

Azodyes as Photoalignment Agents for Polymerizable Liquid Crystals

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ABSTRACT

We show that sulfuric bisazodyes, earlier distinguished as highly effective photoalignment materials for conventional liquid crystals (LC), exhibit excellent photoalignment of polymerizable liquid crystals (PLC). These dyes excel in high affinity to various substrates, extremely low exposure dose (less than 50 mJ/cm²) for PLC alignment, and insolubility in LC and their solutions. The alignment can be easily patterned using minimal number of masks and exposure steps. We emphasize potential of new photoalignment materials for the production of patterned optical films requested by modern LCD technologies.

1. INTRODUCTION

The development of polymerizable liquid crystals (PLC), whose oriented state can be frozen by polymerization [1], opened unique opportunities for manufacturing of anisotropic optical films used as retardation or compensation films [2-5], interference color filters [2] and dichroic polarizers [6]. The anisotropic films of semiconducting PLC are of great interest for OLEDs, because of capability of polarized emission [7].

To demonstrate its unique properties, PLC should be properly aligned before solidification. There is some difference in the alignment demands for conventional low-molecular-weight LC and PLC. On the one hand, the demands for PLC are weaker: photoalignment layer should maintain alignment of PLC only for a short time before polymerization, it should not meet strong requirement of the electric field operation, etc. On the other hand, the alignment layer for PLC should meet the following conditions: (1) it should be insoluble in organic solvents used to dissolve PLC for film deposition; (2) it should provide strong anchoring to stabilize PLC alignment during polymerization; (3) it should provide sufficiently high photo and thermal stability of alignment to prevent damage during photo and thermal polymerization, respectively; (4) it should be highly adhesive to different substrates, first of all plastic films commonly used as substrates for compensation films.

The types of treatment of the aligning substrates for PLC are the same as for conventional liquid crystals. The preferred alignment method is a unidirectional rubbing. Its most important drawbacks are complexity of alignment patterning and insufficient alignment uniformity. These problems can be successfully solved by using photoalignment. First Shannon et al. [8] aligned PLC on the layers of dichroic dye blended in polymer matrix. Later on, Schadt et al. [2] applied cinnamate based material for PLC alignment. The materials used in these first attempts did not suit very well for photoalignment of PLC. The polymer blends of dichroic dyes do not keep the photoinduced order very well so that alignment function can be lost some time after the light exposure. In turn, cinnamate based materials commonly need considerably higher exposure dose than the materials containing dichroic dyes.

In the present study, we consider sulfuric bisazodyes, forming perfect layers on different substrates, as photoalignment materials for PLC. Earlier we demon-

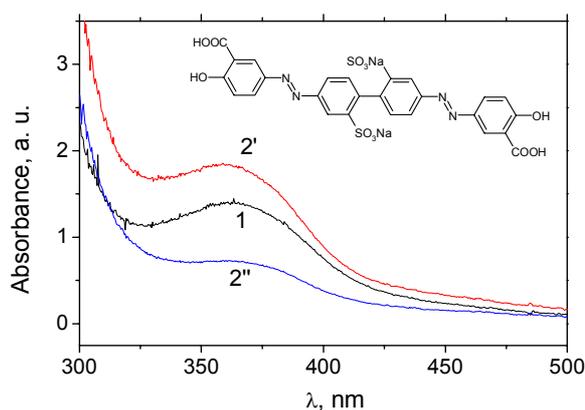


Fig. 1. Chemical formula of sulfuric bisazodye SD1 used as photoalignment agent in the present study and UV/Vis spectra of its film before (1) and after (2', 2'') exposure to polarized UV light (3.3 mW/cm² (in 365 nm emission line), 5 min). Spectral components 2' and 2'' are polarized perpendicular and parallel to polarization direction of exciting beam, \mathbf{E}_{ex} . These spectral changes confirm reorientation of azodye molecules perpendicularly to \mathbf{E}_{ex} .

