Multiple Bragg Diffractions with Different Wavelengths and Polarizations Composed of Liquid Crystal/Polymer Periodic Phases

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ABSTRACT: We first fabricated holographic polymer-dispersed liquid crystals (HPDLCs) that produce multiple Bragg diffractions with different polarization states for every angle of incidence, through a photopolymerization-induced phase separation by one-time interferential exposure. The polarizations of the Bragg diffractions were well-controlled at individual wavelengths in the fabrication process by the compositional ratio of LCs to monomers. The raw mixtures of extremely low-functionality monomers having very different viscosities were used to reduce the domain size in phase separation and subsequently to form elaborate periodic structures of the LC and polymer phases. A cross-linker (1-vinyl-2-pyrrolidione) and a prepolymer with urethane groups were employed to strengthen the polymer network. Note that the diffractions of our HPDLCs are regarded as not purely but mostly Bragg type, according to the evaluation with the established criteria. The devices, which are monolithic but versatile in diffractive behaviors, have advantages of simple manufacturing and handling.

1. INTRODUCTION

A versatile diffractive device that allows us to efficiently steer multiple light waves is useful in various areas ranging from all-purpose optical elements to cutting-edge photonic applications. From the point of view of manufacturing, this device should have a simple fabrication procedure and moreover an integrated but monolithic durable structure. These constraints on the device properties do not conflict but can be realized with holographic polymer-dispersed liquid crystals (HPDLCs). Conventional HPDLCs have produced only a single Bragg diffraction regulated by a simple periodic structure. However, our HPDLCs are capable of displaying multiple Bragg diffractions with different wavelength and polarization properties for every angle of incidence. These HPDLCs are made with a single interferential exposure while only adjusting fabrication conditions (liquid crystal/monomer mixture ratio and exposure temperature) and selecting appropriate raw materials to control the phase separation morphology and orientation-ordering distribution. These diffractive structures were formed through photopolymerization-induced phase separation (PPIPS) developed by interferential exposure to the prescribed raw materials. Thus, the devices with the HPDLCs are expandable to a wide range of fundamental and advanced optical (photonic) applications. For instance, the devices possess an integrated monolithic structure and allow us to unite optical pickup components of multiformat disk drives, which separate and combine several light beams with different wavelengths.1,2 Such multiple periodic structures have a potential for applications to optical nonlinear resonators and distributed Bragg reflector or distributed feedback lasers.3−5

Generally, HPDLCs are made of regularly arranged double-phase structures with mesoscale (submicrometer- to micrometer-scale) domains. LC molecules aggregate to form discrete or coalesced droplets that are periodically distributed in polymer networks on the scale of optical wavelengths. An essential property of HPDLCs is the ability to produce Bragg diffraction with a strong optical polarization, resulting from the orientation ordering of the LC molecules in the droplets. Coupled wave theory, an established general theoretical framework for analyzing thick optical gratings first described by Kogelnik, is based on scalar wave equations in electromagnetic wave optics.6,7 Two-wave coupled wave theory, an extension of the Kogelnik’s theory developed for analyzing particularly thick HPDLC gratings,8−11 accounts accurately for the individual p- and s-polarization components in the Bragg diffractions, that is, the polarizations parallel and perpendicular components of the light beams. The advantage of the coupled wave theory is that it can be applied to all types of wave fields, including cases with nonsinusoidal wave forms and wave fields with high-order spatial harmonics.

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HPDLCs can be formed through PPIPS, achieved by a spatially periodic intensity modulation during holographic or interferential exposure. Linearly polarized Bragg diffraction is produced by the orientation ordering of LC molecules, which is uniaxial along the grating vector and can be switched by applying an electric field. Following the demonstration of switching the polarization states in the diffraction by Sutherland,\textsuperscript{14} Boiko et al. developed an electrically controlled four-state switch using orthogonal polarized diffractions by combining two HPDLCs with a polarization rotator.\textsuperscript{15} Lu et al. produced a polarization beam splitter that can precisely switch between states with orthogonal polarizations using an electric field.\textsuperscript{16} This polarization switchability has given rise to many fundamental and pioneering photonic applications, such as photonic crystals, tunable wavelength lasers, tunable focal length lenses, and all-optical switches using azo-benzene dyes.\textsuperscript{17} Recently, HPCLCs with fine and complex structures were fabricated using elaborate techniques of holographic exposure such as multibeam, multiple, or nonlinear irradiation.\textsuperscript{24–27} For instance, reflective HPDLC gratings with a half pitch equal to the interferential fringe spacing have been fabricated through PPIPS by holographic exposure using a femtosecond laser and a two-photon absorptive dye.\textsuperscript{27} Future HPDLCs will soon be required to display more complex and finer structures. Furthermore, a simplification of fabrication processes will make devices readily applicable to practical use.

