

38.2: Azodye Aligning Layers for Liquid Crystal Cells

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Abstract

The photo-induced alignment of liquid crystal onto a photochemical stable azo dye film is studied for the liquid crystal display (LCD) applications. The photo-aligning of azo dye takes place due to the pure reorientation of the molecular absorption oscillators perpendicular to the UV-light polarization. The order parameters $S = -0.4$ (80% of the maximum absolute value $S_m = -0.5$) was measured at the wavelength of 372 nm from the polarized absorption spectra. The temperature stable pretilt angle of 5.3° was obtained by a two-step exposure of azo-dye film using normally incident polarized light followed by oblique non-polarized light. The azimuthal anchoring energy of the photo-aligned substrate was $A_\phi > 10^{-4} \text{ J/m}^2$, which is of the same magnitude as the anchoring of the rubbed PI layer. VHR value of the photo-aligned LC cell was also found to be very high (98-99%) at room temperature and more than 95% at $T = 80^\circ\text{C}$. The thermal stability of the photo-aligned azo-dye layers is sufficiently high, while UV-stability has to be improved e.g. by polymerization. The bright perspectives for the new LCD aligning technology are envisaged.

Introduction

Recently we have shown the possibility of obtaining a high quality non-contact photo-alignment layers using the azo dye structures [1]. Photochemical stable azo dye layers are an excellent example of pure reorientation of the absorption oscillator of the azo dye molecules perpendicular to the polarization of the activating UV-light. As was discussed earlier by one of the authors [2], the photochemical mechanisms, such as cross-linking, photo-degradation and even cis-trans isomerization are most likely avoided in case of certain organic materials, such as azo-dye layers in our case. The negligible contribution of the cis-trans isomerization process into the photo-aligning of the azobenzene dyes in solid films was also observed in Ref. [3]. When the azo dye molecules are optically pumped by a polarized light beam, the probability for the transformation is proportional to the square of the cosine θ , the angle between the transition dipole moments of the molecules and the direction of the polarization of the activated light. Therefore, the azo dye molecules that have their transition dipole moments parallel to the direction of the polarized light will most probably get the excess in energy, which results in their reorientation from the initial position. This process can be described statistically as a diffusion motion of the dye molecules

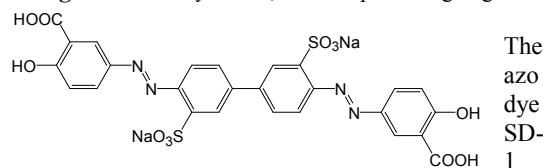
in the potential field of the polarized light [4]. This results in an excess of chromophores in a direction at which the absorption oscillator is perpendicular to the polarization of the UV-light. The function $f(\theta)$ of the statistical distribution of the dye molecules along the various orientations θ , which is $f = 1/4\pi$ in the initial state will tend to $f = \delta(\theta - \pi/2)$ for the sufficiently high exposure time. Hence, a thermodynamical equilibrium in the new oriented state will be established. When the illumination light source is removed, the induced order relaxes to the less ordered state. However, if the illumination exposure time is high enough the self-induced ordering can be observed due to the internal average field of the chromophore molecules, which are in the highly ordered state [5,6]. Consequently, the anisotropic dichroism and optical retardation are photo-induced permanently and the associated order parameter as a measure of this effect can be very large in some of these materials.

The temperature stable aligning was successfully demonstrated in the mixtures of azo dye molecules with various polymers [6-8]. However the pure azo-dye layers can be also used as photo-aligning agents [9]. In this paper we provide some important parameters of the LC cells produced on the basis of the photo-aligned azo dye layers, such as pretilt angle, azimuthal anchoring energy and VHR ratio. The thermal stability of the photo-aligned azo-dye layers is sufficiently high. The azo-dye layers can be a good photo-aligning material for AM-LCDs, including LCOS structures.

Experimental

The dye molecule, which was synthesized for the studies of photo-induced alignment, is shown in Fig. 1. It was synthesized by azo-coupling of 4,4'-diamino-3,3'-biphenyldisulfonic acid with o-hydroxybenzoic acid according to the literature [10]. The products were purified by recrystallization and column chromatography.

