Formation of Microscopic Polymer Structure in LCs by Patterned UV Irradiation using Polymerization Inhibitor

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Abstract  We controlled the fine-pitch polymer aggregation in liquid crystals (LCs) two-dimensionally via patterned ultraviolet (UV) irradiation, where a photomask was used to precisely control the light distribution. The combination of high-intensity UV light and a polymerization inhibitor suppressed polymerization in the masked area, and improved the uniformity of LC alignment between fine-pitch polymer structures. We were able to electrically control the diffraction patterns of polymer-dispersed LCs.

Keywords: Liquid crystal, Polymer dispersed liquid crystal, Polymer aggregation, Polymerization inhibitor, Pattern UV irradiation

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) have attracted considerable attention because they allow for excellent control of light distribution, and are mechanically strong due to their unique internal polymer aggregation. PDLCs have found applications in privacy windows, and in both flexible and viewing-angle-controllable displays. However, it is challenging to precisely control light distribution through the PDLCs because of the difficulties associated with management of fine-pitch polymer aggregation. We previously aimed to control such structures by delivering anisotropically diffused ultraviolet (UV) light through a micro lens placed on the surface of the substrate. This distributed UV light unevenly into the LC-monomer mixture; monomers were phase-separated and polymerized along the direction of light when illuminance was high. A layered structure formed because of polymerization-induced phase separation. The polymer structure thus controlled light distribution.

However, it is difficult to apply this technique in a two-dimensional plane; the UV light evenly irradiates all LC cells. Two-dimensional control of light distribution permits local viewing angle control of displays. For example, the functionality of automotive displays is enhanced, improving driver safety. In addition, if the LC alignment between fine-pitched polymer structures could be controlled, LC-spatial light modulators (LC-SLMs) with fine pixel pitch could be realized. These devices would immediately find applications in novel electrical holographic displays, and improve the field of view of existing holographic displays through precise control of the two-dimensional phase of light.

Here, we controlled the fine-pitch polymer aggregation in LCs two-dimensionally via patterned UV irradiation using a photomask (Fig. 1). In this fabrication process, a mixture of a LC, a monomer, and a small amount of photoinitiator are injected into the empty cell and then irradiated with UV light through a photomask (Fig.1(a)). The LC and monomer are phase-separated and form a polymer aggregation structure in the irradiated area (Fig.1(b)). This method is not a conventional interference irradiation technique and can be applied to easily control polymer structure over a large area.

Polymer aggregations in LCs created via UV patterning using a photomask have often served as spacers in flexible LCDs. The spacer pitch is about 100 µm and the monomer concentration is about 15 wt%.

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for optical diffusers, holographic displays and other electrically switchable phase gratings\(^{(22)}\), the pitch is only a few micrometers and the monomer concentration exceeds 50 wt\%. Hence, monomer diffusion and polymerization in the masked area must be considered. In this paper, we optimized the UV intensity and added a polymerization inhibitor when creating fine-pitch polymer aggregates. The direction of alignment of LCs between the fabricated fine polymer structures was controlled; the two-dimensional diffraction patterns by the fine-pitch lattice-shaped polymer structures are also described.

### 2. Experimental

We precisely controlled the internal polymer aggregation in LCs via patterned UV exposure through a photomask. A polarizing microscope (BX-50; Olympus) fitted with a crossed-Nicols polarizer was used to evaluate aggregation. The dark and bright regions indicate optically isotropic polymer and birefringent LCs, respectively, which allows polymer aggregation to be evaluated.

