

Dependence of Retardation Dispersion on the Ultraviolet Polarization Direction During Photopolymerization of Self-organized Smectic Reactive Mesogen Molecules

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(Received April 2, 2018 : revised May 4, 2018 : accepted June 8, 2018)

We investigated the dependence of the retardation dispersion on the polarization direction of ultraviolet (UV) light during the photopolymerization of self-organized smectic reactive mesogen (RM) molecules. RM retarder film that was photopolymerized with UV light linearly polarized parallel to the layer plane showed negative dispersion (ND) of retardation for a wide range of UV polymerization temperatures. On the other hand, film that was photopolymerized with unpolarized UV light showed negative dispersion in a narrow range of UV polymerization temperatures. With a certain UV polymerization temperature, the dispersion of retardation was converted from positive to negative, depending on the UV polarization.

Keywords : Retarder, Negative dispersion, Photo-polymerization, UV polarization, Reactive mesogen
OCIS codes : (260.1440) Birefringence; (260.2030) Dispersion; (120.2040) Displays; (310.6860) Thin Films, optical properties

I. INTRODUCTION

Retarder films are widely used in display devices to compensate for viewing-angle dependence. Retarder films generally have a positive dispersion (PD) of retardation $Re(\lambda) = \Delta n d$, where λ is the wavelength of light, Δn is the birefringence, and d is the thickness of the film [1]. PD of $Re(\lambda)$ means that $Re(\lambda)$ decreases for longer λ . Meanwhile, a retarder with negative dispersion (ND) of $Re(\lambda)$ has been recently developed by several groups [2-7]. The $Re(\lambda)$ of an ND retarder increases for longer λ . The ND retarder is especially useful for the antireflective (AR) film of an organic light-emitting diode (OLED) display. A commercial OLED AR film is a quasicircular polarizer composed of a linear polarizer (LP) and a quarter-wave plate (QWP) [1, 8-11]. The ND retarder is used as the QWP and can render the phase retardation $\Gamma(\lambda) = 2\pi \Delta n d / \lambda$ constant, independent of λ . Thus the reflectance from an OLED can be minimized throughout the whole visible-wavelength range, provided that the ND retarder has an ideal dispersion of $Re(\lambda)$.

There have been several approaches to making an ND retarder [3-14]. The previous approaches can be classified as single-layer [3-7] or multilayer types [8-14]. The single-layer ND retarder has the benefits of simple fabrication process and slimness, whereas the multilayer ND has superior viewing-angle properties. Future flexible displays require a thinner retarder film for reliability during the bending and folding; hence the single-layer ND retarder is expected to be mainstream. Single-layer ND retarders can be made of stretched polymers [2, 3] or reactive mesogen (RM) molecules [4-7]. A retarder film made of RMs is generally thinner than a stretched film, and draws much attention for flexible-display components [15-17].

Our group has reported a ND retarder using two-dimensional self-organization of smectic RM molecules (Fig. 1) [5-7]. The HCM026 absorbs shorter-wavelength light, compared to the N2, as described in our previous paper (Fig. 1(a)) [17]. When the N2 molecules were parallel to the layer plane, the refractive index n_x along the layer-normal direction smoothly decreased, while n_y along

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the layer-parallel direction rapidly decreased, showing ND of $Re(\lambda)$ (Fig. 1(b)). On the other hand, when the N2 molecules were orthogonally oriented to the layer plane, PD of the $Re(\lambda)$ was shown [17]. In the previous paper, we changed the photopolymerization temperature to vary the molecular orientation; in this paper, we have changed the UV polarization direction and investigated its effect on the dispersion of $Re(\lambda)$. We have found that the ND of $Re(\lambda)$ is promoted by UV light polarized along the layer-parallel direction (Fig. 1(b)), and that ND of $Re(\lambda)$ is suppressed by UV light polarized orthogonal to the layer plane. In addition, ND of $Re(\lambda)$ was shown across a wide range of UV polymerization temperatures.

