Study of azo dye surface command photoalignment material for photonics applications

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We provide detailed quantitative characterization of sulfonic bisazodye SD1 as a photoalignment material for photonics applications. The reversibility of photoalignment was tested for transformations between planar and 90° twist orientation states in a liquid crystal (LC) cell using polarized UV light. No degradation was observed for 100 cycles of transformations. A given twist angle of the LC orientation was obtained in a single step, as well as in a sequence of gradually increasing angles. A hysteresis is revealed in the latter case for planar–twist–planar cycles. The material was used for obtaining patterned orientation of a LC polymer providing similarly good quality photoalignment for UV as well as visible light. High efficiency large area and high spatial frequency optical axis gratings (or, polarization gratings) were demonstrated on a polycarbonate substrate. We show the opportunity of obtaining photoalignment in a multilayer system with single exposure to a polarized light. Finally, we provide evidence of a positive feedback in the dynamics of photoalignment due to the orientational effect of an increasing number of aligned molecules.   © 2010 Optical Society of America

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1. Introduction

Photoalignment techniques developed with the goal of modernizing the production technology of liquid crystal (LC) displays have opened up new opportunities for a wide range of photonics applications [1–3]. The feasibility of fabricating material layers with spatially distributed variation of optical axis orientation have led to the demonstration of optical components such as azimuthal and radial wave plates and polarizers, patterned wave plates and polarizers, polarization converters, and optical axis gratings (OAGs) (polarization gratings) [4–11].

These components proved to be highly valuable in imaging, microscopy, nanophotonics, micromanipulations involving laser beams, formation of laser beam profile, security labeling, etc. [12–21].

Still, neither the possibilities nor the spectrum of applications of such components have been fully explored. One of the problems hindering development of new components and applications is that photoalignment materials are practically unavailable commercially. A class of such materials for research can be obtained from Rolic Technologies Ltd. However, those products are constantly modified, and the materials you may have spent many hours studying turn sometimes unavailable later. There are a number of laboratories that synthesize different classes of photoalignement materials

[1–4,22]; however, they are in the research stage or not available commercially. Thus, it is very important to study the properties and capabilities of various photoalignment materials.

In the present work, we study one of the most promising materials for photonics applications. Compared to cinnamate-based photopolymerizable polymers (LPPs), the material known as SD1 [1,23,24] has a number of distinct advantages. 1) Photoalignment with SD1 requires significantly lower exposure energy. 2) The spectral sensitivity of SD1 peaks at 372 nm, extending to over 450 nm, as opposed to the 320–330 nm peak sensitivity wavelength of cinnamate-based LPPs. Thus, SD1 could be efficiently used for photoaligning using longer wavelength UV and even visible light sources. 3) It allows erasure of previously recorded alignment pattern and rerecording, making it easier to obtain a variety of compositions of alignment patterns. Thus, the azo dye SD1 acts as a photoaddressable command layer for LCs or LC polymer (LCP) overlays. Note that photoalignment with SD1 takes place in the direction perpendicular to the polarization direction of the light. 4) SD1 is characterized by azimuthal anchoring energy of $>10^{-4} \text{ J/m}^2$, which is comparable to that of rubbed polyimide and is higher than that for other photoalignment materials. This makes it an ideal candidate for producing OAGs. 5) SD1 produces very thin uniform layers of 3 to 12 nm thickness, as opposed to ~50 nm for cinnamate-based LPPs. Because of layer thinness, coloring and optical retardation introduced by a single SD1 layer are small. Note also that SD1 is insoluble in LCs and LCPs [25].

2. Photoalignment Process for Multiple SD1 Layers

The chemical formula of the bisazodye SD1 is shown in Fig. 1. 1 wt. % solution of SD1 in N, N-dimethylformamide (DMF) is spin coated on a glass substrate at 3000 rpm for 60 s. The substrate is dried on a hot plate at 100 °C for 30 min before exposure to a linearly polarized UV light. We used a pair of optical filters, a WG295 UVC cut-off filter and a UG11 UV bandpass filter from Schott, to select a $\lambda = 365$ nm illumination wavelength from a UV source. A high transmission calcite Glan polarizer was used to obtain the desired direction of linear polarization. The UV exposure time was 5 min at 10 mW/cm^2 intensity.