#### 2.1 Sample preparation

We prepared a mixture of nematic LC (E-7; Merck) and UV-curable monomer (NOA65; Norland Products) (1:1 w/w). Empty cells were fabricated from polyethylene-terephthalate (PET) substrates (thickness: 50 \(\mu\)m) without any alignment treatment and the LC/monomer mixture was added through capillary injection. Plastic bead spacers were used to control cell thickness (5 \(\mu\)m). The cell was irradiated with collimated nonpolarized UV light (JATEC Co. Ltd.) through a photomask; this triggered phase separation. The center wavelength was 365 nm and the light was normally incident to the cell substrate. The photomask was striped; the width of the masked area was 1 \(\mu\)m and the pitch was 2 \(\mu\)m. Phase separation of the polymer network and the LCs of PDLCs is markedly affected by temperature during UV irradiation\(^{(23)-25)}\). If the monomer concentration is high, the temperature must be above that of the nematic-isotropic phase transition temperature, \(T_{NI}\), of the LC/monomer mixture. If the temperature is lower than that value, the LCs enter the nematic phase and scatter the UV light\(^{6} 26) 27)\). Therefore, we operated at 50°C; the \(T_{NI}\) was 35°C.

#### 2.2 Effect of UV intensity on polymer aggregation

The intensity of the UV light greatly affects the rates of phase separation and polymerization, and thus polymer aggregation. We fabricated LC cells under UV irradiation of 2, 10, and 25 mW/cm\(^2\) at 50°C, and observed the samples using a polarizing microscope fitted with a crossed-Nicols polarizer. The amount of integrated UV light was 6.0 J/cm\(^2\) to fully polymerize the monomer. We also measured the distribution of diffracted light through the PDLCs, and thus the diffraction efficiency to evaluate the polymer structures, using an angle-luminance analyzer (Conoscope; Autronic-MELCHERS GmbH) fitted with a collimated white light-emitting diode (LED). The light was normally incident on all samples. For precise control of polymer aggregation, suppression of polymerization in the masked area is important; however, this becomes more difficult at higher monomer concentrations. The residual polymer network in the masked area reduces the difference in refractive index between LCs and the polymer structures, thereby degrading PDLC diffraction efficiency.

The diffraction efficiency \(\eta\) is defined as follows:

\[
\eta = \frac{P}{P_0}
\]

where \(P\) is the diffracted power of first-order diffracted light and \(P_0\) is the incident power.

#### 2.3 Effect of a polymerization inhibitor

We investigated whether a polymerization inhibitor could facilitate the control of polymer aggregation\(^{(28)}\). In the presence of the inhibitor, polymerization is more rapid in UV-exposed areas; in masked regions, polymerization is readily terminated. Thus, monomers diffuse to light-exposed areas and aggregate therein. The excessive inhibitor affects the polymer structures in UV-exposed areas, therefore, we optimized a concentration and added a 3.5 wt\% polymerization inhibitor (Osaka Organic Chemical Industry) to the LC mixture and delivered UV at 25 mW/cm\(^2\) and 50°C. Samples were completely irradiated to polymerize all residual monomers, and then subjected to polarizing microscopy and diffraction analysis.

#### 2.4 LC alignment in finely pitched polymer structures

When the monomer concentration is high, the alignment of the bulk LC is affected by residual monomers and surface anchoring of polymer structures\(^{(29)}\). We evaluated the uniformity of LC alignment when the pitch of the striped photomask was 2, 4, and 10 \(\mu\)m. Cells were fabricated with two PET substrates. We spin-coated a photo alignment material film (TO2; Nissan Chemical) onto the substrates and baked them at 100°C for 1 min.
Next, we irradiated both substrates with linearly polarized UV light to obtain LCs that were aligned parallel to the polymer stripes. The center wavelength was 313 nm and the integrated light level was 252 mJ/cm². The LC alignment directions were 0° and 45° to the polarizer axis.

3. Results and Discussion

3.1 Effect of UV intensity on polymer aggregation

Figure 2 shows micrographs of PDLCs fabricated under UV irradiation of 2, 10, and 25 mW/cm². It is clear that the striped polymer structures became more uniform as the UV intensity increased.

