Mol. Cryst. Liq. Cryst., Vol. 530: pp. 13/[169]–18/[174], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.496288

Fabrication of Broadband Cholesteric Liquid Crystal Films by Photopolymerization-Induced Phase Separation

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We optimized fabrication conditions of cholesteric liquid crystal (CLC) films; 1) amount of photo-initiator, 2) exposure conditions. Based on these conditions, we could succeed in fabricating broadband CLC films with $\Delta\lambda \approx 250$ *nm. We also examined the spatial helical pitch gradient structure fabricated here using a field emission-scanning electron microscope (FE-SEM) at a freeze-fractured cross-section of the fabricated CLC films.*

Keywords Cholesteric liquid crystals (CLC); field emission scanning electron microscope (FE-SEM); pitch gradient; selective reflection

1. Introduction

Cholesteric liquid crystals (CLCs) exhibit wavelength- and polarization-selective reflection due to the helical arrangement of their molecules; in other words, CLCs selectively reflect circularly polarized light with the same handedness as a helix. This phenomenon is a type of Bragg reflection and makes CLCs one of the most interesting one-dimensional self-assembled photonic crystals [1].

For the normal incidence of light along the helical axis, selective reflection occurs when the wavelength λ_R of the light is of the order of the pitch p of the helix: [2]

$$\lambda_R = np,$$

where n is the average refractive index calculated as $(n_o + n_e)/2$ (n_o and n_e are the ordinary and extraordinary refractive indices of the CLC, respectively). Selective reflection occurs within a bandwidth $\Delta\lambda = \Delta n p$, where $\Delta n = n_e - n_o$ is the birefringence. Thus, the reflection bandwidth $\Delta\lambda$ is proportional to the birefringence Δn. CLC films

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with a reflection bandwidth can be used for manufacturing optical components such as polarizers, mirrors, and colour filters.

However, CLCs have a relatively narrow reflection bandwidth because Δn is small ($\Delta n \leq 0.2$); this narrow bandwidth is rather limited for specific wideband applications (e.g., wideband polarizers). In general, the bandwidth $\Delta\lambda$ is less than 100 nm in the visible spectrum with typical values of around 50 nm [3]. Several methods have been proposed to overcome this limitation. For example, CLC films with broad reflection bandwidth can be fabricated by exposure to UV illumination with an intensity gradient across the film thickness [4,5]. Another approach is to induce diffusion between two different CLCs [6–9]. Wideband CLC films can also be fabricated by diffusing small molecules into the polymerized film [10].

In this work, we fabricated CLC films by varying the following parameters: the doping concentration of the photoinitiator, intensity of irradiating UV-light, and irradiation time. By optimizing the fabrication conditions, we succeeded in fabricating wideband CLC films with $\Delta\lambda \approx 250$ nm. The spatial pitch gradient structure fabricated here was confirmed using a field-emission scanning electron microscope (FE-SEM) at a freeze-fractured cross section of the fabricated CLC films.

2. Experimental

2.1. *Materials*

A photo-reactive liquid crystal (LC) with a mono-acrylate functional group was employed as a host material. Its nematic temperature ranged from 76°C to 149°C. CM223 (BASF) and Igacure 907 (Ciba-Geigy) were used as a chiral dopant and a photoinitiator, respectively. CM223 has di-acrylate functional groups and can also react with the host LC during photoreactions. The chemical structures of the materials used in this work are depicted in Figure 1. The CLC mixture contained approximately 95 wt% of the host LC and 5 wt% of CM223 with a small amount (0.5–2 wt%) of the photoinitiator.

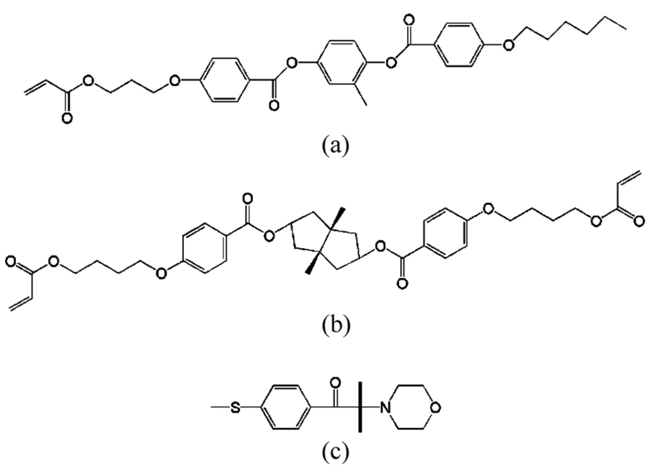

Figure 1. Chemical structures of (a) liquid crystal, (b) chiral dopant (CM223, BASF), and (c) photo-initiator (Irgacure 908, Ciba Geigy).

