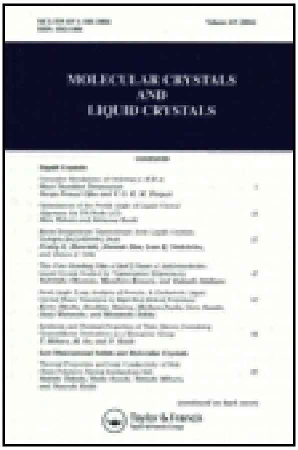

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Thermally Stable Binary Optical Films Based on Photocrosslinkable Liquid Crystalline Polymers Containing Azodyes

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Thermally Stable Binary Optical Films Based on Photocrosslinkable Liquid Crystalline Polymers Containing Azodyes

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We developed thermally stable binary optical films based on azodye-containing liquid crystalline polymers (ACLCPs) through two-step exposure of linearly polarized light with the wavelength of 488 nm together with subsequent exposure for photo-crosslinking by ultraviolet light under nitrogen atmosphere. Our fabricated optical films with two in-plane optic axes showed high thermal durability and little degradation of optical efficiency less than 5% at 200°C. Due to the large birefringence acquired during the photo-alignment, the binary optical films can be used as a variety of patterned retarders for mobile display applications.

Keywords: azodye-doped; binary optical film; liquid crystalline polymer (LCP); photo-alignment; thermal stability

I. INTRODUCTION

Photoreactive polymeric materials have great interest due to their excellent physical and optical properties suitable for organic-based optical and/or electronic device applications. Particularly, photo-crosslinkable liquid crystalline polymers (LCPs) have been widely used for producing binary optical elements such as optical retarders [1], color filters [2], polarization converters [3], and interference filters [4]. For fabricating such optical components, the LCP should be

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processed into an optically anisotropic film structure with in-plane bi-optic axes so that an alignment technique, for instance, the use of a rubbed surface [5] or a photo-treated surface [2,3] is inevitably required. However, the former often involves mechanical damages and contamination, and the latter suffers from the weak anchorage of the LCP [6,7].

In this paper, we present a new method of fabricating thermally stable binary optical films based on azodye-containing LCPs (ACLCPs). The volume-alignment of the doped azodyes in a bulk of the LCP is achieved by the exposure of linearly polarized (LP) light along the direction perpendicular to the polarization direction. The ACLCP optical films with two in-plane optic axes are produced using two-step exposures of the LP light through a photo-mask [8,9] together with subsequent exposure for photo-crosslinking by ultraviolet (UV) light under nitrogen (N_2) atmosphere. The photo-crosslinked ACLCP films show high thermal stability and little degradation of optical efficiency at 200°C. Moreover, due to the large birefringence acquired during the photo-alignment, the ACLCP films with two optic axes can be used as in-cell patterned retarders for mobile display applications [10].

II. EXPERIMENTAL CONSIDERATIONS

It is well known that azodye molecules experience a conformation change (photoisomerization) between *trans*-stable and *cis*-excited states when irradiated to resonant light. Light with polarization parallel to the longitudinal direction of the *trans*-isomers causes the *trans*-isomers to be transformed to the *cis*-isomers that thermally relax to the *trans*-isomers oriented randomly. Through the repeated excitation and relaxation processes, there is a statistical enrichment of the *trans*-isomers perpendicular to the polarization of light. As a result, the azodye molecules tend to align perpendicularly to the polarization of the irradiation light [11,12].

The LP light irradiation at the absorption wavelength ($\lambda = 488\,\mathrm{nm}$) of doped azodyes was performed to align the LCP molecules through the effective orientation of azodyes perpendicular to the polarization direction of irradiated light. The unpolarized UV exposure was subsequently carried out for photo-crosslinking under N_2 atmosphere.

A commercial photocrosslinkable LCP material, RMS 03-001C (E. Merck), was doped with an azobenzene copolymer of poly-((methyl methacrylate)-co-(Disperse Red 1 acrylate)) (Sigma-Aldrich) of 1% by weight. Figure 1 illustrates a binary patterned retarder with two different optic axes. A solution, filtered through a filter with the pore size

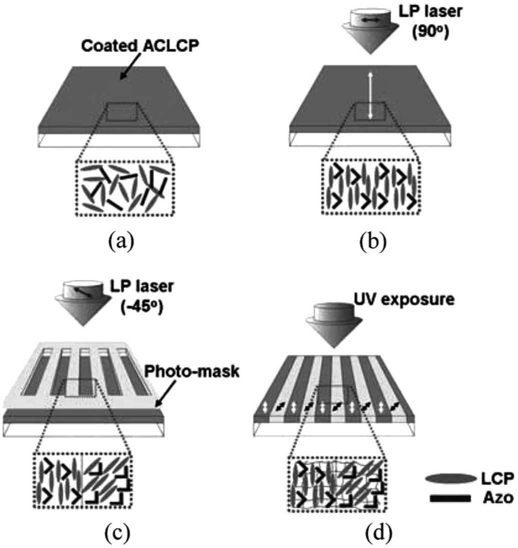

FIGURE 1 Schematic diagram of binary ACLCP film with different optic axes: (a) coated ACLCP material, (b) first irradiation of LP blue laser in the whole region, (c) second selectively irradiation of LP laser through photo-mask, and (d) UV exposure for curing the binary patterned retarder.