The processes of localized aggregation and uniaxial orientation ordering of LC molecules during PPIPS have been reliably investigated using Fourier transformation infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and dynamic light scattering (DLS) measurements.\textsuperscript{28–32} Real-time FTIR spectroscopy and photo-DSC, which are useful for tracking processes of LC orientation ordering and acrylate polymerization, revealed the role of monomer functionality in structural formation during PPIPS.\textsuperscript{33,34} NMR and DLS measurements provided information on the diffusion and orientation-ordering behaviors of LC molecules constrained during PPIPS, in particular, the anchoring effect at the LC/polymer interfaces and the diffusion rates influenced by the LC/monomer compositional ratio.

The orientation-ordering dynamics of LC molecules during PPIPS was explained by diffusion theory including polymerization reactions\textsuperscript{35–37} and by the thermodynamics of spatiotemporal fluctuations within LC/monomer mixtures.\textsuperscript{38–41} Because the photopolymerization rate depends on the (sinusoidal-distributed) irradiation intensity during interferential exposure, inhomogeneous polymerization is the driving force to segregate monomers and LCs and consequently to order the orientation of LC molecules. The diffusion coefficient of monomers depends on their molecular weight and reactivity. Therefore, a variety of monomer molecular weights or functional numbers yield the complex distribution of polymer and LC phases. For instance, a simulated mixture of LC and prepolymer with tri- and hexa-functionalities displays a much more complex distribution than expected when using sinusoidal intensity in interferential exposure because of the difference in diffusion coefficients between tri- and hexa-functional oligomers.\textsuperscript{42} The formation of LC droplet distribution and the orientation orderings of LC molecules during PPIPS were theoretically explained in terms of the free energy of liquid–liquid (de-)mixing, molecular orientation ordering, and polymer network elasticity. For instance, the inhomogeneous aggregation that produces discrete LC droplets with orientation ordering was numerically reproduced using the time-dependent Ginzburg–Landau model combined with Flory–Huggins and Maier–Saupe theories, assuming Gaussian-type cross-linked polymer chains.\textsuperscript{43}

The shape of LC droplets and the molecular orientation within them are generally dominated by the temperature, LC/monomer compositional ratio, and polymer network density.\textsuperscript{44–47} Boots and Serbutoviez et al. theoretically and experimentally studied droplet morphology during PPIPS under spatially uniform irradiation and reported that the shape and size are influenced by the cross-linking density of the polymer network surrounding the droplets.\textsuperscript{38,41} The LC droplet size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily. Pogue et al. adjusted the monomer functional number from 2 to 5 and observed the LC size decreases in a loose network because LC molecules permeate the polymer network easily.
droplet morphology. Their statistical analysis revealed the dependence of the LC droplet size, shape, or distribution on the monomer functionality. The influence of the monomer functional number on the LC droplet size was examined to improve the diffusion efficiency. This efficiency was maximized for a monomer functional number of approximately 1.5 because the phase separation morphology yielded a smooth sinusoidal periodic structure that could reduce light scattering. Because smaller LC droplets may produce more elaborate structures in phase separation and suppress residual light scattering, we reduced the LC droplet size by using monomer (prepolymer) mixtures with low functional numbers as low as 1 or 2. However, phase separation may fail to occur with such low-functionality monomers, as previous studies suggested that the elasticity in a low-dimensionality polymer network may be insufficient to segregate LC molecules. We therefore used a prepolymer containing urethane groups to strengthen the polymer networks. A mixture of monomers (prepolymer) with a wide viscosity range was used. Such a monomer system is expected to diffuse at different rates and, consequently, to polymerize into complicated periodic structures as a result of interventional irradiation. Furthermore, a small amount of 1-vinyl-2-pyrrolidione (NVP) was added because it generally fulfills three purposes: first, as a diluent to homogenize the monomer mixture; second, as a cross-linker in the polymer network; and third, as an agent to reduce LC droplets.