II. METHODS

Figure 1 shows the chemical structures of the RM molecules used in this study. The HCM026 (HCCH), N2, and a photoinitiator (Irgacure 651, Ciba Chem) were mixed in a weight ratio of 58.8:39.2:2.0. The materials were diluted in chloroform solvent and stirred at 80°C for 10 min. The weight fraction of the solid contents in the solution was 10 wt%. For planar alignment of the RM molecules, a commercial polyimide (PI) (PIA-X189-KU1, JNC) was spin-coated on the substrate, baked at 230°C for 1 h, and then rubbed with a cotton cloth. Then the RM mixture was spin-coated on the polyimide-coated substrate. The RM-coated sample was heated up to the target temperature and baked for 3 min, and then was exposed to UV light with an intensity of 40 mW/cm² for 3 min. with a nitrogen-gas purge. The temperature of the sample was maintained using a heating stage (Linkam) with a variation of less than 0.1°C. To compare the effect of the UV polarization, a linear UV polarizer (Edmund Optics) was

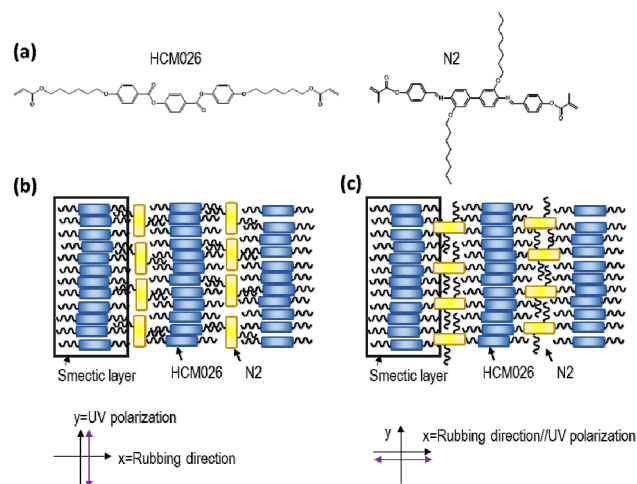


FIG. 1. (a) Chemical structures of the RM molecules used in this study, and schematic illustrations of the RM-molecule orientations when the UV polarization was (b) parallel and (c) orthogonal to the layer plane.

placed in front of the sample and the transmission axis of the polarizer was oriented parallel or perpendicular to the smectic layer of the RM mixture. The transmission center wavelength and the full width at half-maximum (FWHM) of the UV polarizer were 365 and 10 nm respectively.

For the measurement of $Re(\lambda)$ of the retarder film, the probe beam consecutively passed through a linear polarizer, the sample, and a polarimeter (Thorlab). The slow axis of the sample was tilted 45° from its transmission axis. The Stokes parameter was measured after transmission through the sample, and $Re(\lambda)$ of the sample was calculated. The details of the optical measurement are described in our previous paper [17]. The UV-vis absorption spectrum of the sample was measured with a commercial UV-vis spectrophotometer (UV2700, Shimadzu) with a broadband UV polarizer.

III. RESULTS AND DISCUSSION

To investigate the effect of UV polarization during the photopolymerization process, we prepared three types of samples: The first was photopolymerized in the absence of the UV polarizer, the second with UV polarization parallel to the plane of the smectic layer, and the third with UV polarization orthogonal to the smectic-layer plane.

Figure 2 presents photographs of the fabricated films positioned between a pair of crossed-polarizers. The retarder film photopolymerized in the absence of the UV polarizer showed homogeneous brightness, when the rubbing direction was at 45° to the polarizer (Fig. 2(a)), but showed some light leakage when the rubbing direction was parallel to the polarizer (Fig. 2(d)). The film photopolymerized with UV polarization parallel to the layer plane also showed a large extinction between crossed polarizers (Figs. 2(b) and 2(e)). Moreover, this film showed much less light leakage when the rubbing direction was parallel to the polarizer (Fig. 2(e)). Because the thickness of the RM was the same

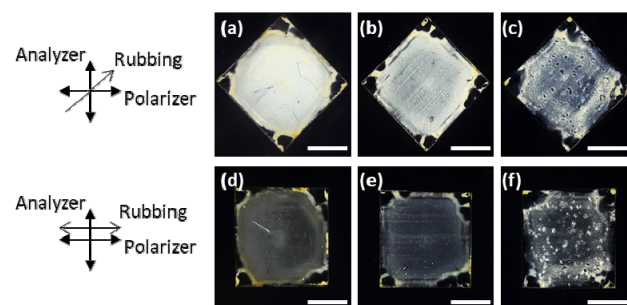


FIG. 2. Photographs of the fabricated retarder films, observed between crossed polarizers. The UV light was (a) unpolarized and linearly polarized (b) parallel to and (c) orthogonal to the smectic layer. The rubbing direction was 45° from the transmission axis of the polarizer for the samples in (a)-(c), and was at 0° in (d)-(f). The samples were photopolymerized at 100°C with the UV light. The scale bars correspond to 10 mm.