of 0.2 μm, was spin-coated on an indium-tin-oxide (ITO) glass substrate at the spinning speed of 500 rpm for 5 sec, then at 3000 rpm for 25 sec. The solution-coated ITO glass substrate was baked at 65°C for 1 min to remove the remaining solvent and to promote the adhesion of the azodye-doped LCP molecules as shown in Figure 1(a). An Ar-ion laser with the wavelength of 488 nm at the intensity of 200 mW/cm^2 was used as a pump beam for reorientation of azodyes. The polarization state for the first photo-exposure as a whole and that for the second photo-exposure through a photo-mask were denoted as 0° and 45°, respectively, as shown in Figures 1(b) and 1(c). After two-step photo-exposure, the ACLCP films with two optic axes were exposed to unpolarized UV light with the wavelength of 365 nm at the intensity of a 40 mW/cm^2 for 300 sec under N_2 atmosphere for photo-crosslinking as shown in Figure 1(d).

The phase retardation and the thickness of each film were measured using a photo-elastic modulation (PEM) method [13] at the wavelength of 632.8 nm and an alpha-step profiler, respectively. The thermal stability was monitored in terms of the retardation change in time at 150°C and 200°C. Note that the two temperatures correspond to the baking temperature of the LC alignment layer and the deposition temperature of metal electrodes.

III. RESULTS AND DISCUSSION

Figure 2 shows microscopic textures of the binary optical film of the ACLCP observed with a polarizing optical microscopy (POM, Optiphot2-Pol, Nikon) under crossed polarizers. Figures 2(a) and 2(b) correspond to such textures that one of two crossed polarizers makes an angle of 0° and 45° with respect to the optic axis of the binary optical film, respectively. It is clear that two in-plane optic axes were well defined in the ACLCP film.

As shown in Figure 2(a), the binary optical film shows bright and dark states along the directions of 0° and 45° between the bi-pattern of the LCP film as an optical retarder and one of crossed polarizers. Small white and gray arrows coincide with bi-domains with the directions of 0° and 45° aligned patterns, respectively. Figure 2(b) shows microscopic texture when the binary LCP optical film was rotated by an angle of 45° with respect to Figure 2(a). In this case, the bright and dark states were reversed. The measured optical retardation, $2\pi d\Delta n/\lambda$, of the binary optical film using the PEM technique was about 1.978 of the wavelength used. A He-Ne laser of 632.8 nm was used as a light source. This can be interpreted by the aligning power of the oriented azodyes.

Figure 3 shows normalized optical retardations of both the ACLCP optical film and the LCP optical film fabricated onto a photo-treated surface. The closed circles, triangles, and rectangles denote phase retardations of the LCP optical film fabricated onto a photo-treated layer with dependent of curing times, 10 sec, 60 sec, and 600 sec, respectively. After heating at 200°C for 6 hr, the initial phase retardations

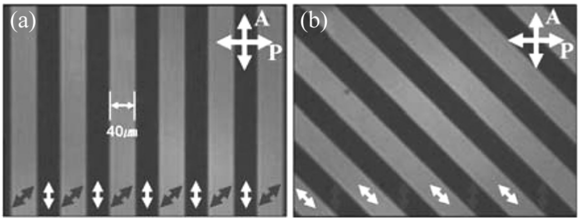

FIGURE 2 Microscopic texture of a binary ACLCP film on the glass observed under crossed polarizer: (a) an angle of 0° and (b) 45° between the direction of retardation layer and the rear polarizer. White and gray arrows denote 45° and 0° aligned ACLCP region.

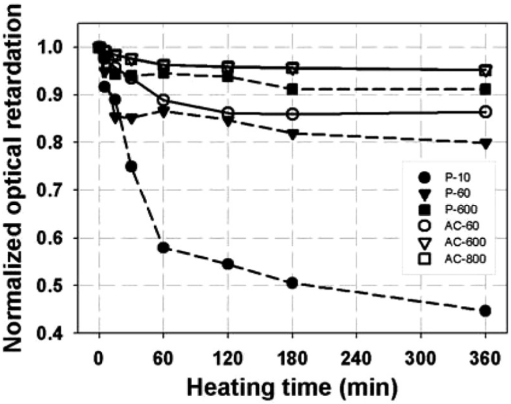

FIGURE 3 The normalized optical retardations of the photoalignment-induced LCP optical films and the binary ACLCP optical films with different curing times. The open circles, open triangles, open rectangles, closed circles, closed triangles, and closed rectangles denote the ACLCP optical films with different curing times, 60 sec (AC-60), 600 sec (AC-600), and 800 sec (AC-800), and the photoalignment-induced LCP optical films with different curing times, 10 sec (P-10), 60 sec (P-60), 600 sec (P-600), respectively.