2. RESULTS

The diffraction efficiency spectrum was measured for different angles of incidence. Each spectrum displayed either a single peak or plural peaks, of which the intensity and wavelength varied as a function of the angle of incidence. Characteristic results, measured at 25 °C, are plotted for the samples with X = 50 mol % and Tex = 55 °C (Figure 1) and X = 50 mol % and Tex = 55 °C (Figure 2), as a function of the wavelength λ and the angle of incidence θ, where X is the molar ratio of LC to the raw mixture and Tex is the exposure temperature, as detailed in section 2.3. The vertical bars in the graphs denote the diffraction efficiencies for the p- and s-polarizations, ηp and ηs. The broken curves in the λ−θ plane represent the theoretical estimates of the Bragg formula for a periodic structure with a pitch of Λ/N, that is, λ = 2(Λ/N) sin θ, where Λ is the periodic interval of the sinusoidal intensity fringes produced by the interventional irradiation and N = 1, 2, 3, ...
The value of \( \Lambda \) was determined to be 1.03 ± 0.03 \( \mu m \) from optical microscopy as detailed below. The measured diffraction efficiencies satisfy the Bragg formula for each \( N \).

For \( N = 1 \), \( \eta_p \) is large and satisfies the Bragg formula over a wide range of \( \theta \), as represented by the data located on the curves (\( N = 1 \)) in Figures 1a and 2a. On the other hand, \( \eta_s \) is approximately zero over the \( \theta = \lambda \) plane, as shown by the data on the curves (\( N = 1 \)) in Figures 1b and 2b. For \( N = 2, \eta_p \) and \( \eta_s \) are essentially zero, as shown by the data on the curves (\( N = 2 \)) in Figure 1a,b, but have nonzero values over a wide range of \( \theta \) when the sample was prepared with another condition, as shown by the data on the curves (\( N = 2 \)) in Figure 2a,b. Some diffraction is also apparent along the curves, corresponding to \( N \geq 3 \), for all the samples prepared. We examined a thicker sample, as shown in Figure 3a,b. The results are of an optical grating of a thickness of 29 \( \mu m \), which was prepared with \( X = 56 \text{ mol} \% \) and \( T_{ex} = 40 \degree C \). The measured data show that \( \eta_p \) for \( N = 1 \) is mostly 90\% and \( \eta_s \) for \( N = 2 \) is about 60\%, and they depend strongly on the polarization state.

We sampled the diffraction efficiencies for \( N = 1 \) and 2 at \( \theta = 30\degree \), at wavelengths of approximately 1.0 and 0.5 \( \mu m \), respectively. The diffraction property is generally characterized by its polarization and magnitude. In this paper, the diffraction polarization \( \alpha \) is defined as \( \alpha = (\eta_p - \eta_s)/(\eta_p + \eta_s) \) and equals \(-1, 0, \) or 1 when the diffraction is completely s-polarized, nonpolarized, or p-polarized, respectively. The values of \( \alpha \) for \( N = 1 \) and 2 are mapped as a function of \( X \) and \( T_{ex} \) as expressed by the color scale in Figure 4a,b, respectively. The magnitude of the diffraction \( \beta \) is defined as the maximum diffraction efficiency achieved by rotating the polarization azimuth and is expressed by the contours superposed on the same figures. As shown in Figure 4a, the diffraction for \( N = 1 \) retains p-polarization (\( \alpha > 0 \)) over a wide range of \( T_{ex} \) and \( X \), whereas \( \beta \) increases as \( X \) increases. The increase of \( \beta \) is particularly strong around \( X = 50 \text{ mol} \% \), as indicated by the high contour density. Figure 4b shows the diffraction for \( N = 2 \) changing from p- to s-polarization as \( X \) increases. The transition from green to red shows the polarization switching rapidly from the p-state (\( \alpha > 0 \)) to the s-state (\( \alpha < 0 \)) as \( X \) increases past 50\% of \( T_{ex} \). This change appears significantly at approximately \( T_{ex} = 40 \degree C \). These rapid changes in \( \beta \) for \( N = 1 \) and in \( \alpha \) for \( N = 2 \) near \( X = 50 \text{ mol} \% \) are mostly independent of \( T_{ex} \).

