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Azodyes as Photoalignment Materials for Polymerizable Liquid Crystals

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We demonstrate the excellent photoalignment capability of sulfuric azodyes for polymerizable liquid crystals (PLC) whose anisotropic films are extensively studied as basic elements of many passive optical devices (e.g., retardation films, polarizers, and color filters). These dyes exhibit a high affinity to various substrates and insolubility in PLC and organic solvents commonly used for their dilution. An extremely low exposure dose (less than 50 mJ) is needed to induce an excellent planar alignment of PLC. This alignment can be easily patterned using minimal numbers of masks and exposure steps. No sign of alignment deterioration is observed after photopolymerization. These imply that new photoalignment materials can be effectively used for the industrial production of optical films based on PLC. Particularly, they suit the continuous manufacturing process for such films. [DOI: 10.1143/JJAP.46.2995]

KEYWORDS: polymerizable liquid crystal, photoalignment, azodye, retardation film, polarizer

1. Introduction

In contrast to that of conventional liquid crystals (LCs) the structure of polymerizable liquid crystals (PLCs) can be "frozen" by thermal or photoinduced polymerization that causes the solidification of PLC.¹⁾ This property opens a new field of application for LCs. It includes the manufacturing of passive optical elements, such as retardation or compensation films,^{2–5)} interference color filters,²⁾ and dichroic polarizers.⁶⁾ Anisotropic films of semicoducting PLCs are of great interest for organic light-emitting diodes (OLEDs), because of their capability of polarized emission.⁷⁾

To demonstrate their unique properties, PLCs should be properly aligned before solidification. There is some difference in alignment demands between conventional lowmolecular-weight LCs and PLCs. On the one hand, the demands for PLCs are less strict: the photoalignment layer should maintain PLC alignment only within a short time before polymerization, thus the usual strict requirements for LC alignment layers can be partially sacrificed. On the other hand, (1) the alignment layer should be insoluble in the organic solvents used to dissolve PLCs for film deposition; (2) it should provide strong anchoring to stabilize PLC alignment during polymerization; (3) it should provide sufficiently high photostability and thermal stability of alignment to prevent damage during photopolymerization and thermal polymerization, respectively; and (4) it should be highly adhesive to different substrates, particularly plastic films commonly used as substrates for compensation films.

For PLCs, same as for conventional LCs, the alignment treatment of bounding substrates is commonly used. The prevalent alignment method used is unidirectional rubbing. This method can hardly provide alignment patterning and sufficient alignment uniformity. To avoid these problems, photoalignment process for PLC films was proposed. Shannon *et al.*⁸⁾ aligned PLCs between a pair of substrates containing a photoalignment layer from the inner side. The photoalignment material was dichroic dye blended in a polymer matrix. Later on, Schadt *et al.*²⁾ used only one photoalignment layer for the alignment of PLC films. In the latter case, a cinnamate-based photoalignment material was employed.



Fig. 1. Chemical formula of sulfuric azodye SD1 as photoalignment agent.

Nevertheless, for industrial implication, photoalignment layers for PLC films should be improved. The polymer blends of dichroic dyes used in ref. 8 do not keep the required photoinduced order so that the alignment function can be lost some time after the light exposure. Besides, usually, the photoinduced order in these materials is not very high that leads to a moderate LC anchoring strength. In turn, cinnamate-based materials generally require a considerably higher exposure dose than materials containing dichroic dyes.

In this study, we consider adsorbed layers of sulfuric bisazodyes as photoalignment layers for PLCs. According to our previous results, this type of dyes can be effectively used for the alignment of conventional nematic 9,10 and ferroelectric smectic¹¹⁾ LCs. The chemical formula of the main dye utilized in the present study is shown in Fig. 1. It is designated as sulfuric dye 1 (SD1). The SD1 molecule contains groups that enable good adhesion to various surfaces. UV exposure causes an effective reorientation of SD1 molecules perpendicular to the polarization direction of activated light, which is practically not accompanied by trans-cis photoizomerization that takes place in azopolymers and polymer blends.¹²⁾ The thickness of the alignment film is very low (2-12 nm) so that coloring and optical retardation produced by this film can be neglected. SD1 and similar dyes are insoluble in PLCs and solvents commonly used to dilute them (e.g., toluene and cyclohexanone). The latter preserves their alignment function in the case of contact with PLCs or PLC solutions.