Figures 3 and 4 show the diffraction patterns and the relationship between diffraction efficiency and UV intensity, respectively. A He-Ne laser (05-LHP-151; Melles Griot) was used to study the diffraction properties; the light was normal to each sample. At a UV intensity below 10 mW/cm², the light was linearly transmitted rather than diffracted. When the UV intensity was over 10 mW/cm², the diffraction efficiency increased monotonously as the UV intensity increased. At low UV intensity, phase separation is slow, but is ultimately complete in large-pitch polymer structures. However, when fabricating fine pitch structures, we considered that phase separation should be rapid (under high-intensity UV light) to suppress monomer diffusion to the masked area. The UV light was diffracted by the fine-pitch mask, triggering polymerization of residual monomers in the masked area. Thus, high UV intensity facilitated control of fine polymer structure and the photomask pattern was replicated.

3.2 Effect of polymerization inhibitor

Figures 5 and 6 show micrographs and diffraction patterns of PDLCs fabricated in the presence of 3.5 wt%}

![Fig. 2 Microscopic images of fabricated PDLCs with UV irradiations at (a) 2 mW/cm², (b) 10 mW/cm² and (c) 25 mW/cm².](image)

![Fig. 3 Diffraction pattern of PDLC fabricated with UV irradiations at 2 mW/cm² and 25 mW/cm².](image)

![Fig. 4 Relationship between diffraction efficiency and UV intensity.](image)

![Fig. 5 Microscopic images of fabricated PDLC (a) without polymerization inhibitor and (b) with polymerization inhibitor.](image)

![Fig. 6 Diffraction pattern of PDLC fabricated with polymerization inhibitor.](image)
polymerization inhibitor, respectively. Compared to the case without inhibitor, polymer precipitation in the masked area was suppressed. Also, third-order light diffraction was evident and the diffraction efficiency improved from 0.12 to 0.15. The inhibitor suppressed polymerization in the masked area and increased the difference in refractive index between LCs and polymer structures, thus enhancing PDLC quality (Fig. 7).

3.3 Evaluation of LC alignment in fine-pitch polymer structures

In general, alignment films on upper and lower substrates control LC alignment. However, for LC cells with fine-pitch polymer structures, bulk LC alignment is affected by the residual polymer network of the LCs and the surface anchoring of polymer structures. Figure 8 shows micrographs of PDLCs in parallel alignment. If the LC molecules align uniformly parallel to the polarizer axis, the entire micrograph is dark. PDLCs fabricated in the absence of polymerization inhibitor leaked light (Fig. 8(a)), attributable to LC alignment distortion by the residual polymer network. When polymerization inhibitor was added, light leakage was suppressed, the uniformity of LC alignment improved as polymer pitch was reduced. Thus, uniform LC alignment was feasible on addition of polymerization inhibitor with fine-pitch polymer structures, reducing the level of residual polymer and improving spatial anisotropy.

3.4 Two-dimensional control of polymer aggregation

Finally, we attempted to control polymer structure two-dimensionally via patterned UV irradiation using a photomask. We used 50-µm-thick PET substrates without alignment layers. The UV irradiation pattern of the LC layer was affected by the diffraction of the fine-pitch photomask. First, we calculated the UV irradiation pattern at the LC layer by the lattice-shaped photomask using the angular spectrum method. The width of the masked area was 2 µm, the pitch was 7 µm, and the distance between the photomask and the LC layer was 50 µm. Figure 9(a) shows the calculation result. The UV illuminance distribution pattern at the LC layer differed from that of the photomask, therefore, the pattern of the photomask was optimized by consideration of diffraction.

We placed the above-mentioned photomask at the position of the LC layer and irradiated it with the light from the side of the LC layer. We calculated the illuminance distribution at the actual location of the photomask by the angular spectrum method. This illuminance distribution becomes a necessary pattern of the photomask and the calculation result was shown in Fig. 9 (b). We fabricated PDLCs using the polymerization inhibitor and the new photomask, and subjected the samples to polarizing microscopy (Fig. 10) and diffraction analysis (Fig. 11). Polymer structure and
diffraction efficiency improved on addition of the polymerization inhibitor, and electrical control of the diffraction pattern was achieved (Fig. 11(b)). The applied voltage was 80 V.