For spectral measurements, ten layers of the material were spin coated at 1000 rpm, each of them dried at 100 °C for 10 min. The resultant absorption spectrum taken for the spectrometer light parallel and perpendicular to the optical axis of the film is
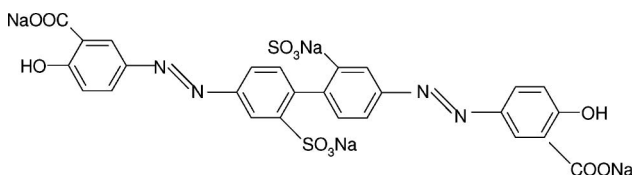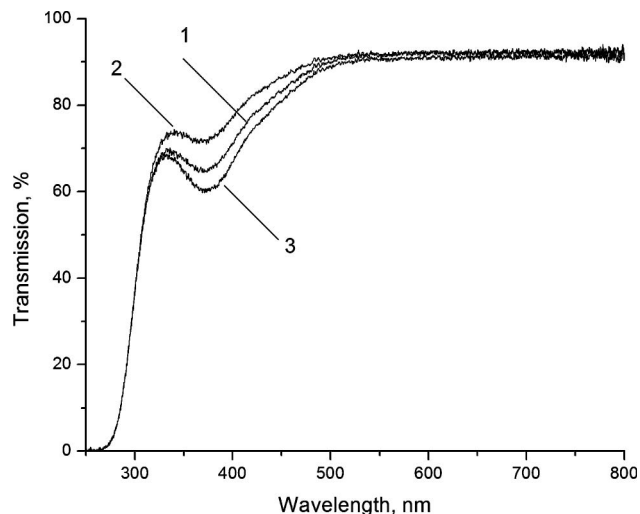

Fig. 1. Chemical formula of the bisazodye SD1.

Fig. 2. Transmission spectra of SD1 photoalignment layer resulting from ten deposition procedures on a glass substrate before (1) and after photoalignment obtained with a light polarized parallel to the photoalignment direction (2) and perpendicular to it (3).

shown in Fig. 2. The photoalignment was performed only once, after depositing all ten layers. No birefringence is exhibited between crossed polarizers. The evaluated effective layer thickness is ~32 nm for five layers. To verify the homogeneity of the obtained multilayer system, we compared five spectra taken at a 4 mm distance from each other. The standard deviation of transmission variation at the absorption peak was found to be 0.6, which was only ~1% over 20 mm range.

3. Patterned Photoalignment of Liquid Crystal Polymer with Ultraviolet and Visible Radiation

The spectral sensitivity of SD1 extends to over 450 nm, allowing realization of photoalignment not only with UV, but with radiation of visible wavelengths, as well. To compare these two opportunities, we produced LCP layers with patterned alignment with UV as well as visible light; see Fig. 3. The glass substrate was spin coated by SD1 solution and illuminated with linearly polarized UV light for 3 min. Then the polarization of the UV light was rotated by 45° and the substrate was illuminated a second time through a mask of a rectangular pattern for 5 min. Finally, the substrate was spin coated by LCP ROF 5102 (Rolic Ltd.) at 1000 rpm for 60 s and polymerized with unpolarized UV light at nitrogen atmosphere for 10 min. The resulting film, when placed between crossed polarizers, reveals areas of the two states of orientation (Fig. 3). Thus, the second UV exposure realigns the molecules of the SD1 at 45° with respect to the first exposure.

The patterned alignment structure shown in Fig. 3(a) is not uniform. Homogeneous orientation is achieved with longer exposure energy [Fig. 3(b)]. In this case, the entire area of the substrate with SD1 coating was exposed to UV light for 5 min, and then the central part was illuminated through a mask with a circular opening for 7 min.
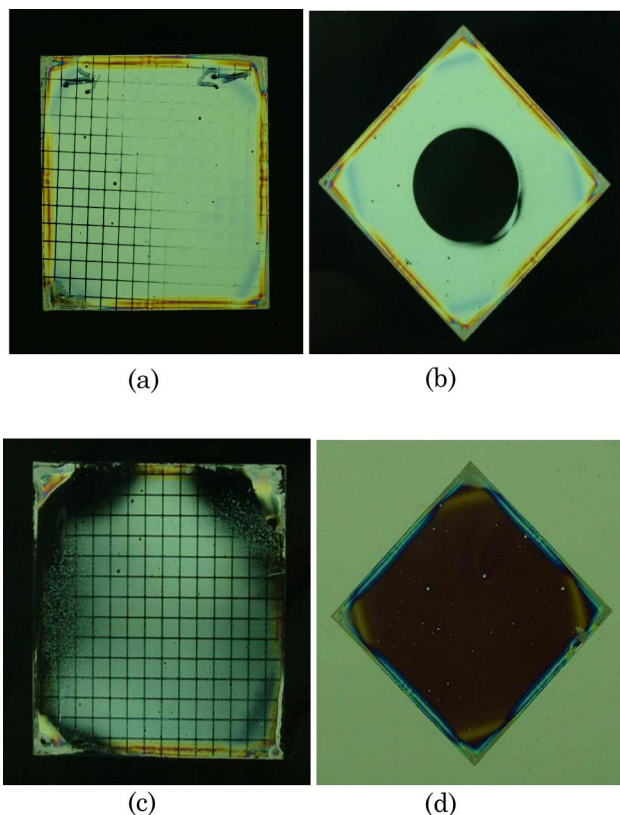
Fig. 3. (Color online) Photos of LCP films with patterned orientation obtained between crossed polarizers with a mask containing openings of circular and rectangular patterns: (a) and (b) photoalignment with UV light (365 nm), and (c) and (d) photoalignment with visible light (>450 nm).