strated high efficiency of these dyes for the alignment of conventional nematic [9,10] and ferroelectric smectic [11] LC. The chemical formula of the main dye utilized in the present studies is shown in Fig. 1. It is designated as SD1. In the central and peripheral parts this molecule contains groups providing good adhesion to various surfaces. The SD1 molecules show effective reorientation under UV exposure perpendicularly to polarization direction of light (Fig. 1), which is practically not accompanied with *trans-cis* photoisomerization taking place in azopolymers and polymer blends [12]. The thickness of the alignment film is very low (3-15 nm) so that coloring and optical retardation introduced by this film can be neglected. As we additionally checked, SD1 and similar dyes are insoluble in PLC and solvents commonly used to dilute them (toluene, cyclohexanone, etc.). The latter preserves their alignment function in case of contact with PLC or PLC's solutions.

2. FILM PREPARATION

The SD1 was dissolved in DMF at concentration of 1 wt.%. The filtered to 0.2 μm solution was spin coated on the substrates at 800 rpm over 10 s following with 3000 rpm over 60 s. The substrates were glass slides or plastic PES films. Before coating alignment layer, the substrates were cleaned in an ozone cleaner over 10 min. The SD1 coated substrates were baked at 100°C over 30 min to remove remained solvent and strengthen adhesion of dye 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 by a cut-off filter. In the major irradiation procedure, the light was linearly polarized by UV polarizer and directed normally to the substrate. The intensity of irradiation in the emission line 365 nm was 3.3 mW/cm^2 , while the time of irradiation was 5 min (exposure dose is about 1 J/cm^2).

The PLC films were obtained by disposing PLC on one substrate or filling it in a sandwich cell containing two substrates with photoalignment layers from the inner side. In the first case we used two highly viscose 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 25 wt.%. The PLC films were obtained by spin coating PLC solution at 3000 rpm over 30 s. In the following the substrates were kept at 60°C over 1 min, to remove the residual solvent and improve PLC alignment, and exposed to unpolarized UV light (20 mW/cm^2 in 365 nm emission line) over 30 s. The photo-polymerization of RMM256C and UCL017 mixtures was carried out in air, while photo-

polymerization of UCL011 mixture in nitrogen atmosphere. The thickness of PLC layers obtained was 1.5-2 μm . The low-viscosity mixture UCL011 was also aligned between two photoaligning substrates. The treatment conditions for SD1 layers were the same as above. The photopolymerization was provided by exposing to a non-polarized UV light (20 mW/cm^2 in 365 nm emission line) over 1 min in an air atmosphere. A thickness of PLC film was controlled by the size of spacers maintaining gap between the aligning substrates. It was varied in a range 2-5 μm . The further increase of the film's thickness resulted in considerable deterioration of PLC alignment after photopolymerization.

3. FILM PROPERTIES

The films of RMM256C and UCL017 spin coated on SD1 alignment layer show excellent uniform alignment (Fig. 2). The study of these films with transmission null ellipsometry technique [13,14] reveals planar alignment with optical properties of positive A plate (Fig. 3). The films of UCL011 have splayed structure with planar alignment at SD1 layer and high tilt at interface with air.

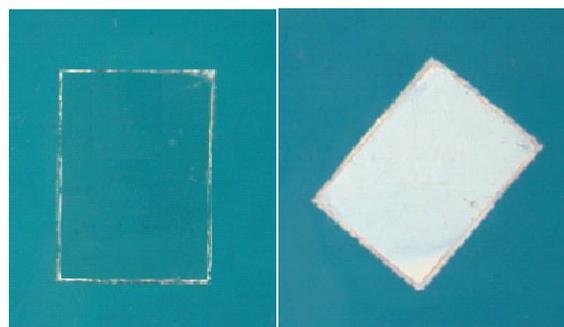


Fig. 2. The photographs of anisotropic RMM256C film viewed between a pair of crossed polarizers. The film is uniformly aligned by SD1 photoalignment layer in the long side direction of the rectangular glass slide (slow axis of the film).