of the LCP films decreased about 55% (10 sec), 20% (1 min), and 10% (10 min), respectively. According to previous experiments, the reduction of optical properties about ACLCP optical film with dependent of curing times over 60 sec were measured after heating at 200°C for 6 hr. As shown in Figure 3, the open circles, triangles, and rectangles denote phase retardations of the ACLCP optical films with different curing times, 60 sec, 600 sec, and 800 sec, respectively. The measured results decreased nearly 13% (60 sec), 5% (600 sec), and 5% (800 sec) as compared with initial phase retardations, respectively. The reductions of phase retardations about ACLCP optical films are smaller than those about LCP optical films for reasons that the aligning capability of photo-aligned by the oriented azodyes containing within the ACLCP bulk is higher than that of a surface-induced of photo-alignment layer. In addition, the measured results of the ACLCP optical films are saturated under 5% reduction value of optical efficiencies and thus, the curing time over 10 min enough to fabricated ACLCP optical films.

Figure 4 shows the measured thermal stability of the ACLCP optical films in time dependence at 150°C and 200°C, which temperatures correspond to the baking temperature of the LC alignment layer and the deposition temperature of metal electrodes fabricated onto the optical films. The initial phase retardation of the LCP film was about

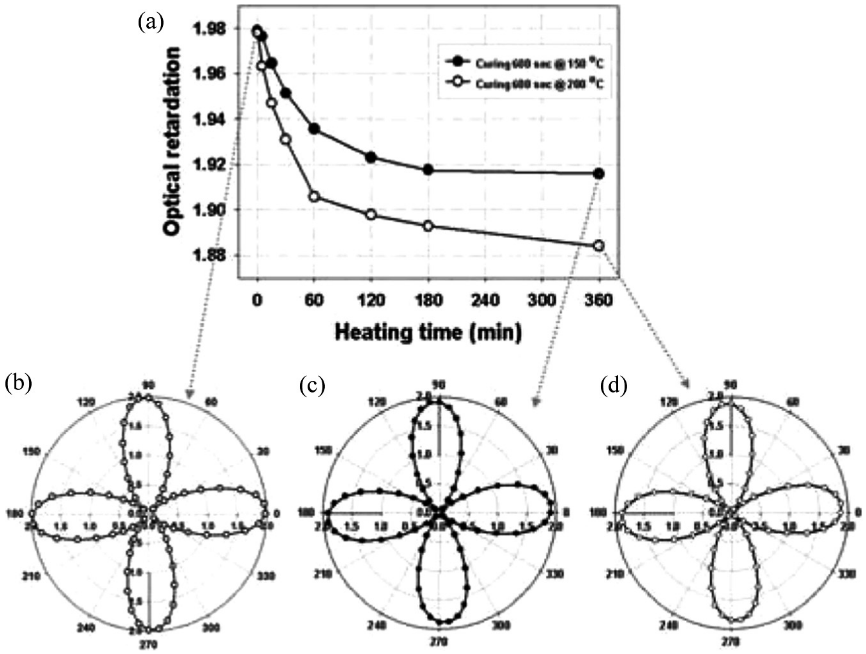

FIGURE 4 (a) The high stability of a binary ACLCP optical film measured at 150°C and 200°C after 6 hr. (b) Initial optical retardation of the ACLCP optical film. The optical retardation of the ACLCP optical film at (c) 150°C and (d) 200°C after 6 hr.

1.978 and the measured optical retardations of the ACLCP film with curing times of 10 min were about 1.9159 at 150°C and about 1.884 at 200°C after heating for 6 hr, respectively. In conclusion, reductions of the phase retardation of the ACLCP film at different heating temperatures were observed about 3% and under 5%, respectively. The measured results are on the high stable level with that (20% reduction ratio) of the photoalignment-induced and that (10% reduction ratio) of the rubbing-induced LCP optical film with adequate curing time, over 10 min. Consequently, our binary optical LCP film has enough thermal stability and lower degradation of optical efficiency.

IV. CONCLUSION

We developed thermally stable binary ACLCP optical films without any alignment layer. Due to be induced an orientation of azodyes perpendicular to the polarization direction of light by LP light irradiation, two-step LP light irradiations through a photo-mask could fabricate a bi-patterned states of the ACLCP layer. After double light treatments, the ACLCP was photocrosslinked by a UV exposure under N_2 atmosphere. In our fabricated ACLCP optical film, measured degradations of the optical retardation are on the high stable level with adequate curing time, over 10 min as compared with photo-alignment-induced LCP optical films. For reasons of aligning capability of volume-induced by the orientation of azodyes doped within the LCP bulk is higher than that of a surface-induced by the photo-alignment layer, the degradations of optical properties about ACLCP optical films are smaller than that about LCP optical film onto the photo-treated substrate. Consequently, our fabricated optical film has not only good performance as a retarder with appropriate birefringence and bi-optic axes, but also high temperature stability because the optical films were photocrosslinked by UV curing at two patterned state with higher degree of the aligning capability. Moreover, the in-cell binary optical films fabricated by using simple fabrication steps are much thinner, which is a strong request for mobile applications.

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