The tests with radiation of visible wavelengths were performed using a cut-off filter to block shorter wavelengths of the light source used in this study, and the substrate containing the photoalignment layer was exposed to light with wavelengths longer than 440 nm. The intensity of the visible portion of the light was ~10 mW/cm² and it was linearly polarized. Large area homogenous birefringent films could be obtained for exposure times of less than 2 min (Fig. 3). Extending the exposure duration resulted in deterioration of the film quality. Thus, the quality of the patterning is comparable for photoalignment with UV as well as visible wavelengths, requiring considerably smaller exposure time in the latter case. Note that patterned photoalignment of an LCP layer was demonstrated earlier for SD1; however, it was performed with UV light only and the result was not directly compared with photoalignment performed by visible radiation [25].

4. Fabrication of Optical Axis Gratings

We tested SD1 as a photoaligning layer for fabricating LCP OAGs based on LCP ROF 5102 (Rolic Ltd.). As we mentioned in Section 1, SD1 is characterized by azimuthal anchoring energy of $>10^{-4}$ J/m², comparable to that of rubbed polyimide and higher than that for other photoalignment materials, which

makes it best suited for producing OAGs with high spatial frequency.

The wavelength of the He–Cd laser used in these tests, 325 nm, was considerably far from the peak absorption wavelength of SD1 (372 nm). Hence, longer exposure times were required for producing scatter-free polymer polarization gratings compared to what could be expected for radiation of 372 nm wavelength. The first tests with an illumination time of a few minutes resulted in low-quality polarization gratings. Scatter-free LCP gratings of 6 μm spacing with practically 100% efficiency were obtained with exposure times over 10 min with 9.5 mW/cm² power density of orthogonal circularly polarized beams [Figs. 4(a) and 4(b)].

In the second series of experiments, the entire area of the glass substrate with an SD1 coating was first illuminated by a linearly polarized single beam for 3 min. Next, the substrate was illuminated for 10 min with interfering orthogonal circularly polarized beams. Finally, the substrate was spin coated with LCP ROF 5102 at 1000 rpm for 60 s and polymerized under a nitrogen atmosphere. This procedure resulted in the formation of a good-quality cycloidal grating over a large area of the substrate [Figs. 4(c) and 4(d)]. Almost no difference can be seen in the spectra of the grating fabricated by single and double exposure (Fig. 5). The photo of a high-efficiency OAG produced on a polycarbonate substrate is shown in the insert of Fig. 5. Note that fabrication of a LC OAG using SD1 was attempted earlier [26]. The LC layer was too thick in that case, violating the stability condition for a cycloidal orientation pattern. Hence, it behaved like a low-efficiency conventional phase grating. Note also that the capability of SD1 to act as a photoalignment material
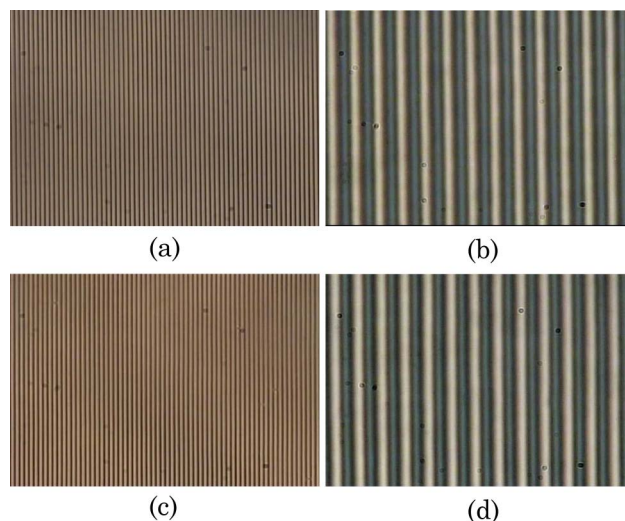

Fig. 4. (Color online) Microstructures of LCP cycloidal OAGs of 6 μm spacing fabricated using SD1 photoalignment material on a polycarbonate substrate. Photos are taken with an optical microscope between crossed polarizers at 20× and 100× magnification. (a) and (b) Single exposure, and (c) and (d) double exposure.
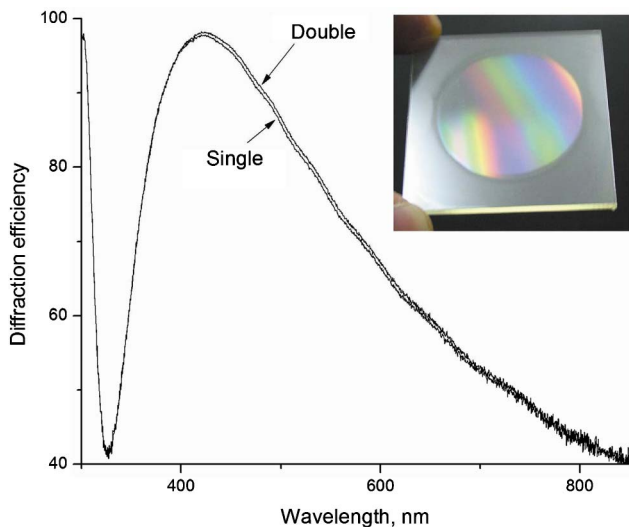
Fig. 5. (Color online) Diffraction efficiency of LCP OAGs fabricated using SD1 as a photoalignment material with single and double exposures. The insert photo shows a high-efficiency OAG of 2 in. (5 cm) diameter.