in both samples, the homogeneous dark state in Fig. 2(e) indicates the uniform orientation of the RM molecules when the UV polarizer was used. On the other hand, the film photopolymerized with UV polarization orthogonal to the layer plane showed heterogeneous orientation (Figs. 2(c) and 2(f)); the contrast between the crossed polarizer was very small, compared to the other films. We omitted the optical evaluation of this sample, due to its heterogeneous orientation.

As a next step, we measured the $\text{Re}(\lambda)$ of the retarder film photopolymerized in the absence of the UV polarizer, *i.e.* the film was photopolymerized with unpolarized UV light (Fig. 3). The RM-coated film was photopolymerized at 100°C. The film showed PD of $\text{Re}(\lambda)$, and $\text{Re}(550 \text{ nm})$ was 183 nm (Fig. 3(a)). Δn of the film was 0.131 at $\lambda = 550 \text{ nm}$. Figure 3(b) corresponds to the normalized $\text{Re}(\lambda)$, divided by $\text{Re}(550 \text{ nm})$. $\text{Re}(450 \text{ nm})/\text{Re}(550 \text{ nm})$ was 1.32, and $\text{Re}(650 \text{ nm})/\text{Re}(550 \text{ nm})$ was 0.91.

Figure 4(a) shows $\text{Re}(\lambda)$ of the retarder film photopolymerized with the UV polarizer when its transmission axis was parallel to the smectic-layer plane (see also Fig. 1(b)). This retarder film showed ND of $\text{Re}(\lambda)$ throughout

the visible wavelengths of light. This film was made from the identical RM compound and photopolymerized under the same conditions (same UV intensity, UV curing temperature, and UV curing time), except for the UV polarizer; therefore, this result implies that UV polarization plays an important role in the dispersion of $\text{Re}(\lambda)$. Figure 4(b) shows the normalized $\text{Re}(\lambda)$, divided by $\text{Re}(550 \text{ nm})$. The dashed line represents the ideal achromatic dispersion of $\text{Re}(\lambda)$, and we see that the experimental data were close to the ideal dispersion, except for the points at 450 and 650 nm.

We must note that the magnitude of $\text{Re}(\lambda)$ in Fig. 4(a) is much smaller than in Fig. 3(a). As described in our previous papers [5-7], ND of $\text{Re}(\lambda)$ appears when the N2 molecules are orthogonally aligned with the long axes of the HCM026 molecules (Fig. 1(b)). Because the core two RM molecules are orthogonally oriented, the net birefringence decreases. The thickness of the sample exhibiting ND in Fig. 4 was 1.3 μm , and Δn calculated from $\text{Re}(550 \text{ nm})$ was 0.054. On the other hand, when the N2 molecules are oriented parallel to the long axes of the HCM026 molecules, the net birefringence increases, showing PD of $\text{Re}(\lambda)$, as seen in Fig. 3(a).