The diffraction properties of the samples prepared with a high-functionality monomer or dipentaerythritol pentaerythrylate (DHPHA) were examined in comparison with the present low-functionality monomer system. The values of \( \alpha \) and \( \beta \) are mapped as a function of \( X \) and \( T_{ex} \) in the same way as Figure 4, for \( N = 1 \) and 2, respectively, as shown in Figure 5a,b. For \( N = 1 \), the values of \( \alpha \) and \( \beta \) are the largest at around \( X = 55\text{–}60 \text{ mol} \% \) and \( T_{ex} \) below nematic-to-isotropic (NI) transition temperature, which decrease monotonically as \( X \) or \( T_{ex} \) deviates from there, as shown in Figure 5a, whereas the values of \( \alpha \) and \( \beta \) for the samples obtained from low-functionality monomers remain large in the wide range of \( X \) and \( T_{ex} \) particularly even at \( T_{ex} \) higher than the NI transition point, as shown in Figure 4a. For \( N = 2 \), as shown in Figure 5b, \( \beta \) reaches its maximum value of 0.06 at around \( X = 57 \text{ mol} \% \) and \( T_{ex} = 40 \degree C \), and \( \alpha \) remains positive. On the other hand, as shown in Figure 4b, \( \beta \) is averagely quite larger than that in Figure 5b, and \( X \) can control \( \alpha \) well between negative and positive. The results indicate that the samples made of high-functionality monomers produce single diffraction only for \( N = 1 \) and suggest a microscopic view that the periodic structure of phase separation forms sinusoidal distribution of refractive index modulation.

Figure 6a,b shows the diffractions efficiencies as a function of the polarization azimuth for \( N = 1 \) and 2, respectively. The data refer to four specific samples with different values of \( X \) at \( T_{ex} = 40 \degree C \), denoted I to IV in Figure 4. In Figure 6a, the diffraction polarization for \( N = 1 \) remains in the p-state as \( X \) increases, whereas in Figure 6b, the diffraction for \( N = 2 \) changes from p-polarization to nonpolarization and to s-polarization states, as shown by samples I to IV. Figure 6c,d shows the diffraction efficiencies as a function of the polarization azimuth for \( N = 1 \) and 2, respectively, when samples I to IV were heated up and maintained at 70 \degree C. The polarization properties of the HPDLCs were found to appear and vanish reversibly at temperatures below and above the NI transition point. This result ensures that the diffraction polarization is caused by the LC orientation orderings that were inhomogeneously formed through PPIPS in the interferential exposure.

The parameter \( S \), which quantitates the orientation ordering at 25 \degree C (i.e., a temperature below the NI transition point of K15 (35 \degree C)), is mapped out as a function of \( T_{ex} \) and \( X \) in Figure 7. \( S \) is very close to zero near \( X = 33 \text{ mol} \% \), regardless
of $T_{ex}$ and is consistent with the result shown in Figure 4a,b. That is, the diffraction property near 33 mol % for $N = 1$ and 2 is nonpolarized or nondiffracted. $S$ increases with increasing $X$ initially, and much more steeply as $X$ passes 50 mol %, albeit with some local irregularities.

Microscopic optical anisotropy in the periodic structures of samples I to VI was observed when the grating vector was rotated to 45° in the azimuth from the polarizing directions of the crossed-nicols polarizers, as shown in Figure 8a–f. The inset photographs in Figure 8a–d were captured under the same exposure, to allow a comparison of the average optical anisotropy between samples I, II, III, and IV. The fringes are arranged along the direction of the grating vector (arrow labeled p in the image). The pitch of 1.03 ± 0.03 μm corresponds to the interferential interval of the exposure. This indicates that anisotropic and isotropic phases were formed with a spatial periodicity by PIPS in the interferential exposure and suggests that the LC molecules in the LC-rich phase are ordered in their orientation along the grating vector, whereas the polymer-rich phase is isotropic. The periodic contrasts increase with increasing $X$, as shown in the insets. This result is consistent with the increase in $S$ as shown in Figure 6. Samples V and VI, of which $X$ is 57 mol %, revealed smooth and obvious periodic contrasts within the image resolution, as shown in Figure 8e,f, in comparison with the image of sample IV, of which $X$ is nearly the same.