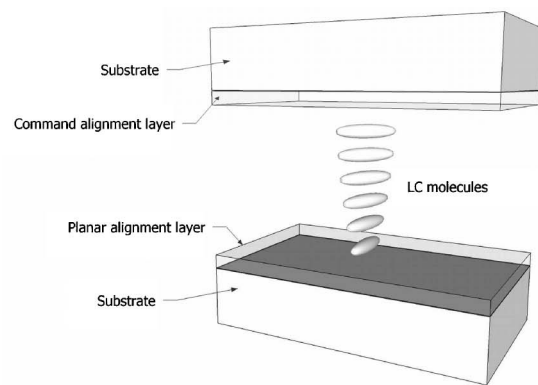on a plastic substrate was demonstrated earlier, but on an unspecified substrate [27].

5. Characterization of Reversibility of Photoalignment Process

The reversibility of photoalignment with the aid of SD1 was suggested for developing rewritable displays [1,27,28]. We characterize below the key features of reversibility with the aid of LC cells similar to the ones used for demonstrations in [27,28].
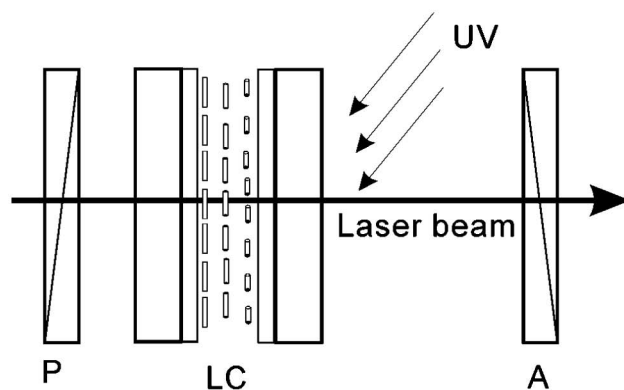
One of the substrates in LC cells fabricated in this study impose strong and permanent planar anchoring. It was obtained with photoalignment material LPP ROP-108 (Rolic Ltd.). This material was spin coated on a glass substrate at 3000 rpm for 60 s. The substrate was dried on a hot plate for 10 min at 100 °C to remove any residual solvent.

The second substrate of the cell was made using an SD1 layer as described in Section 2. The exposure times were 5 and 12 min for the substrate with the SD1 layer and the LPP ROP-108 layer, respectively. The cell was assembled using $10\,\mu m$ thick Teflon spacers between glass substrates, and was filled with LC 6CHBT [29] by capillary action. The material LPP ROP-108 orients the LC parallel to, while SD1 induces orientation perpendicular to, the polarization direction of the UV illumination. This circumstance needs to be taken into account when assembling the cell in order to get the desired initial (for example, planar) orientation of the LC.

The schematic of the LC cell and the setup for characterization of the photoalignment process are shown in Fig. 6. A probe He–Ne laser beam with 10 mW power was expanded by a system of lenses of $L1 = 10\,mm$ and $L2 = 500\,mm$ focal length. The central part of the expanded beam was selected by a diaphragm with an 8 mm aperture. The cell was placed between crossed polarizers at a 5° angle with

(a)

(b)

Fig. 6. (a) Schematic of the LC cell. (b) Schematic of the setup for characterization of reversibility of photoalignment of SD1: P and A, polarizer/analyzer pair; LC, LC cell.

respect to the propagation direction of the beam. The substrate with the surface command layer (SD1) faced the UV illumination at an incident angle normal to the cell. The angle between the direction of linear polarization of the UV light and the direction of the fixed alignment on the first surface was varied by a Glan polarizer.

The dynamics of the probe beam power propagated through the polarizer–LC-cell–analyzer system was measured during the illumination of the LC cell by the UV beam. A 90° twist-aligned LC cell was used in the first test. The initial transmission state of the cell was, therefore, maximal between crossed polarizers. Illumination of the SD1 layer with UV light polarized parallel to its initial alignment resulted in transformation of the LC orientation from twist to homogeneous planar, leading to decreasing transmission (Fig. 7). Changing the polarization direction of the UV light by 90° restores twist orientation of the LC, switching the transmission of the cell back to the initial high state (Fig. 7). Note that the twist angle of the LC director was rotated between 12° and 62° in an earlier study, and it was induced with a visible light of 440 nm wavelength [1].
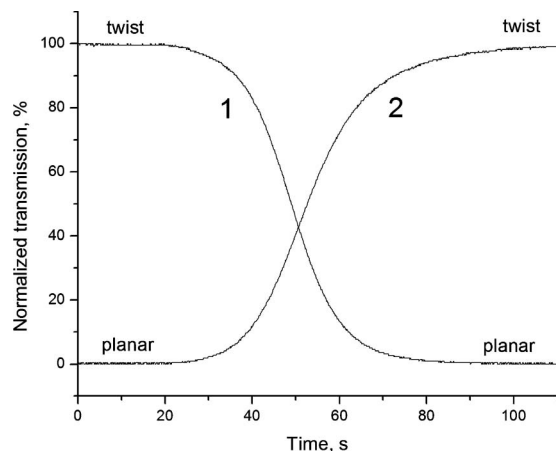
Fig. 7. Controlling the transmission state of an LC cell containing SD1 surface command layer: 1 transformation from a twist to homogeneous planar orientation with UV light polarized in a direction parallel to the initial alignment direction of the SD1; 2 transformation from a planar to twist orientation with UV light polarized in a direction perpendicular to the original alignment direction of the SD1.