4. Conclusion

In this study, we precisely controlled the polymer aggregations in LCs two-dimensionally via UV irradiation using a photomask for precise control of the light distribution pattern and the phase of light. High-intensity UV achieved fine-pitched polymer structures by suppressing monomer diffusion into the masked area. A polymerization inhibitor suppressed polymerization in the masked area, thereby enhancing the fine polymer structures in LCs. The inhibitor reduced the polymer network, providing highly uniform LC alignment by the fine-pitched polymer structures enhancing a spatial anisotropy. The diffraction pattern could be precisely controlled, therefore, our method could facilitate the fabrication of future functional displays and high-quality holographic displays.

References

1) J.Y. Kim & P. Palffy-muhoray, "Phase Separation Kinetics of a Liquid Crystal- Polymer Mixture," Molecular Crystals and Liquid Crystals, 203, pp.93-100 (1991)
2) P.S. Drzaic, "Polymer dispersed nematic liquid crystal for large area displays and light valves," J. Appl. Phys. 60(6), 2142-2148 (1986)
3) J.W. Doane, N.A. Vaz, B.-G. Wu and S. Zumer, "Field controlled light scattering from nematic microdroplets," Appl. Phys. Lett. 48(4), 269-271 (1986)
4) Y. Hisatake, Y. Kawata and A. Murayama, "Viewing Angle Controllable LCD using Variable Optical Compensator and Variable Diffuser Cell Structure," SID Symp. Dig. Tech. Pap., 31(1), pp.1218-1221 (2005)
5) T. Ishinabe, Y. Horii, Y. Shibata, H. Fujikake, "Light distribution control of layer-structured PDLC fabricated by using micro lens structure and anisotropically diffused UV light," Optics Express, 27(9), pp.13416-13429 (2019)
6) Y. Horii, Y. Shibata, T. Ishinabe and H. Fujikake, "Polymer Distribution Control of Polymer-Dispersed Liquid Crystals by Unidirectionally Diffused UV Irradiation Process," IEICE Trans. Electron, E101-C(11), 857-862 (2018)
7) K. Maeda, S. Ishizuka, T. Tsujino, H. Yamamoto and A. Takigawa, "Optical performance of angle dependent light control glass," Opt.
Mater. Tech. Energy Efficiency Sol. Energy Conversion 1536, 138-148 (1991)
8) T. Okita, K. Kawamura, T. Ohno, M. Ueda, S. Kitayama and S. Hozumi, "A polymer film that controls light transmission - LUMISTY," Kusuri No Chishiki, pp.37-48 (1991)
9) M. Honda, S. Hozumi and S. Kitayama, "A novel polymer film that controls light transmission," 3rd Pacific Polym. Conf., pp.159-169 (1993)
10) T. Uematsu, S. Maenosono, A. Watanabe and Y. Yamaguchi, "Angular dependence in the transmittance from self-organized striped pattern of refractive indices in photopolymer," J. Polym. Sci., B, Polym. Phys. 40(2), pp.216-225 (2002)
11) S. Seo, M. Nishizawa, Y. Horii, Y. Shibata, T. Ishinabe and H. Fujikake, "Proposal of novel optical model for light-diffusing film having alternating polymer layers with different refractive indices," IEICE Trans. Electron. E100-C(11), 1047-1051 (2017)
12) Y. Sekiguchi, T. Ishinabe, S. Seo, Y. Shibata and H. Fujikake, "Diffraction mechanism of a light-diffusing film with an alternate-polymer-layer structure," Appl. Opt. 56(34), 9564-9572 (2017)
13) Z. Zhang, Z. You, D. Chu, "Fundamentals of phase - only liquid crystal on silicon (LCSOS) devices," Light Sci Appl., 3(10), e213 (2014)