2.2. *Film Fabrication*

The CLC mixture was introduced into sandwiched cells composed of two parallel glass substrates by capillary action at 80°C. The spacing of 4.75 μm was maintained by glass beads. These cells were then annealed for 1 h for the LC molecules to align homogeneously. The planar structure in which the helical axis of the CLC molecules is perpendicular to the glass substrates results from the capillary action. A cholesteric Grandjean (planar) texture was clearly observed between crossed polarizers. The transmittance spectrum was measured in situ by UV-visible spectroscopy while the LC cells were on the hot plate. The CLC films were kept at 80°C to allow a large displacement between the constituents during the UV-light exposure (wavelength: 365 nm). Then, cross-linked CLC films with a spatial helical pitch gradient were fabricated.

2.3. *Measurement*

To confirm the existence of a spatial helical pitch gradient, transmittance spectra were measured (Agilent 8453 UV-Visible spectroscopy, Agilent Technologies). Cross-sectional images of the CLC films were obtained using an FE-SEM system (LEO SUPRA 55 FE-SEM, Carl Zeiss).

3. Results and Discussion

3.1. *Optimizing Amount of Photoinitiator*

Figure 2 shows the transmittance spectra of the CLC films prepared with several different photoinitiator concentrations and exposure times. Before UV irradiation, the observed reflection wavelength (λ_{centre}) and the bandwidth exhibited by the pure CLC films were 590 nm and 50 nm or less, respectively. Then, the CLC films were irradiated with UV light of intensity 50 μWcm^{-2}.

UV-light irradiation was carried out until the photoreaction of the precursor was fully terminated, and the termination time was determined by a photo-differential scanning calorimeter (photo-DSC). The observed termination times for photoinitiator concentrations of 0.5, 1, and 2 wt% were 90, 70, and 25 s, respectively, at an irradiation intensity of 50 μWcm^{-2}. For concentrations of 0.5 and 1 wt%, the final bandwidths were approximately 150 and 250 nm, respectively. In contrast, for a concentration of 2 wt%, the film exhibited the widest bandwidth that varied from 420 nm to over 900 nm. However, the band profile gradually decreased and deformed because light scattering was enhanced by highly cross-linked networks. Therefore, we chose the intermediary condition with a photoinitiator concentration of 1 wt% in order to fabricate the wideband CLC film.

3.2. *Optimizing Exposure Conditions*

The transmittance spectra of the CLC films irradiated with various UV-light intensities (50, 100, and 500 μWcm^{-2}) and exposure times are shown in Figure 3. In this case, the precursor contained 1 wt% of the photoinitiator. As the UV-light intensity increased, the photoreaction of the precursor terminated more quickly. The termination time was determined by photo-DSC. When the precursor was irradiated with the highest intensity (500 μWcm^{-2}), the observed bandwidth could not be effectively

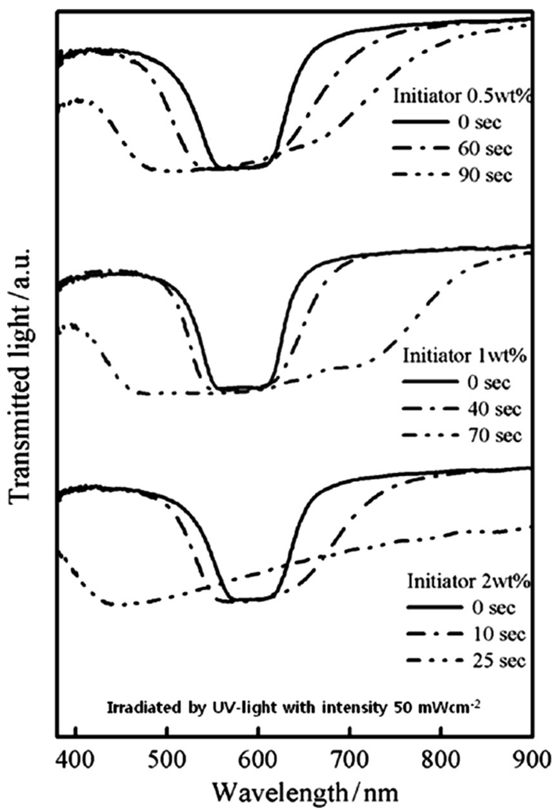

Figure 2. Transmittance spectra of the CLC films prepared with several different concentrations (0.5, 1, and 2 wt%) of photo-initiator and exposure times.

broadened, that is a spatial helical pitch gradient could not be induced e. This was because the strong intensity accelerated the photoreaction quickly, thereby impeding the diffusion of the constituents. Thus, CLC films with a narrow pitch gradient ($\Delta\lambda < 100$ nm) could be fabricated. Among the three conditions that were tested, the CLC film treated by the weakest UV-light intensity of 50 μWcm^{-2} over long periods exhibited the largest bandwidth of at least 250 nm. From these results, it is clear that weak UV-light irradiation over a long period was most effective in increasing the bandwidth of CLC films. This is because such irradiation for a photoreaction can effectively induce the gradual diffusion of the constituents along the film thickness.