The transmission of the optical system under study can be set at different levels by changing the linear polarization direction of the UV light [Fig. 8(a)]. In the tests, starting from the initial planar orientation, the LC cell was brought to different twist orientations using 15° increments. The cell was brought back into its initial planar orientation before a new switching cycle [Fig. 8(b)]. More than 100 reorientation cycles were completed without any sign of cell degradation.

Figure 9 shows the dynamics of the output power of the probe beam for different thicknesses of LC cells due to transformation between planar and twist states induced by linearly polarized UV light of $15\,\mathrm{mW/cm^2}$ intensity and a 5 min duration.

In the next series of tests, the LC cell was brought from an initial planar state to 90° twist state gradually, in 15° increments, without intermediate restoration of the planar state [Fig. 10(a)]. The LC orientation was brought back into the planar state in the same manner after achieving the 90° twist state [Fig. 10(b)]. This process exhibits hysteresis, as shown in Fig. 11.

The maximal width of the hysteresis loop is about 20%. The origin of the hysteresis could be explained by the fact that each subsequent transmission state was achieved from the previous state and hence acquired a higher UV radiation dosage. For instance, the 90° twist state was achieved from the previous 75° twist state, which already was affected four times with the $15\,\mathrm{mW/cm^2}$ intensity and 5 min duration of the UV illumination.

6. Discussion

These results prove the conclusion that the photoalignment material SD1 is highly suitable for producing a large variety of photonics components [30], including the most complex and demanding ones,
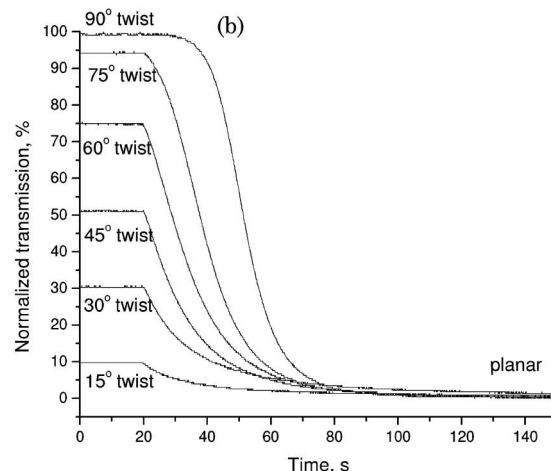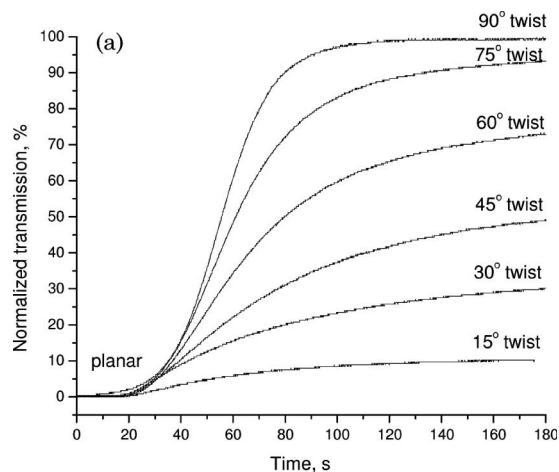

Fig. 8. (a) Obtaining different twist angles from planar oriented state. (b) Restoring planar orientation from states with different initial twist angles. Data correspond to a $10\,\mu\mathrm{m}$ thick LC cell.

such as OAGs, with very high spatial resolution. It was important to verify that the orientation obtained with this material is fully reversible and can be cycled numerous times (up to 100 times tested in this paper) with no signs of degradation. Also, and most importantly, high-quality oriented films could be obtained within irradiation times of less than 3 min, as opposed to Rolic's photoalignment materials, which required over 10 min.