Figure 1. Azo-dye SD-1, used for photo-aligning.



was dissolved in N,N-dimethylformamide at a concentration of 1 wt%. The solutions were spin coated

onto glass substrates with ITO electrodes and dried at 100°C. The spin-coated film was uniform and very adhesive to the glass substrate. UV light was irradiated onto the surface of the layer using a super-high pressure Hg lamp, interference filter at 365 nm, and polarizing filter. The light intensity on the surface of layer is 15 mW/cm² for polarized light and 40 mW/cm² for nonpolarized light.

Two glass substrates were assembled to form liquid crystal cell with a cell gap of 10 μm. Liquid crystal mixture 11-3323 (from Dainippon Ink and Chemicals) was injected into the cell in an isotropic phase by capillary action.

Results

1. Polarized absorption spectra

In order to study the photoreorientation of the azo dye molecules by the linearly polarized UV exposure, we measured polarized absorption spectra for the layer before and after the irradiation with the linearly polarized UV light. The spectra were measured using incident light with polarization directions parallel and orthogonal to the polarization direction of the activated linearly polarized UV light. Figure 2 shows the absorption spectra before (curve 1) and after (curves 2 and 3) the UV irradiation.

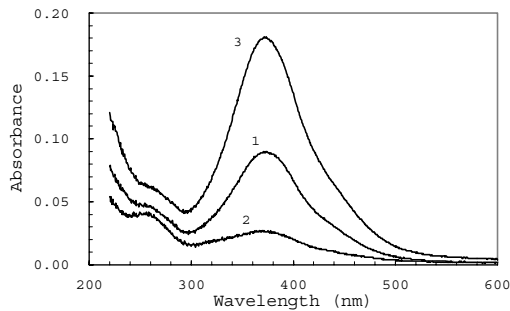


Figure 2. Absorption spectra of SD-1 layer before the polarized UV exposure (curve 1). Curves 2 and 3 show the polarized absorption spectra after the exposure by a polarized UV light in the direction parallel and perpendicular to the activating light polarization accordingly.

Before the irradiation the absorption of the azo dye layer does not depend on the polarization of the light, used in measurements. After the irradiation by linearly polarized UV light, the absorption of light with the polarization direction parallel to the polarization direction of the activated light decreases (curve 2, Fig.2) while that one with orthogonal polarization direction increases (curve 3, Fig. 2). The evolution of the absorption spectra after UV-illumination does not reveal any noticeable contribution of cis-trans isomerization [2,3] as the average absorption $A_{ave} = (A_{\parallel} + 2A_{\perp})/3$ remains the same. The order parameter S of the azo dye chromophores can be expressed as [11]:

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$$

where A_{\parallel} and A_{\perp} are absorption (optical density) of parallel and orthogonal polarized light to the polarization of the activated UV light. The order parameter S is equal to -0.4 at $\lambda_m = 372$ nm (absorption maximum), which is 80% from its maximum absolute value $S_m = -0.5$ in our case.

2. Pretilt angle.

In order to achieve pretilt of liquid crystal, we tried four kinds of exposure method illustrated in Figure 3. To measure the pretilt angle, the liquid crystal cells were assembled with substrates antiparallel to UV irradiation directions and were filled with liquid crystal mixture. The crystal rotation method was used to measure their pretilt angles [11]. Pretilt angle of 0.7°, 0.1°, 5.3°, and 3.8° is obtained with the exposure method (a), (b), (c), and (d), respectively (Fig.3). We believe, that oblique irradiation of non-polarized light is the most efficient in order to obtain large pretilt angles. The dependence of the pretilt angle on the exposure energy in (c) is shown in Figure 4.