3.3. *Confirming Pitch Gradient*

The pitch gradient can be visualized using FE-SEM at a freeze-fractured cross-section of the fabricated CLC films. The pitch varies gradually across the thickness of the film. Figure 4 shows the cross-section micrograph of the CLC film with a photoinitiator concentration of 1 wt% and an irradiation intensity of 50 μWcm^{-2} for a 70s time interval. As seen from Figure 4, both the dark and the less-dark regions are observed in alternate positions. Two neighbouring dark or less-dark

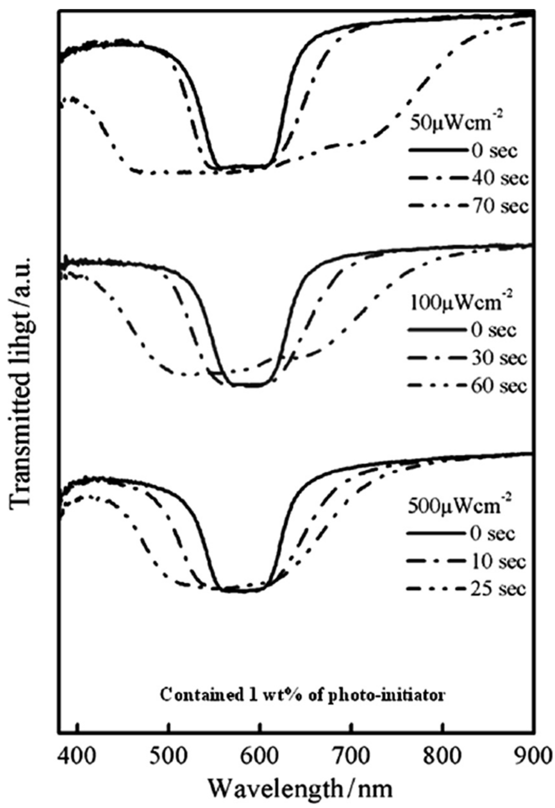

Figure 3. Transmittance spectra for the CLC films irradiated with various UV-light intensities ($50\,\mu Wcm^{-2}$, $100\,\mu Wcm^{-2}$, and $500\,\mu Wcm^{-2}$) and exposure times.

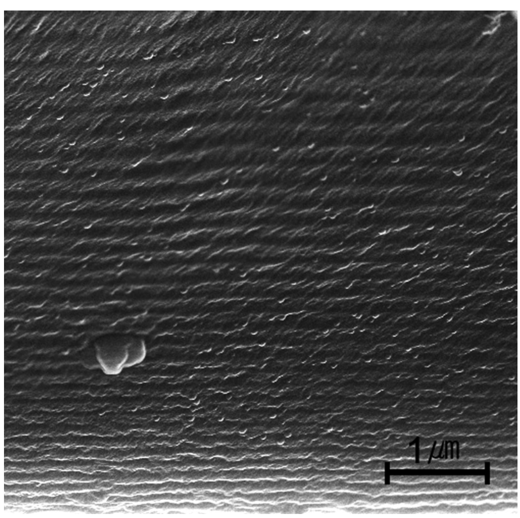

Figure 4. FE-SEM micrograph of cross section of CLC film with pitch gradient. The top substrate was closest to the UV light source during UV-crosslinking reaction.

regions correspond to one-half of the helical pitch $P_0/2$, that is, the LC director rotates 180° across the film thickness. A spatial pitch gradient across the film thickness is clearly apparent from Figure 4; the pitch is longest near the UV-light source and it gradually decreases in length as we move towards the opposite substrate.

4. Conclusion

We fabricated CLC films by varying several fabrication parameters: the doping concentration of the photoinitiator, intensity of UV-light irradiation, and irradiation time. Under optimal conditions, we succeeded in making broadband CLC films with a bandwidth $\Delta\lambda \approx 250$ nm. We also confirmed the spatial pitch gradient structure using a FE-SEM at a freeze-fractured cross section of the fabricated CLC films.

Acknowledgments

This research was supported by the Kyung Hee University Research Fund in 2009 (KHU-20090728).

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