The obtained results shed light on fundamental aspects of photoalignment process in azodye material systems. Namely, the normalized transmission T_N we have plotted for different conditions is related to the angle α made by the direction enforced by the photoalignment layer (the direction of easy axis orientation) with respect to the polarizer axis as $T_N = \sin(2\alpha)$. Since the orientational relaxation time of the LC in relatively thin cells is shorter than the observed photoalignment times, we can assume that the orientation of the LC follows the change in the direction of alignment enforced by the photoalignment layer. The time dependence of the angle α calculated from the transmission formula thus carries
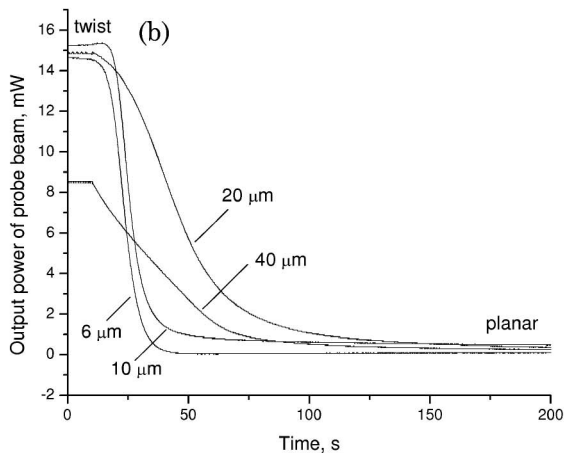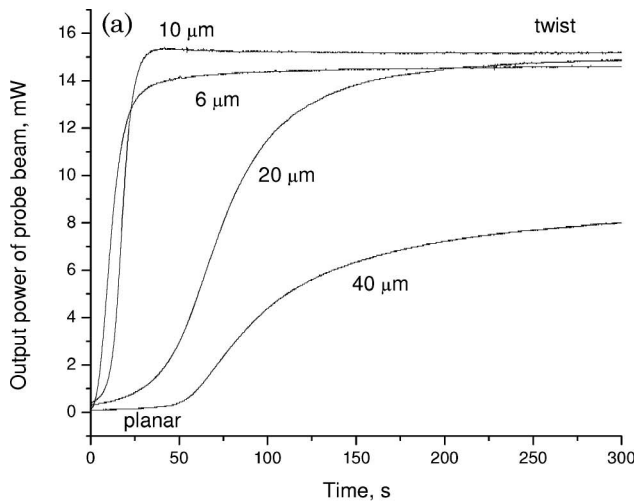
Fig. 9. Reorientation dynamics of LC cells of different thickness due to photoalignment of SD1 layer by UV illumination of $15\,mW/cm^2$ intensity and 5 min exposure: (a) transformation from initial planar to 90° twist orientation and (b) transformation from initial twist to planar orientation.
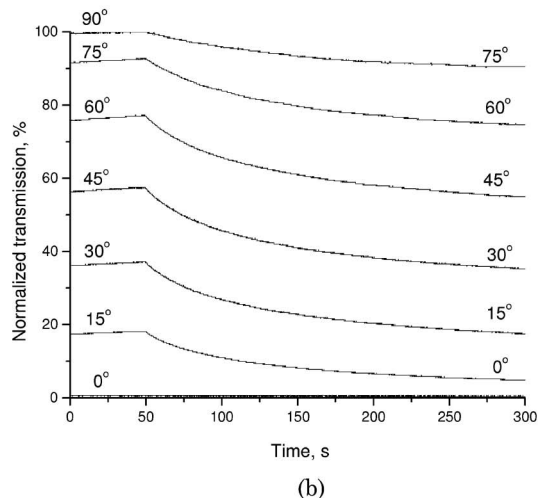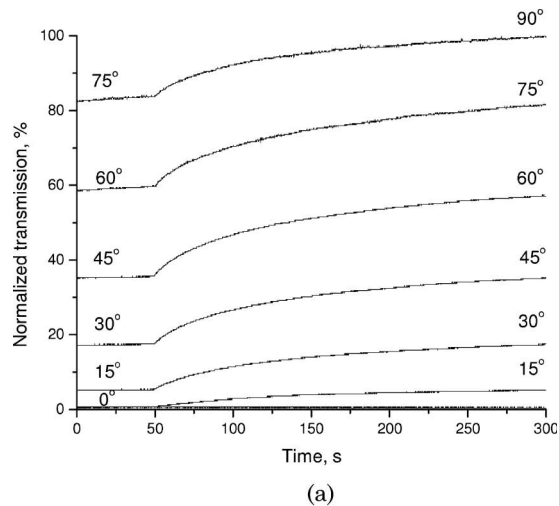

Fig. 10. (a) Normalized transmission for a $20\,\mu m$ thick LC cell in the probe beam setup for UV-induced reorientation in consecutive steps: (a) transformation from planar to 90° twist orientation and (b) from twist to planar.

information on the dynamics of processes in the photoalignment layer that is otherwise hard, if possible at all, to detect, given its thinness.

