10 mW/cm². Finally, the film was irradiated with UV light (λmax, 365 nm; light intensity, 5 mW/cm²) to fix the induced molecular orientation.

The diffraction property of the resultant film was measured with the optical setup as shown in Fig. 2c. A right- or left-circularly polarized beam was obtained from a He-Ne laser (λ = 633 nm) by adjusting the angles of the quarter-wave plate and polarizer. Evaluating diffraction angle of the beam, we calculated the lattice period (Λ) from the following equations:

\[ \alpha = \arctan\left(\frac{D}{l}\right) \]  
\[ \Lambda = \frac{m\lambda}{s \sin \alpha} \]

where \( \alpha \) denotes the diffraction angle, \( D \) the distance between the 0th and 1st order diffracted beams that appeared on the screen, \( l \) the distance between the sample and the screen, \( m \) the diffraction order, \( \lambda \) a wavelength of incident light. To quantitatively evaluate the diffraction behavior of cycloidal orientation patterns in the film, we calculated the diffraction efficiency (\( \eta \)) by the following equation:

\[ \eta = \frac{I_n}{I_0} \times 100 \]

where \( I \) and \( I_n \) are defined as the intensity of the incident beam and n-th order diffracted beam passing through the film, respectively. The light intensity was measured with an optical power meter.

3. Results and discussion

The sample mixture was irradiated with various patterns by scanning UV light to induce uniform cycloidal molecular orientation by SWaP. We employed four types of UV patterns (\( \Lambda = 26.1, 31.3, 36.6, 41.8 \) µm) with unirradiated widths of 5.2 µm, 10.4 µm, 15.7 µm and 20.9 µm, respectively, keeping the irradiated rod-shaped area with a width of 20.9 µm. By using these designed UV patterns, the films (Cyc26.1, Cyc31.3, Cyc36.6, Cyc41.8) were fabricated by SWaP with the light scanning rate of 15 µm/s. The polarized optical microscope (POM) images of the obtained films showed different textures depending on the periodicity of UV patterns (Fig. 3). The Cyc31.3 and Cyc36.6 films clearly showed a grating structure, and each periodicity was consistent with that of the designed optical patterns (Fig. 3b,c). The grating vector was perpendicular to the light scanning direction. On the other hand, the POM images of Cyc26.1 and Cyc41.8 films showed obscure grating structure (Fig. 3a,d). The POM observation with a tint plate (\( R = 530 \) nm) was carried out to evaluate the molecular orientation in the grating structures of Cyc31.3 and Cyc36.6 films. The additive and subtractive colors periodically appeared. The ratio of additive-colored area to

![Fig. 3. Polarized optical micrographs of Cyc26.1 (a), Cyc31.3 (b), Cyc36.6 (c), Cyc41.8 (d). The left and right columns show the images observed with and without a tint plate, respectively. Scale bars, 100 µm.](image)
subtractive-colored area in the patterns in Cyc$_{31.3}$ and Cyc$_{36.6}$ films resulted in 0.79 and 0.67, respectively. The ratio should be 1 if the cycloidal molecular orientation is perfectly symmetric to the irradiated rod-shape patterns. The Cyc$_{31.3}$ film showed a larger value, indicating that the unirradiated area width of 10.4 μm is more suitable to induce cycloidal orientation, probably due to the appropriate arc in the rod-shape pattern.

Effect of the scanning rate in SWaP on the cycloidal molecular orientation was examined to achieve high-performance CDWs. The sample was irradiated with the rod-shape pattern of $\Lambda = 31.3$ μm at scanning rates of 5, 10, 15, and 20 μm/s. The retardation of the obtained films was determined by POM equipped with both an interference filter ($\lambda = 546$ nm) and a Berek compensator. The retardation depended on the scanning rate, and showed the maximum value of 429 nm at a scanning rate of 15 μm/s as shown in Fig. 4. The scanning rate which has a relationship with exposure energy in SWaP affects a molecular flow. Thus, this result suggests that the most appropriate flow to direct precise cycloidal molecular orientation is induced under this condition.

To evaluate the optical property of the induced cycloidal molecular orientation under optimized photopolymerization conditions, we investigated diffraction behavior of the He-Ne laser beam from the film. For this measurement, we prepared a film with a retardation of 340 nm, which is similar to the half wavelength of the He-Ne laser beam ($\lambda = 633$ nm). The film diffracted circularly polarized incident light in different directions depending on its handedness; the right- and left-circularly polarized light was diffracted on the +1st and –1st orders, respectively (Fig. 5). On the other hand, the linearly polarized incident light was diffracted in both directions. The lattice period calculated from the diffraction angle was 31.9 μm, which corresponds to the periodic cycloidal molecular orientation pattern ($\Lambda = 31.3$ μm). Diffraction efficiency of the Cyc$_{31.3}$ film with the retardation of 340 nm is summarized in Table 1. When the right-circularly polarized light was normally incident on the film, the +1st order diffraction showed the higher diffraction efficiency of 15.0% compared to the –1st order diffraction. The left-circularly polarized incident beam showered the opposite tendency; +1st and –1st order diffraction efficiencies were 4.7% and 14.9%, respectively.

The selective diffraction behavior of circularly polarized light implies that the fabricated LC polymer films function as a CDW. A conventional half-wave plate has orthogonal fast and slow axes to cause the retardation of incident light. In the case of the film with cycloidal molecular orientation, the fast and slow axes gradually rotate according to the molecular orientation. As a result, the light passing through the film has the spatial distribution of the phase of inverted circular polarization, leading to the selective +1st and –1st order diffraction depending on the handedness of the incident light.

![Fig. 4. Retardation of the Cyc$_{31.3}$ films as a function of scanning rate.](image)

![Table 1. Diffraction efficiency of the Cyc$_{31.3}$ film.](image)

![Fig. 5. Photographs of the diffraction pattern of the linearly (a), right-circularly (b), and left-circularly (c) polarized incident light passing through the obtained film on a screen.](image)
Irradiated with the rod-shape pattern, we achieve high-performance CDWs. The sample was exposed to light with a maximum value of 429 nm at a scanning rate of 15 µm/s as shown in Fig. 4. The scanning rate which corresponds to the half wavelength of the He-Ne laser beam (λ = 632.8 nm) and a Berek compensator was used. The retardation of the obtained films was determined by measuring the wavelengths of the film with cycloidal molecular orientation, the –1st order diffraction (Fig. 6). Considering linearly polarized light as the incident light, both +1st and –1st order diffraction occurred equally.

4. Conclusion
In summary, we fabricated LC polymer films by SWaP under various light irradiation conditions and successfully obtained optically transparent films with the highly symmetric cycloidal molecular orientation over a large area. We optimized SWaP conditions; the uniform cycloidal molecular orientation was precisely prepared by irradiating the rod-shape patterns with a width of 20.9 µm and a distance of 10.4 µm at a scanning rate of 15 µm/s. The CDW fabricated by SWaP exhibited circular-polarization selective diffraction behavior, and right- and left-circularly polarized light was diffracted in different directions. We believe that SWaP provides a sophisticated way to fabricate next-generation photonic devices.

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