By sandwiching UCL011 mixture between two SD1 layers we realized uniform parallel and 90° twisted alignment (positive A plate and twisted A plate, respectively). The photographs of the corresponding cells are shown in Fig. 4. A good alignment in all configurations was observed for neat PLC mixtures and the mixtures doped with dichroic dyes as well.

In the following we demonstrate that photoalignment of PLC on SD1 can be easily patterned. Because SD1 molecules can be readily reoriented by light, patterning procedure is simplified by reduction of mask and

number of exposure steps. Fig. 5 shows alignment patterns obtained for the neat PLC film, while Fig. 6 for

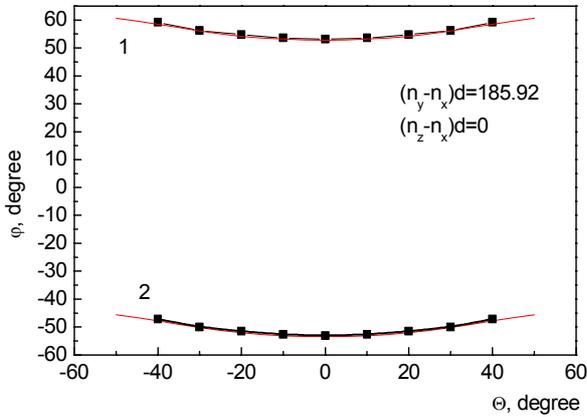


Fig. 3. The analyzer vs. sample rotation angle curves (experimental points) measured by transmission null ellipsometry technique for the optical film presented in Fig. 2. The upper and lower curves correspond to horizontal and vertical orientation of slow axis of the film. The continuous curves are results of fitting. According to the fitting, the film is optically equal to positive A crystal plate with slow axis perpendicular to polarization direction of actinic light used for photoalignment processing and in-plane retardation 186 nm.

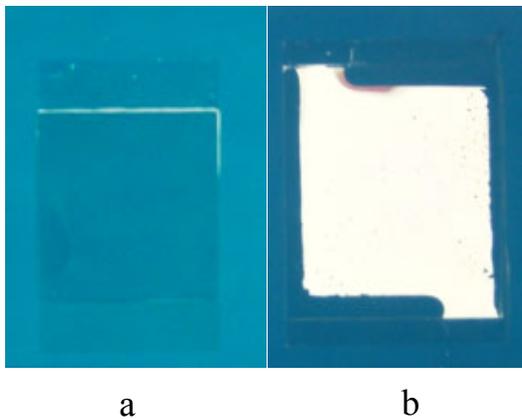


Fig. 4. The photographs of ULC-011 films sandwiched between two SD1 photoalignment layers coated on glass slides. The gap between substrates is 4.5 μm . The angle between alignment directions is 180° (a) and 90° (b). Correspondingly, antiparallel and 90° twist LCP director distribution is realized.

the dyed PLC film. One can see uniform alignment within the patterns with sharp border between them. The absorption dichroic ratio of the latter films amounted to 10.