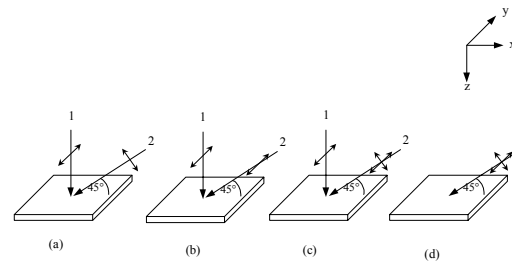


Figure 3. Various methods of UV light irradiation to attain the pretilt angle of LC layer on the photo-aligned azo dye film. Case (a): two step exposure by y- polarized light vertical to the plane of the azo dye film (xy plane) and oblique p-polarized light ; (b): case (a) with s-polarized light used at the second step, (c): case (a) with non-polarized light at the second step; (d): one step exposure with oblique non-polarized light. The activated UV light propagates in xz plane at an angle of 45° with the substrate.

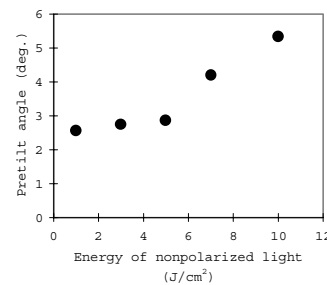


Figure 4. Dependence of the pretilt angle on the energy density of the obliquely irradiated nonpolarized light after the irradiation of vertical polarized light with the energy density of 10 J/cm².

3. Anchoring energy

Anchoring energy of the azo dye layer was measured according to the method, already used by one of the authors for the photo-aligned substrate [12]. A substrate with rubbed polyimide alignment layer and

that with photo-aligned azo dye layer were assembled with an 80° twisted nematic configuration. The liquid crystal was injected into the cell with gap of 10 μm. Azimuthal anchoring energy of the azo dye alignment layer was calculated from the equation

$$A_{\phi} = \frac{2 K_2 \Delta \phi}{d \sin(\Phi - \Delta \phi)},$$

where Φ , $\Delta \phi$, K_2 , and d is 80°, twist angle, twist elasticity constant of liquid crystal (6.0×10^{-12} N), and cell gap, respectively. The measured twist angle $\Delta \phi$ was about 80° with the accuracy of 1°, for the whole range of the UV-light exposure energies between 1 J/cm² and 10 J/cm², which states, that the anchoring energy $A_{\phi} > 10^{-4}$ J/m², which is comparable with the anchoring energy of the rubbed polyimide layer.

4. VHR and LC electrooptical response.

Figure 5 compares the transmission voltage characteristics of the of 90° twisted nematic LC cell (TN-LC) based on photo-aligned azo dyes SD1, SD2 film and rubbed polyimide PI 2424 layer. The azo-dye structure of SD2 is very close to SD1 and was described earlier [1]. The transmission-voltage curves (TVCs) are similar and very good contrast as the result of a perfect LC alignment can be measured directly. It is greater than 70:1 at the normal incidence. The electrooptical response does not change even in case the SD1 photo-aligned cell is heated up to 200°C during 2 hours. The VHR was measured by a standard technique, when the voltage pulse of $V_0=5V$ was applied during 64 μsec and the voltage $V(t)$ on LC cell dropped down during $\tau=16$ msec after the pulse is switched off at $t=0$. The VHR value of the photo-aligned LC cell was found to be very high (98-99%) at room temperature, and still more than 95% at $T=80^\circ C$. VHR value of the photo-aligned LC cell appeared to be even larger, than for LC cell based on the rubbed polyimide (PI) layer.

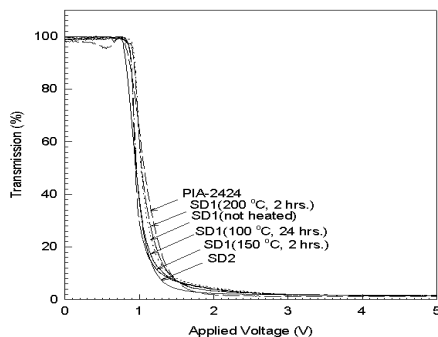


Figure 5. The comparison of transmission –voltage curves (TVCs) for 90° twisted nematic LC cell (TN-LC) based on photo-aligned azo dyes SD1 and SD2 films and rubbed polyimide PI 2424 layer. Heating the cell up to 100°C, 150°C and 200°C during 2 hours does not have any effect to the TVC curve.