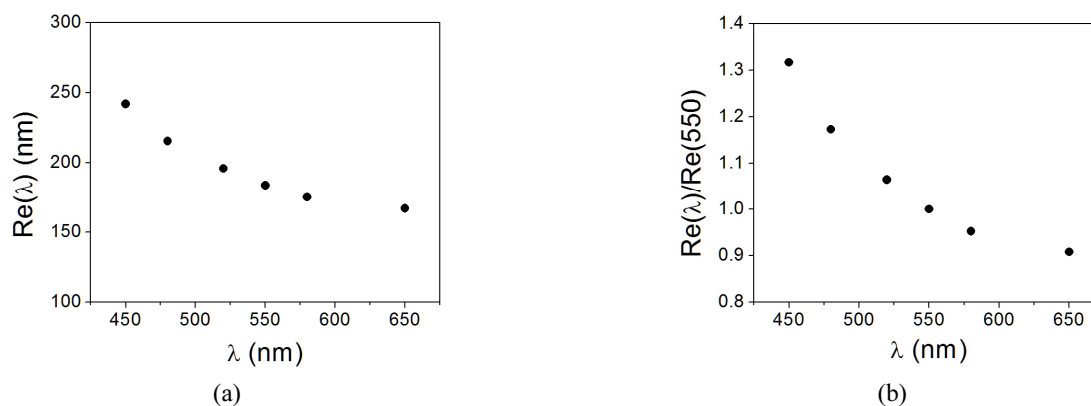


FIG. 3. (a) $\text{Re}(\lambda)$ of the retarder film photopolymerized with unpolarized UV light, as a function of λ . (b) Normalized $\text{Re}(\lambda)$, divided by $\text{Re}(550 \text{ nm})$. The films were photopolymerized at 100°C.

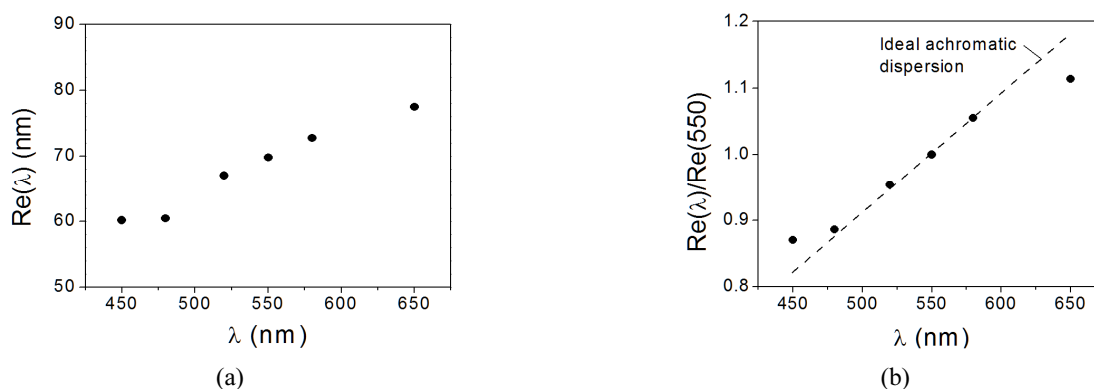


FIG. 4. (a) $\text{Re}(\lambda)$ of the retarder film photopolymerized with linearly polarized UV light, as a function of λ . The UV polarization was parallel to the smectic-layer plane. (b) Normalized $\text{Re}(\lambda)$, divided by $\text{Re}(550 \text{ nm})$. The dashed line corresponds to ideal achromatic dispersion of $\text{Re}(\lambda)$. The films were photopolymerized at 100°C with the UV light.

We also investigated the dependence of $\text{Re}(\lambda)$ dispersion on the UV polarization state with varying UV curing temperature (Fig. 5). To compare the dispersions of $\text{Re}(\lambda)$, the derivative $d\text{Re}(\lambda)/d\lambda$ was plotted as a function of the UV curing temperature. A positive sign of $d\text{Re}(\lambda)/d\lambda$ indicates ND of $\text{Re}(\lambda)$, while its sign being negative indicates PD of $\text{Re}(\lambda)$. In case of the film photopolymerized with unpolarized UV light (black squares), ND of $\text{Re}(\lambda)$ was seen when the UV polymerization temperature was 90°C. On the other hand, the film photopolymerized with UV light polarized along the layer-parallel direction showed ND of $\text{Re}(\lambda)$ when the UV curing temperature was 90–110°C. Thus, ND of $\text{Re}(\lambda)$ was seen in a wider range of UV curing temperature when the film was photopolymerized with UV light polarized along the layer plane. This result clearly shows that linearly polarized UV light can promote the ND of $\text{Re}(\lambda)$ and widen the processing-temperature range.