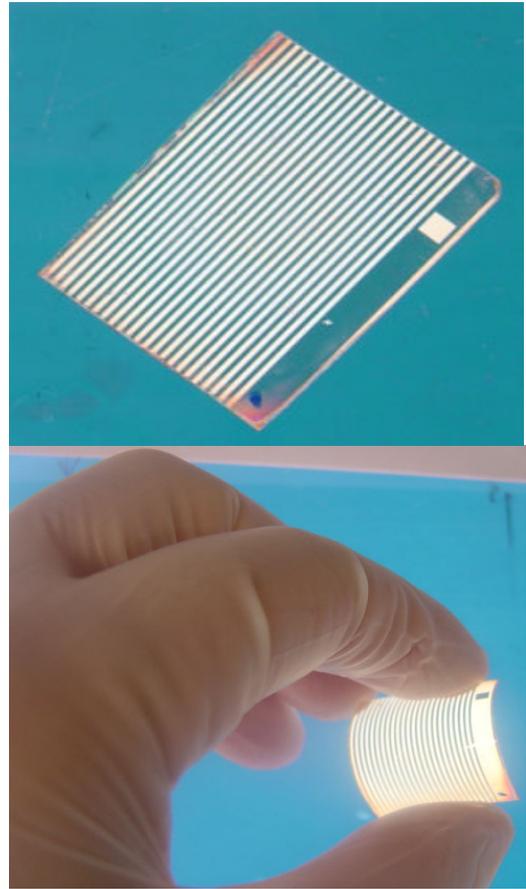


Fig. 5. The photographs of anisotropic film of neat PLC RMM256C viewed between a pair of crossed polarizers. The film contains two kinds of patterns with 45° angle between alignment directions. To pattern PLC alignment, SD1 layer is first entirely exposed to polarized UV light over 3 min then exposed through mask over 5 min again with rotation of UV light polarization in 45°. The intensity of UV light 3.3 mW/cm^2 in 365 nm emission line.

Then we estimated minimal exposure dose of SD1 layers needed for good PLC alignment. For this purpose the multi-domain SD1 layers were prepared with the domains differing by the exposure dose. By covering these layers with PLC films we revealed that alignment on the domains exposed to the doses higher than 50 mJ/cm^2 is indistinguishable. To our best knowledge, so low alignment dose was never achieved for photoalignment materials.

Finally we note rather high thermal stability of PLC alignment on SD1 films, which endures baking process used for solvent evaporation from PLC films and better PLC alignment.

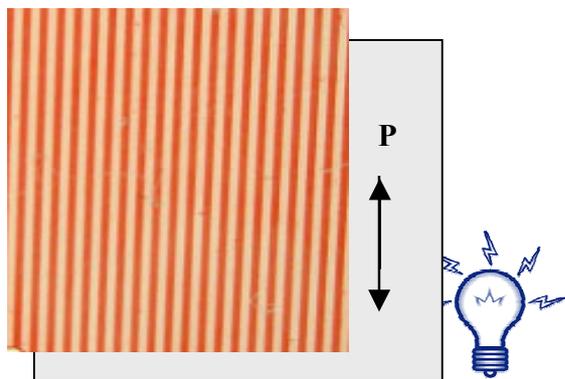


Fig. 6. The photograph of anisotropic optical film made from PLC RMM256C doped with 1 wt.% of DR1 azodye. The film is aligned by SD1 photo-alignment layer coated on PES plastic film and exposed to polarized UV light in two steps to create alignment patterns with angle between alignment directions of 90° . The width of strip like patterns is 1 mm. The sample is placed on polarizer and illuminated from the bottom. The optical density contrast between the dark and bright strips is about 5.

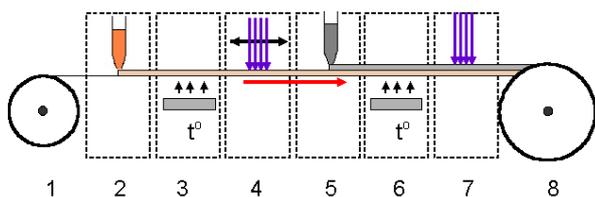


Fig. 7. The scheme of continuous manufacturing process of anisotropic PLC films. (1) roll of plastic substrate; (2) alignment layer deposition; (3) alignment layer backing; (4) photoalignment processing; (5) deposition of polymerizable liquid crystal; (6) PLC tempering; (7) polymerization of PLC film; (8) roll with PLC coated plastic film.

4. CONCLUSIONS

In summary, we propose photoalignment materials, which suit very well for the alignment of PLC and so can be integrated in the manufacturing process of anisotropic optical films. They are especially useful to pattern PLC alignment needed to produce patterned

compensators and polarizers highly requested by latest developments of LCD (transflective LCD, stereoscopic displays, etc.) [15]. The high affinity of studies materials to flexible plastic substrates and their high photosensitivity make possible continuous manufacturing process of optical films schematically shown in Fig. 7.

5. Acknowledgment

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6. References

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