14) Y. Isomae, Y. Shibata, T. Ishinabe, H. Fujikake, "Design of 1-µm-pitch liquid crystal spatial light modulators having dielectric shield wall structure for holographic display with wide field of view," Opt. Rev. 24(2), pp.165-176 (2017)
15) Y. Isomae, T. Ishinabe, Y. Shibata and H. Fujikake, "Alignment control of liquid crystals in a 1.0-µm-pitch spatial light modulator by lattice-shaped dielectric wall structure," J. Soc. Inf. Disp., 27(4), pp.251-258 (2019)
16) M. Date, Y. Takeuchi and K. Kata, "A memory-type holographic polymer dispersed liquid crystal (HPDLC) reflective display device," J. Phys. D Appl. Phys. 31(18), 2225-2230 (1998)
17) K. Kato, T. Hisaki and M. Date, "Alignment-Controlled Holographic Polymer Dispersed Liquid Crystal for Reflective Display Devices," Jpn. J. Appl. Phys. 38(2B), 805-808 (1999)
18) K. Tanaka, K. Kata and M. Date, "Fabrication of holographic polymer dispersed liquid crystal (HPDLC) with high reflectivity efficiency," Japanese J. Appl. Physics, Part 2 Lett., 38(3A) (1999)
19) H. Sato, H. Fujikake, Y. Iino, M. Kawakita and H. Kikuchi, "Flexible Grayscale Ferroelectric Liquid Crystal Device Containing Polymer Matrices and Networks," J. Jpn. Appl. Phys., 41, pp.5052-5056 (2002)
20) Jong-In Baek, Jong-Ha Shin, Min-Cheol Oh, Jae-Chang Kim and Jong-In Baek, "Formation of High-Performance Polymer Walls in a Liquid Crystal Cell by Phase Separation of Fluorinated Polymer Mixture," Journal of Information Display, 7(1), pp.7-11 (2006)
21) T. Ishinabe, S. Takahashi, Y. Shibata and H. Fujikake, "Evaluation of Capability to Maintain Thickness of LC layer of Flexible LCDisplays with Bonding Polymer Spacers," ITE Trans. Media Technol. Appl., 7(4), pp.183-189 (2019)
22) Anup K. Ghosh, Yoichi Takehata, Ken Ishikawa and Hideo Takezoe, "Electrically controllable polarization-dependent phase grating from photocurable liquid crystals," Journal of Applied Physics, 95, 5241 (2004)
23) P. Kumar and K.K. Raina, "Morphological and electro-optical responses of dichroic dispersed liquid crystal films," J. Appl. Phys. 7(6), pp.636-642 (2007)
24) R.B. Deshmukh and M.K. Malik, "Effect of temperature on the optical and electro-optical properties of poly (methyl methacrylate)/ET polymer-dispersed liquid crystal composites," J. Appl. Phys. Sci. 109(1), pp.627-637 (2008)
25) S. Ohta, S. Inasawa and Y. Yamaguchi, "Size control of phase-separated liquid crystal droplets in a polymer matrix based on the phase diagram," J. Polym. Sci., B, Polym. Phys. 50(12), pp.863-869 (2012)
26) C. Shen and T. Kuo, "Spinodals in a polymer dispersed liquid crystal," J. Chem. Phys. 102(1), pp.556-562 (1995)
27) D. Nwabuzma, K.J. Kim, Y. Lin, L.C. Chien and T. Kuo, "Phase Diagram and Photopolymerization Behavior of Mixtures of UV-Curable Multifunctional Monomer and Low Molar Mass Nematic Liquid Crystal," Macromolecules 31(20), pp.6806-6812 (1998)
28) Françoise Lartigue-Peyrou, "The use of phenolic compounds as free-radical polymerization inhibitors," Industrial Chemistry Library, 8, pp.489-505 (1996)
29) B. Jerome, "Surface effects and anchoring in liquid crystals," Reports Prog. Phys., 54(3), pp.391-451 (1991)
30) J.W. Goodman, Introduction to Fourier optics, Roberts & Co (2005)

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