Figure 12 shows the angle α calculated from the transmission curve for a 90° rotation of the optical axis of a $10\,\mu m$ thick LC. It is interesting to note that the speed of reorientation increases at the last stages of the process, indicating a positive feedback. Such a feedback can be a result of the effect of boundary conditions on photoalignment of azobenzene molecules. As discussed in [31], the process of trans-cis-trans photoisomerization cycles in the presence of an easy axis is affected by the orienting effect of the alignment layer. At the initial stages of the process, the aligning effect of the easy axis on the azo dye molecules is strong, preventing them from aligning into the direction perpendicular to the light polarization. With an increasing number of azo dye molecules oriented perpendicular to the light polarization, the direction of the easy axis is switched, thus increasing the efficiency of orientation of azo dye molecules in

the direction perpendicular to the light polarization. It could be interesting in the future to study the photoalignment dynamics in more detail to find
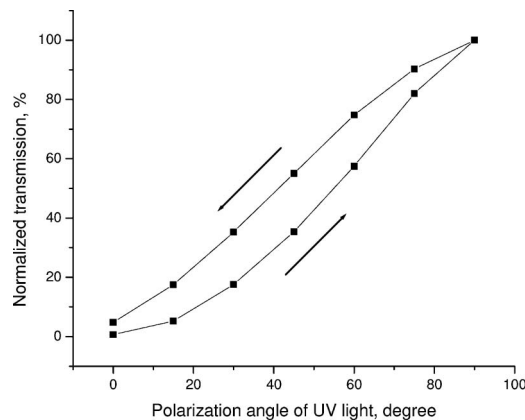

Fig. 11. Transmission hysteresis as a function of the angle between the direction of linear polarization of the UV light and the planar orientation when changing the twist angle in consecutive steps.
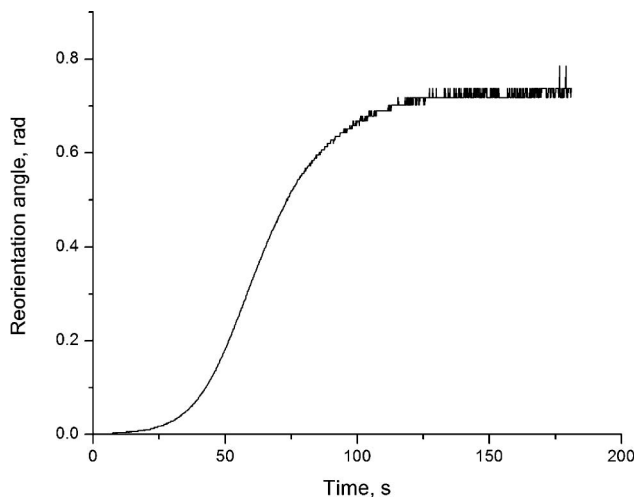
Fig. 12. Dynamics of changing of the easy axis orientation calculated from the transmission curve corresponding to 90° rotation of the optical axis of 10 mm thick LC.

out if it is affected by the LC layer itself and the specifics of the LC material.