Thus the future application in active matrix liquid crystal displays (AM-LCDs), where a high ionic purity of LC cell is required becomes possible.

DISCUSSION AND CONCLUSION

The photo-induced alignment of liquid crystal on a photochemical stable azo dye film is studied for the liquid crystal display (LCD) applications. The photo-aligning of azo dye takes place probably due to the pure diffusive reorientation of the molecular absorption oscillators perpendicular to the UV-light polarization in the field of the polarized activated light. We can not find any noticeable contribution of cis-trans isomerization from the evolution of the polarized absorption in azo-dye layers. The order parameter S saturates for the sufficiently high exposure time contrary to the case of photochemical active substances, when the order achieves its maximum value and then decreases to zero [2].

The high order parameters $S = -0.4$ (80% of the maximum absolute value $S_m = -0.5$) was defined from the polarized absorption spectra at the wavelength of 372 nm. The temperature stable pretilt angle of 5.3° was obtained by a two-step exposure of azo dye film using normally incident polarized light followed by oblique non-polarized light. The azimuthal anchoring energy of the photo-aligned substrate was $A_{\phi} > 10^{-4}$ J/m², which is comparable with the anchoring of the rubbed PI layer. VHR value of the photo-aligned LC cell was also found to be very high (98-99%) at room temperature, and still more than 95% at $T=80^\circ C$. The electrooptical characteristics of azo dye aligned TN LCD samples are excellent and thermo-stable, however, further improvement of the UV stability of the photo-aligned azo dye layer is needed, e.g. by a polymerization. In view of this we have synthesized the SD-1 molecules with polymerizable terminal groups. We succeeded to obtain the polymerization of the new substances both in the solvent and solid films, keeping the high order parameter achieved by preceding UV-illumination. Our results are encouraging and will be published elsewhere. Further applications of azo-dye aligning layers in AM-LCDs, including LCOS structures are envisaged.

REFERENCE

- [1] W.C. Yip, E. K. Prudnikova, V.M. Kozenkov, V.G. Chigrinov, H.S. Kwok, H. Akiyama, M. Fukuda, H. Takada and H. Takatsu, *SID'01 Digest*, p. 1170 (2001).
- [2] V.M. Kozenkov, V.A. Barachevskiy, In *Photosensitive materials and their application in holography*, "Nauka", Leningrad, pp.89-96,1985 (In Russian).
- [3] M. Schönhoff, M. Mertesdorf, and M Lösche: J. Phys. Chem. **100**, 7558 (1996).
- [4] V.G. Chigrinov, H. S.Kwok, W.C. Yip, V.M. Kozenkov, E.K. Prudnikova, B.Z. Tang, F. Salhi, *Proc. of SPIE*, Vol. 4463,p117 2001.
- [5] V. M. Kozenkov, S. G. Yudin, E. G. Katyshev, S. P. Palto, V. T. Lazareva, V. A. Barachevskiy, *Pisma v JTF*, **12**, 1267 (1986) (In Russian).

- [6] J.K. Song , K.Y.Han, V.G. Chigrinov, *IDW' 96 Digest*, p.407, (1996).
- [7] W. Gibbon, P. J. Shannon, S. Sun and B. J. Swetlin, *Nature (London)* **351**, 49 (1991).
- [8] V. Vorflusev, V. Kosenkov and V. Chigrinov, *Mol. Cryst. Liq. Cryst.* **263**, 577 (1995).
- [9] Linli Su, Bin Wang, J.West, Y. Reznikov , *Molecular Crystals & Liquid Crystals*, 359, p.467, 2001.
- [10] J. Szadowski and Z. Niewiadomski: *Dyes and Pigments* **19**, 41 (1992).
- [11] V.G. Chigrinov, *Liquid Crystal Devices: Physics and Applications*, 357 pp., *Artech-House*, Boston-London, 1999.
- [12] V.P. Vorflusev, H.S. Kitzerow, V.G. Chigrinov, *Jap.J.Appl.Phys.,P.2*, **34**, p.L1137 (1995).