2. Experimental Procedure

SD1 was dissolved in dimethylfolmamide (DMF) at a

concentration of 1 wt %. A filtered to 0.2 µm solution was spin-coated on the substrates at 800 rpm for 10 s then at 3000 rpm for 60 s. The substrates were glass slides or plastic poly(ether sulfone) (PES) films. Before coating the alignment layer, the substrates were cleaned in an ozone cleaner for 10 min. The SD1-coated substrates were baked at 100 °C for 30 min to remove the remaining solvent and to strengthen the adhesion of the azodye molecules to the substrate. Subsequently, the alignment layers were exposed to UV irradiation from a high pressure mercury lamp from Oriel. The UV component of the irradiation was extracted using a cutoff filter. In the major irradiation procedure, light was linearly polarized by a UV polarizer and directed normally to the substrate. The intensity of irradiation in the emission line at $365 \text{ nm was } 3.3 \text{ mW/cm}^2$, and the time of irradiation was 5 min (exposure dose was about 1 J).

PLC films were obtained by disposing PLCs on one substrate or filling them in a sandwich cell containing two substrates with photoalignment layers on the inner side. In the first case, we used two planar nematic mixtures, RMM256C from Merck and UCL017 from DIC, and nematic mixture UCL011 having no planarization agents. The mixtures were dissolved in toluene at 30 wt %. PLC films were obtained by spin coating PLC solution at 3000 rpm for 30 s. Then the substrates were kept at 60 °C for 1 min to remove residual solvent and improve PLC alignment, and exposed to unpolarized UV light $(20 \text{ mW/cm}^2 \text{ in } 365)$ nm emission line) for 30 s. The photopolymerization of RMM256C and UCL017 mixtures was carried out in air, whereas the photopolymerization of UCL011 mixture in a nitrogen atmosphere. The thicknesses of the PLC layers obtained were $1.5-2\,\mu m$.

The low-viscosity mixture UCL011 was also aligned between the two photoalignment substrates. The treatment conditions for SD1 layers were the same as above. Photopolymerization was performed by exposure to a nonpolarized UV light (20 mW/cm^2 in 365 nm emission line) for 1 min in an air atmosphere. The thickness of the PLC film was controlled by the size of spacers maintaining the gap between the alignment substrates. The gap was varied in the range of $2-10 \mu m$.

The film anisotropy was studied by transmission null ellipsometry capable of measuring in-plane and out-of-plane film retardations.¹³⁾ In these experiments, the light beam from the He–Ne laser ($\lambda = 0.63$ nm) passed through an optical system consisting of a fixed polarizer, an anisotropic sample, a quarter wave plate and a rotating analyzer and was registered with a photodiode. The polarizer axis formed angles of 45° with the sample's slow axis and 0° with the slow axis of the retardation plate. The analyzer rotation angle φ corresponding to the minimal transmittance of the laser beam was experimentally measured for different incidence angles of this beam on the sample, i.e., for different sample rotation angles θ . The measured φ vs θ curves were fitted in a frame of the most suitable orientational model. The fitting yielded in-plane and out-of-plane retardations and a spatial orientation of the optical axis.

3. Results and Discussion

Figure 2 shows photographs of the typical film viewed between a pair of crossed polarizers. PLC layers were



Fig. 2. Photographs of anisotropic RMM256C film viewed between pair of crossed polarizers. The film is uniformly aligned by an SD1 photoalignment layer in the long-side direction of the rectangular glass slide (slow axis of film).



Fig. 3. Analyzer angle φ vs sample rotation angle θ curves (experimental points) measured by transmission null ellipsometry for optical film shown in Fig. 2. The upper and lower curves correspond to the horizontal and vertical orientations of the slow axis of the film. The continuous curves are the results of fitting. According to the fitting, the film is optically equal to the positive A crystal plate with a slow axis perpendicular to the polarization direction of the actinic light used in photoalignment processing. The in-plane retardation is 185.9 nm.

uniformly aligned. The alignment qualities were similar for different types of substrates.

Figure 3 shows the curves obtained for the RMM256C film (Fig. 2). They correspond to a uniaxial planar (homogeneous) alignment of PLC molecules in the direction perpendicular to the polarization direction of the actinic light used for the photoalignment treatment of the SD1 layer. The same type of orientational structure is detected in the UCL017 film. Optically, these films are equal to the positive A plate.²⁾ In contrast, a hybrid structure with a planar alignment at the SD1 alignment layer and a high molecular tilt at the PLC-air interface is detected in UCL011 films.

To confirm photoalignment sensitivity, multidomain SD1 layers were prepared with domains differing depending on exposure dose. By covering these layers with PLC films, we found that alignment on the domains exposed to doses higher than 50 mJ/cm^2 is indistinguishable. To the best of our knowledge, such a low alignment dose has never been achieved for photoalignment materials.^{2–6)}

The photostability of the alignment layers was further confirmed. In these experiments, the intensity and time of



b

Fig. 4. Photographs of RMM256C film with patterned alignment. The film is aligned by an SD1 layer coated on a PES plastic film and exposed to polarized UV light in two steps to generate alignment patterns with an angle between alignment directions of 45°. The sample is placed between a pair of polarizers: (a) polarizers are parallel, and (b, c) polarizers are crossed.

the nonpolarized UV light in photopolymerization were varied. Even for 100 mW/cm^2 (in 365 nm emission line) and 10 min exposure, no signs of alignment deterioration were observed. The possibility of using a highly intensive light allows to speed up the production.