References

1. V. G. Chigrinov, V. M. Kozenkov, and H. S. Kwok, *Photoaligning: Physics and Applications in Liquid Crystal Devices* (Wiley VCH, 2008).
2. K. Ichimura, "Photoalignment of liquid-crystal systems," Chem. Rev. **100**, 1847–1873 (2000).
3. K. Takatoh, M. Sakamoto, R. Hasegawa, M. Koden, N. Itoh, and M. Hasegawa, *Alignment Technologies and Applications of Liquid Crystals* (CRC, 2004).
4. M. Schadt, H. Seiberle, A. Schuster, and S. M. Kelly, "Photogeneration of linearly polymerized liquid crystal aligning layers comprising novel, integrated optically patterned retarders and color filters," Jpn. J. Appl. Phys. **34**, 3240–3249 (1995).
5. M. Schadt, H. Seiberle, and A. Schuster, "Optical patterning of multi-domain liquid-crystal displays with wide viewing angles," Nature **381**, 212–215 (1996).
6. F. Moia, H. Seiberle, and M. Schadt, "Optical LPP/LCP devices: a new generation of optical security elements," Proc. SPIE **3973**, 196–203 (2000).
7. M. Stalder and M. Schadt, "Linearly polarized light with axial symmetry generated by liquid crystal polarization converters," Opt. Lett. **21**, 1948–1950 (1996).
8. M. Schadt and K. Schmitt, "Flat liquid crystal projectors with integrated cholesteric color filters/polarizers and photoaligned optical retarders," in *Society for Information Display Proceedings of International Display Research Conference* (Society for Information Display, 1997), Vol. IDRC97, 219–222.
9. C. Provenzano, P. Pagliusi, and G. Cipparrone, "Highly efficient liquid crystal based diffraction grating induced by polarization holograms at the aligning surfaces," Appl. Phys. Lett. **89**, 121105 (2006).
10. M. J. Escuti and W. M. Jones, "Polarization independent switching with high contrast from a liquid crystal polarization grating," in *Society for Information Display '06 Digest* (Society for Information Display, 2006), Vol. 37, pp. 1443–1446.
11. S. R. Nersisyan, N. V. Tabiryan, D. M. Steeves, and B. Kimball, "Optical axis gratings in liquid crystals and their use for polarization insensitive optical switching," J. Nonlinear Opt. Phys. Mater. **18**, 1–47 (2009).
12. R. Yamaguchi, T. Nose, and S. Sato, "Liquid crystal polarizers with axially symmetrical properties," Jpn. J. Appl. Phys. Part 1 **28**, 1730–1731 (1989).
13. H. Ren, Y. H. Lin, and S. T. Wu, "Linear to axial or radial polarization conversion using a liquid crystal gel," Appl. Phys. Lett. **89**, 051114 (2006).
14. Y. Y. Tzeng, S. W. Ke, C. L. Ting, A. Y. G. Fuh, and T. H. Lin, "Axially symmetric polarization converters based on photoaligned liquid crystal films," Opt. Express **16**, 3768–3775 (2008).
15. L. Marrucci, C. Manzo, and D. Paparo, "Pancharatnam-Berry phase optical elements for wave front shaping in the visible domain: switchable helical mode generation," Appl. Phys. Lett. **88**, 221102 (2006).
16. A. Jesacher, A. Schwaighofer, S. Fürhapter, C. Maurer, S. Bernet, and M. Ritsch-Marte, "Wavefront correction of spatial light modulators using an optical vortex image," Opt. Express **15**, 5801–5808 (2007).
17. G. A. Swartzlander Jr., "Peering into darkness with a vortex spatial filter," Opt. Lett. **26**, 497–499 (2001).
18. S. Bernet, A. Jesacher, S. Fürhapter, C. Maurer, and M. Ritsch-Marte, "Quantitative imaging of complex samples by spiral phase contrast microscopy," Opt. Express **14**, 3792–3805 (2006).
19. I. Nishiyama, N. Yoshida, Y. Otani, and N. Umeda, "Single-shot birefringence measurement using radial polarizer fabricated by direct atomic force microscope stroking method," Meas. Sci. Technol. **18**, 1673–1677 (2007).
20. G. Sinclair, P. Jordan, J. Courtial, M. Padgett, J. Cooper, and Z. J. Laczik, "Assembly of 3-dimensional structures using programmable holographic optical tweezers," Opt. Express **12**, 5475–5480 (2004).
21. D. Ganic, X. Gan, M. Gu, M. Hain, S. Somalingam, S. Stankovic, and T. Tschudi, "Generation of doughnut laser beams by use of a liquid-crystal cell with a conversion efficiency near 100%," Opt. Lett. **27**, 1351–1353 (2002).
22. K. L. Marshall, J. Gan, G. Mitchell, S. Papernov, A. L. Rigatti, A. W. Schmid, and S. D. Jacobs, "Laser-damage-resistant photoalignment layers for high-peak-power liquid crystal device applications," Proc. SPIE **7050**, 70500L (2008).
23. V. G. Chigrinov, H. S. Kwok, H. Takada, and H. Takatsu, "New developments in liquid crystal photo-aligning by azo dyes," in *Society for Information Display '06 Digest* (Society for Information Display, 2006), Vol. 37, pp. 1253–1256.
24. V. Chigrinov, E. Prudnikova, V. Kozenkov, H. Kwok, H. Akiyama, T. Kawara, and H. Takada, H. Takatsu, "Synthesis and properties of azo dye aligning layers for liquid crystal cells," Liq. Cryst. **29**, 1321–1327 (2002).
25. O. Yaroshchuk, J. Ho, V. Chigrinov, and H. S. Kwok, "Azodyes as photoalignment agents for polymerizable liquid crystals," Jpn. J. Appl. Phys. **46**, 2995–2998 (2007).
26. V. Presnyakov, K. Asatryan, T. Galstian, and V. Chigrinov, "Optical polarization grating induced liquid crystal microstructure using azo-dye command layer," Opt. Express **14**, 10558–10564 (2006).
27. X. Li, Ping T. Au, P. Xu, A. Muravsky, A. Muravsky, Z. Liu, V. Chigrinov, and H. S. Kwok, "Flexible photoaligned optically rewritable LC display," in *Society for Information Display '06 Digest* (Society for Information Display, 2006), 37, pp. 783–785.

28. A. Muravsky, A. Murauski, X. Li, and V. Chigrinov, "High efficiency optical rewritable device," in *Proceedings of the 13th International Display Workshops (IDW'06)* (Society for Information Display, 2006), pp. 609–612.

29. Z. Raszewski, R. Dabrowski, Z. Stolarzowa, and J. Zmija, "Dielectric studies on binary mixtures containing 4-trans-4-n-hexyl-cyclohexyl-isothiocyanato-benzene," Cryst. Res. Technol. **22**, 835–844 (1987).

30. V. Chigrinov, H. S. Kwok, H. Takada, H. Takatsu, and H. Hasebe, "Azo-dye alignment for displays and photonics," in *Society for Information Display '07 Digest* (Society for Information Display, 2007), pp. 1474–1477.

31. S. Serak and N. Tabiryan, "Microwatt power optically controlled spatial solitons in azobenzene liquid crystals," Proc. SPIE **6332**, 63320Y (2006).