Detailed morphological information on the phase separation was obtained by observing the cross sections of the polymer phase in samples I to VI using a scanning electron microscope (SEM), after rinsing out the LC phase. The resulting images are shown in Figure 9a–f and magnified in the insets. The cross sections show the periodic variable clarity along the direction of the grating vector (the arrow p in the image) with a periodicity of 1 μm. These periodic layers can reasonably be regarded as consisting of polymer- and LC-rich phases. In the sample with a small $X$, for example, sample I, as shown in Figure 9a, the polymer pervades most of the periodic structure, whereas the LC-rich phase is confined to narrow layers. In samples II and III, as shown in Figure 9b,c, the polymer layers gradually decrease, and the LC molecules most likely permeate the polymer phase with increasing $X$. Then, in sample IV, as shown in Figure 9d, the porous network of the polymer extends, incorporating the LC molecules to form the mixed phases. On the other hand, as shown in Figure 9e,f, samples V and VI possess relatively large holes locally confined in the grating layers, in comparison with sample IV.

3. DISCUSSION

In this study, the optical diffractions measured here are regarded as not purely but mostly Bragg diffraction because they are categorized in the intermediate regime between Raman–Nath and Bragg types but are close to the Bragg regime, according to the criteria proposed by Moharam et al., as detailed below. They proposed two indicators to evaluate the criteria of the diffraction type, that is, the terminology of thin or thick grating, $Q' = 2\pi d/n\Lambda^2 \cos \theta'$, and the modulation parameter of the refractive index, $\gamma = \pi \Delta n d/n \cos \theta'$. The values of $Q'$ and $\gamma$ for our HPDLC gratings can be estimated to be 41.3 and 2.65, respectively. Note that the periodic pitch is $\Lambda = 1 \mu m$, the thickness is $d = 10 \mu m$, the average refractive index is $n = 1.6$, the amplitude of refractive index modulation is $\Delta n = 0.08$, the optical wavelength is $\lambda = 1 \mu m$, and the angle of incidence in the grating medium is $\theta' = 18.2^\circ$, estimated from the angle of incidence in air $\theta = 30^\circ$ through Snell’s law. According to the criteria, an optical diffraction is categorized into the Raman–Nath regime if $Q' < 1$, in the Bragg regime if $Q' > 20$, and in the intermediate regime if the other cases. The values of $Q'$ and $Q'$ for our HPDLCs are estimated to be about 109 and 15.6, respectively, from the above-mentioned parameters. Thus, the diffractions are categorized into the intermediate regime but far from the Raman–Nath regime and close to the Bragg regime.

The occurrence of multiple Bragg diffractions ($N = 1, 2, \ldots$) from the HPDLC with different wavelengths and polarizations for every angle of incidence indicates that the grating possesses a periodic nonsinusoidal modulation of the birefringent refractive index. As shown in Figure 4, the diffraction behavior is rapidly altered around an LC/monomer ratio value, $X = 50$ mol %. The orientation-ordering parameter $S$ also displays a marked change at the same value, $X = 50$ mol %, as shown in Figure 7. These coincident changes in di
traction because measurements of $N$ appear and vanish reversibly by changing the temperature, as shown in Figure 6, the uniaxial orientation orderings are most likely distributed periodically with different periodic pitches $\Lambda$/

![Figure 5. Bragg diffraction efficiency for samples prepared using a high-functionality monomer (DPhPA) mapped as a function of the LC/monomer mixture ratio and the exposure temperature. The data are shown in the same way as in Figure 4. The labels V and VI indicate the measurement points discussed elsewhere in this paper.](image-url)
N at N = 1, 2, ... This complex periodic distribution of the orientation orderings is speculated to result from LC molecular anchorings that occur at the interfaces with the polymer phases.28,31,58,59 At small values of X, the LC molecules aggregate to form isolated droplets surrounded by the polymer network, as shown in Figure 9a,b. These isolated droplets typically display a point-symmetric shape. Therefore, optical anisotropy is not macroscopically exhibited, although each droplet possesses orientation-ordered LC molecules. For large X, the LC droplets coalesce together in the porous polymer networks, as shown in Figure 9c,d. The two-beam interferential exposure may uniaxially produce periodic phase separation along the grating vector and anisotropic coalescent boundaries between the LC molecules and the polymer networks. Consequently, the orientation orderings formed by these anisotropic interfaces are considered to appear macroscopically as optical anisotropy.

Various polarization-operated diffractive switches composed of these HPDLCs can be implemented using this one-time interferential exposure, simply by controlling the preparation conditions. Our HPDLCs allow us to control the diffraction intensity individually at different wavelengths by the polarization state, and the devices can be grouped into three types. The first type is an antisynchronous wavelength selector, that is, the incident light with a given wavelength is diffracted at the p-polarization state and transmitted at the s-polarization state, whereas the incident light with a given different wavelength is diffracted at the s-polarization state and transmitted at the p-polarization state (sample IV, Figure 6a,b). The second type is a synchronous wavelength selector, which switches the diffraction/transmission states synchronously at two given different wavelengths.