The SD1 alignment films were also obliquely treated with a collimated beam of a non-polarized UV light. At incidence angles of $45-70^{\circ}$, a uniform PLC alignment was observed as in the polarized light irradiation case. The ellipsometry studies confirmed the planar alignment of planar PLC mixtures in the incidence plane of actinic light and the optical properties of positive A films. The use of non-polarized light instead of polarized one allows us to simplify the exposure scheme and reduce equipment cost.

Figure 4 shows a PLC film with patterned alignment. To form the pattern, the film was first entirely exposed to polarized UV light (3.3 mW/cm^2 , 5 min), then covered with a mask and exposed again to the polarized light in the polarization direction turned to 45° with respect to the direction in the first step. Azodye molecules in the mask's windows reoriented perpendicular to the polarization direction during the second exposure. Alignment patterns with a 90° difference in alignment directions were also produced. High-quality patterns were formed even with the use of a mask with windows with a linear size of as small as $400 \,\mu\text{m}$. We believe that the pattern size can be further decreased with no substantial change in alignment quality.

The alignment of dyed PLC has also been tested on SD1 photoalignment films. In these tests we used the planar PLC mixtures mentioned above doped with different amounts of



Fig. 5. Photograph of anisotropic optical film made of PLC RMM256C from Merck doped with 1 wt % DR1 azodye. The film is aligned by an SD1 photoalignment layer coated on a PES plastic film and exposed to polarized UV light in two steps to generate alignment patterns with an angle between alignment directions of 90°. The width of striplike patterns is 1 mm. The sample is placed on a polarizer and illuminated from the bottom. The optical density contrast between the dark and bright strips is about 5 : 1.

dichroic azodyes soluble in PLCs. The concentration of azodye was maximized; its value was limited by either solubility in PLC or the efficiency of photopolymerization. For these reasons, the concentration of dye was in the range of 1-5 wt %, depending on the dye properties. Figure 5 shows the PLC RMM256C film doped with Dispersed Red 1 (DR1) dye from Aldrich. This film contains alignment patterns with a 90° difference in the alignment directions. It is evident that the alignment of azodye conforms to the alignment of the PLC matrix due to the host-guest effect. The oriented PLC layer containing dichroic dye works as a linear polarizer adsorbing light polarized in the direction of azodye orientation and transmitting the light polarized in the perpendicular direction. The dichroic ratio DR in the absorption maximum of dye can be used as measure of polarization rate. The DR = 5–6 obtained at $\lambda_{max} = 501$ nm for RMM256C-DR1 film is still low for application, but it can be substantially increased using PLC with highly ordered smectic mesophases.⁶⁾ Figure 5 shows that SD1 photoalignment layers are suitable for realization of patterned dichroic polarizers.¹⁴⁾

The low-viscosity mixture UCL011 can be well aligned in a sandwich cell if a cell gap is lower than $5\,\mu$ m. Further increase in the gap (thickness of PLC film) resulted in a considerable deterioration of PLC alignment after photopolymerization. The parallel and twisted alignment configurations, i.e., positive A plate and twisted A plate, respectively, were realized (Fig. 6). The alignment of the sandwiched PLC layers was easily patterned.

4. Conclusions

Layers of SD1 and similar azodyes can be effectively used for the photoalignment of PLC films and the preparation of optical elements. As demonstrated above, parallel and twisted positive A plates as well as splayed O plates can be produced for twisted nematic and super-twisted nematic LC display (LCD) compensation.¹⁵⁾ SD1 layers can also be effectively used to align dyed PLC for dichroic polarizers. The alignment of neat and dyed PLCs can be easily



Fig. 6. Photographs of ULC-011 films sandwiched between two SD1 photoalignment layers coated on glass slides. The gap between substrates is $4.5 \,\mu\text{m}$. The angles between the alignment directions is 180° (a) and 90° (b). Correspondingly, antiparallel and 90° twist LCP director distributions are realized.

patterned, which is a key problem in patterned compensation films and polarizers demanded by modern developments of LCDs (e.g., multidomain wide viewing angle LCD, transflective displays, and three-dimensional imaging).¹⁶⁾ The indisputable advantage of the sulfuric azodye SD1 is its very low photoalignment dose ($<50 \text{ mJ/cm}^2$) that allows the speeding up production. A simple preparation of photoalignment layers and PLC films suggests that the manufacture of optical films in the form of an assembly belt will soon be realized. It can be further simplified for flexible substrates, when continuous roll-to-roll process can be easily developed. This principle can be used in the manufacture of any functional film containing aligned PLC layers or a stack of them.

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