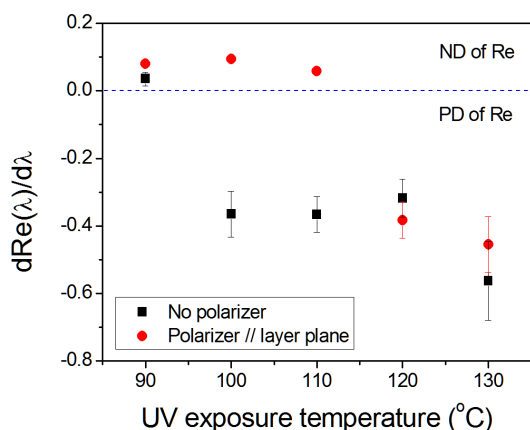


FIG. 5. $d\text{Re}(\lambda)/d\lambda$ of the retarder films photopolymerized with unpolarized or linearly polarized UV light parallel to the layer, versus UV curing temperature. The positive or negative sign of $d\text{Re}(\lambda)/d\lambda$ indicates the negative or positive dispersion of $\text{Re}(\lambda)$ respectively.

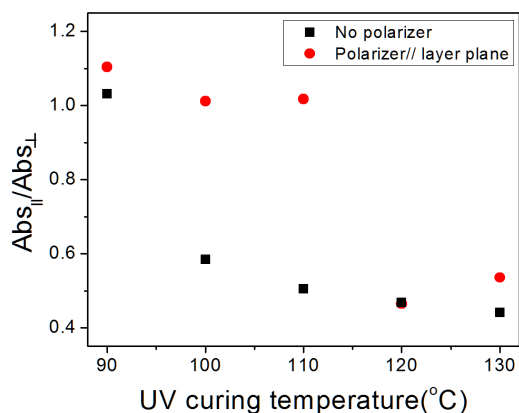


FIG. 6. Ratios of UV absorption intensities of photopolymerized retarder films cured at various temperatures. The absorption intensity was measured at 365 nm with a UV-vis spectrophotometer equipped with a UV polarizer.

To check the anisotropy of the polymer morphology, we measured the UV absorption spectra of the films at $\lambda = 365$ nm (Fig. 6). The absorption spectrum was measured with a UV-visible spectrophotometer equipped with a UV polarizer. We measured the absorption intensities of the films with the UV polarizer parallel and perpendicular to the smectic layer. Figure 6 shows the effect of UV curing temperature on the absorption ratio, defined as the absorption parallel to the layer plane ($A_{||}$) divided by the absorption orthogonal to the layer plane (A_{\perp}). Because the imine group of the N2 molecule strongly absorbs UV light at 365 nm (Fig. 1(a)), a higher absorption ratio means that more of the N2 molecules are aligned along the layer-parallel direction (Fig. 1(b)). The absorption ratio data in Fig. 6 show behavior very similar to that of the $d\text{Re}(\lambda)/d\lambda$ data in Fig. 5. The samples polymerized with the UV polarizer showed greater absorption ratios than those polymerized without the UV polarizer. Therefore, it is thought that more of the N2 molecules photopolymerized with the UV light parallel to the layer plane are aligned parallel to the layer plane, when the UV polarizer is used.

In the previous literature [18–20], it was reported that the morphologies of polymer networks were strongly affected by the UV polarization state. Because the electrical energy of the linearly polarized UV light is strong along the oscillation direction of the electric field, most of the UV energy is absorbed along the polarization direction of the UV light. Consequently, the polymer network also grows along the UV polarization direction (Figs. 1(b) and 1(c)). Thus the N2 molecules in the interlayer space easily absorb the UV energy and can grow in the layer plane. Because the N2 molecules absorb longer-wavelength UV light compared to HCM026 [15], the refractive index along the layer plane n_y rapidly decreases, while n_x orthogonal to the layer plane decreases smoothly, resulting in the ND of $\text{Re}(\lambda)$.

IV. CONCLUSION

In this paper, we investigated the effect of UV polarization on the $\text{Re}(\lambda)$ dispersion of a two-dimensionally self-organized smectic RM retarder film. It was found that UV light polarized along the smectic-layer plane can promote the ND of $\text{Re}(\lambda)$. ND of $\text{Re}(\lambda)$ could be obtained over a wide range of UV curing temperatures. On the other hand, film photopolymerized with UV light polarized orthogonal to the layer plane showed a heterogeneous orientation. We think that these results could be helpful in the fabrication and development of ND retarder films.

ACKNOWLEDGMENT

This research was supported by the Ministry of Trade, Industry, and Economy (MOTIE), the Korea Display

Research Consortium (10051334), and the National Research Foundation (NRF, 2016R1A2B4010361).

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