Figure 6. Polarization azimuth dependence of the diffraction efficiency for samples I to IV, labeled in Figure 4. The results were obtained for wavelengths of (a) λ = 1 μm and (b) λ = 0.5 μm and with an angle of incidence θ = 30°, corresponding to N = 1 and 2, respectively. The data in (c) and (d) are the same, respectively, as those in (a) and (b) but were measured at 70 °C, higher than the NI transition point of the LC material (35 °C), where the data for samples II to IV in (d) are magnified ten times to show them in detail. Note that p- and s-polarizations correspond to 0° (180°) and 90° (−90°) in polarization azimuth, respectively.

Figure 7. Map of the orientation ordering parameter S of the LC in the HPDLCs, as a function of the LC/monomer mixture ratio and the exposure temperature. Measurements were performed at 25 °C. Samples I to IV refer to the labels in Figure 4. The circle symbols represent measured points. The labels I–IV indicate the measurement points discussed elsewhere in this paper. The values of S on the map were linearly interpolated between the measurements. The NI transition point of the LC material (35 °C) is expressed as a broken black line.
wavelengths by rotating polarization azimuth (sample I, Figure 6a,b). The third type switches the diffraction/transmission states of the incident light at a given wavelength depending on polarization azimuth, whereas the light with a given different wavelength remains diffracted regardless of the polarization state (nearly sample III, Figure 6a,b). These types are adjustable in the fabrication process, as mentioned above. Furthermore, the fabrication process could be integrated with other processes, such as multibeam, multiple, or nonlinear irradiation, and potentially produce advanced holographic structures.

4. CONCLUSIONS

In summary, we first produced HPDLCs displaying multiple Bragg diffractions with different wavelengths and different polarizations for every angle of incidence, following PPIPS by a single interferential exposure. We have to note that, strictly speaking, our HPDLCs produce not purely but mostly Bragg diffractions, based on the established criteria. The polarization states of the diffraction were found to be individually controlled from linear to nonpolarized states while retaining a large diffraction efficiency, by carefully adjusting the fabrication parameters and choosing fundamental properties of the raw materials. The fabrication parameters that governed the nonsinusoidal periodic structure of the phase separation were only the LC/monomer compositional ratio and the exposure temperature. The extremely low functionality of the used monomers reduced the domain size in the phase separation. The mixture of plural types of monomers with different viscosities was used, causing diffusion at different rates during PPIPS to form elaborate periodic structures. A cross-linker (NVP) and a prepolymer including urethane groups were employed to strengthen the polymer network. This method is readily adaptable to other fabrication techniques and has a potential for applications to various optical (photonic) diffractive devices.

5. EXPERIMENTAL SECTION

5.1. Mixture of Materials. A nematic LC, 4-cyano-4′-pentylbiphenyl (K15, Merck Corp., molecular weight \(M_w = 249.53\), viscosity \(\eta_v = 30 \text{ mPa s (25}^\circ\text{C)}\)), has refractive indices for ordinary and extraordinary rays \((n_o = 1.5331 \text{ and } n_e = 1.7288)\) and a NI transition point of 35 \(^\circ\text{C}.\) K15 was mixed with a commercial prepolymer (AH600, Kyoeisha Chemical Co., Ltd., \(M_w = 612.7, \eta_v = 2000–4000 \text{ mPa s, and functionality } f = 2)\) that possesses urethane groups in 2-hydroxy 3-phenoxy propyl acrylate (refractive index \(n = 1.5258\)) and hexamethylene diisocyanate \((n = 1.453)\). We mixed dimethylol tricyclo-decane diacrylate (DCPA, Kyoeisha Chemical Co., Ltd., \(M_w = 304, \eta_v = 150 \text{ mPa s, } n = 1.5034, \text{ and } f = 2)\) and 2-hydroxyethyl methacrylate (HO, Kyoeisha Chemical Co., Ltd., \(M_w = 116.1, \eta_v = 6.5 \text{ mPa s, } n = 1.453, \text{ and } f = 1)\) as monomers and NVP (Sigma-Aldrich Co. LLC., \(M_w = 111.4, \eta_v = 2.5 \text{ mPa s, } n = 1.512, \text{ and } f = 1)\) as a cross-linker. The corresponding ratios in the monomer mixtures AH600, DCPA, HO, and NVP were 50, 22, 22, and 6 mol %, respectively. The ratio of the LC and the monomer mixture was \(X:(100 - X), \) where \(X\) varied.
from 33 to 59 mol %.

An initiator, N-phenylglycine (NPG, Tokyo Chemical Industry Co., Ltd., \(M_w = 151.2\)), and a sensitizer, dibromofluoroscein (DBF, Tokyo Chemical Industry Co., Ltd., \(M_w = 490.1\)), were then added to the mixture, in 0.1 and 0.1 wt %, respectively. The whole mixture was stirred while increasing the temperature gradually to 50 °C and was then confirmed to have dissolved uniformly after cooling down to 20 °C.

In addition, samples were prepared using a higher functionality monomer in the same way as aforementioned. K15 was mixed with a monomer DPHPA (mixture of tetra-, penta-, and hexa-acrylate) (Polysciences, Inc., \(M_w = 524.5, n = 1.490, f \approx 5\)). The corresponding ratios in the monomer mixtures DPHPA and NVP were 94 and 6 mol %, respectively. The ratio of the LC and the monomer mixture was \(X:(100 - X)\), where \(X\) varied from 44 to 70 mol %. NPG and DBF with 0.1 wt % were added to the monomer mixtures. The whole mixture was stirred in the same way as above, except that the temperature was increased to 70 °C, and was then confirmed to be uniformly dissolved.

5.2. Photopolymerization Procedure. The mixtures were injected into a 10 μm gap formed between two glass substrates of size 20 × 25 × 1 mm, where the actual measured gap in the experiment was 9.6 ± 0.6 μm. The substrate surfaces were untreated to avoid favoring any particular orientation of the LC molecules and were cleaned by ultrasonication and ozonization. Two-beam interferential exposures were carried out to enable PPIPS of the mixtures in the gaps. The light source was a continuous-wave single-mode Nd:YVO₄ laser with a wavelength of 532 nm (J150GS, Showa Optronics Co., Ltd.). The laser light was expanded, collimated, and split into two pathways, each with an intensity of 20 ± 2 mW cm⁻². Then, the two beams were superposed on the cells at angles of incidence of 15° and −15° relative to the plane perpendicular to the cell surface for fabricating HPDLCs. The superposition was designed to produce sinusoidal intensity fringes with a 1 μm pitch in the cell. During exposure, the mixture in the cell was maintained at a constant temperature \(T_{ex}\) that was varied between 25 and 70 °C. After an interferential exposure over 5 min, any residual monomer was polymerized by a uniform 5 min irradiation with an ultraviolet lamp of intensity 0.8 mW cm⁻² at room temperature.

5.3. Measurement and Observation. The diffraction intensity was measured for wavelengths ranging from 0.3 to 2.5 μm and an angle of incidence \(\theta\) in air varying between 20° and 60°, using a spectrophotometer (U4100, Hitachi High-Technologies Corp.). The angles of incidence and diffraction were adjusted to satisfy the Bragg condition. The diffraction efficiency was determined by normalizing the diffraction intensity with the incident intensity. This was done separately.
for linear polarizations parallel and perpendicular to the plane formed by the incident and diffracted rays, referred to as the p- and s-polarizations, with diffraction efficiencies $\eta_p$ and $\eta_s$ respectively.\(^{12}\)

Infrared absorption near the 2226 cm\(^{-1}\) peak is an indicator of the molecular orientation of the cyano-biphenyl LC.\(^{60}\) The absorption areas $A_p$ and $A_s$ relating to the p- and s-polarization states, respectively, were measured separately using an FTIR spectrophotometer (Frontier, PerkinElmer Co., Ltd.) together with an infrared polarizer. The orientation ordering of the LC molecules was hence determined as $\Delta A = (A_p - A_s)/(A_p + 2A_s)$. The optical anisotropies of the LC- and polymer-rich periodic phases were observed using a polarizing optical microscope (MT9430, Meiji Techno Co., Ltd.) in a crossed-nicols configuration. Cross sections of the periodic structure were observed using a SEM (S-4300, Hitachi High-Technologies Corp.) after the samples were cut and rinsed with methanol to dissolve the LC droplets. The distribution and shape of the LC droplets were manifested by the holes formed in the polymer.

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**Notes**
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