Azo-Dyes Photo-Aligning: Physics and Applications

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Abstract
This review presents the status of our research in liquid crystal display (LCD) photo-aligning. We present the basic mechanisms of the photo-induced order in various photo-aligning materials and in azo-dye layers in particular and show that photo-aligning methods can provide a controllable pretilt angle and anchoring energy of the liquid crystal cell, as well as its high thermo and UV stability. The photo-aligning of various types of liquid crystal displays is also discussed.

1.   Introduction

The effect of LC-photoaligning is a direct consequence of the appearance of the photo-induced optical anisotropy and dichroism absorption in thin amorphous films, formed by molecular units with anisotropic absorption properties [1]. The first publication on LC photo-alignment appeared in 1988 and discussed the application of the reversible cis-trans isomerization of the azo-benzene molecular layers attached to the solid surface to the switching of the alignment of the adjacent LC layer from homeotropic to the azimuthally random planar orientation [2]. The optical control of LC alignment was made by changing the wavelength of the non-polarized light illumination [2]. Later it was shown that the alignment of a liquid crystal medium could be made by illuminating a dye doped polymer alignment layer with a polarized light [3]. LC molecules in contact with the illuminated area were homogeneously aligned perpendicular to the direction of the laser polarization and remain aligned in the absence of the laser light. Very soon the LC photo-alignment procedure was made using cinnamoyl side-chain polymers [4,5]

and polyimide aligning agents [6]. The area of LC photo-alignment is very rapidly developing and the vast majority of the new materials, techniques and LCD prototypes based on photo-alignment technology appeared recently [7-9]. We present an original review of recent achievements in photo-aligning technology based on azo-dye layers, as new photo-aligning materials [10,11].

2.   Results
2.1   Azo-dye photo-aligning layers
The following mechanisms of the photo-alignment are known: (i) photochemical reversible cis-trans isomerization in azo-dye containing polymers, monolayers and pure dye films; (ii) pure reorientation of the azo-dye chromophore molecules or azo-dye molecular solvates due to the diffusion under the action of polarized light; (iii) topochemical crosslinking in cinnamoyl side-chain polymers; (iv) photodegradation in polyimide materials. The first two processes present the reversible transformations, while the latter two can be referred as irreversible photo-chemical phenomena, taken place in photosensitive aligning films. For cis-trans isomerization the change of the absorption spectra is observed after illumination [12,13], which is not the case for the photo-stable azo-dye molecules, involved in a reorientation and solvate formation process under the action of polarized light [14].

Besides chemical reaction, the UV light can induce an asymmetric potential field under which the stable configuration is characterized by the dye absorption oscillator perpendicular to the induced light polarization. One of the possible photo-aligning mechanism in azo-dye films is a pure reorientation of azo-dye molecules. When the azo-dye molecules are optically pumped by a polarized light beam, the probability for the absorption is proportional to $\cos^2 \theta$, where θ is the angle between the absorption

oscillator of the azo-dye molecules and the polarization direction of the light (Fig.1) [14].
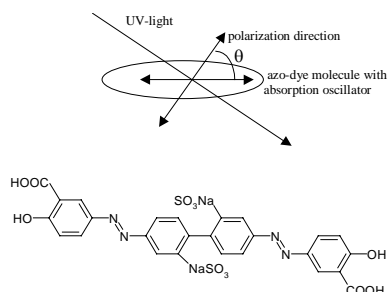
Figure 1. Photo-induced order in photochemical stable azo-dye films. The structure of azo-dye molecule (sulfonic dye, SD-1) is also shown.

Therefore, the azo- dye molecules, which have their absorption oscillators (chromophores) parallel to the light polarization will most probably get the increase in energy, which results in their reorientation from the initial position. Fig. 2 shows the polarized absorption spectra (absorbance or optical density) before (curve 1) and after (curves 2 and 3) the UV
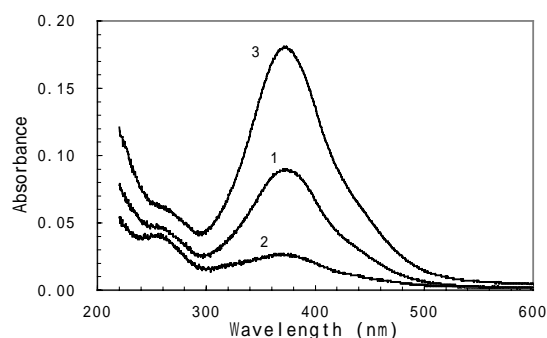

irradiation [10].

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 ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the activating light polarization accordingly [10].

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 ($D_{\parallel}$) decreases (curve 2, Fig.2) while that one with

orthogonal polarization direction ($D_{\perp}$) increases (curve 3, Fig.2). The evolution of the polarized absorption spectra after UV-illumination does not reveal any noticeable contribution of photochemical reactions [12], as the average absorption
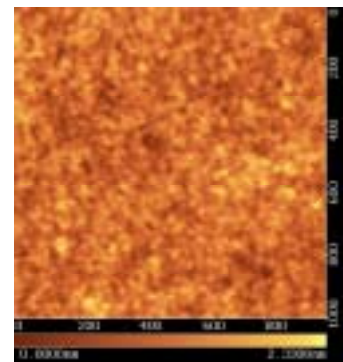
$$D_{ave} = (D_{\parallel} + 2D_{\perp})/3 \qquad (1)$$

remains the same for any fixed value of the exposure time, Fig.2. The order parameter S of the azo dye chromophores can be expressed as [10]:

$$S=(D_{\parallel}-D_{\perp})/(D_{\parallel}+ 2D_{\perp}), \qquad (2)$$

where $D_{\parallel}$ and $D_{\perp}$ are absorption (optical density) of parallel and orthogonal polarized light to the polarization of the activated UV light.

Consequently, the anisotropic dichroism or birefringence is photo-induced permanently and the associated order parameter as a measure of this effect goes to the saturation value, which can be very large in these materials. The order parameter S of azo-dye SD1 is equal to -0.4 at λ_m= 372 nm (absorption maximum), which is 80% from its maximum absolute value S_m = -0.5 in our case. The relative order parameter of azo-dye layer is proportional to the measured normalized phase retardation of the layer and sufficiently high, even for moderate exposure energy of 100-200 mJ/cm^2 (Fig.3). Recently we synthesized the new azo-dye derivatives, capable to make a perfect LC alignment with a minimum energy of 150 mJ/cm^2 for a non-polarized obliquely incident light (45^0) and 20 mJ/cm^2 for a polarized light.

The temperature stable pretilt angle of 5.3^0 was obtained by a two-step exposure of azo-dye film using normally incident polarized light followed by oblique non-polarized light [10,11]. The pretilt angle was temperature stable and does not change after heating the sample up to 100^0C.

Figure 3. Saturation of the normalized photoinduced retardation proportional to order parameter S with time. The intensity of the UV light is also shown.

The azimuthal anchoring energy of a photo-aligned substrate was $W_{\varphi} > 10^{-4}$ J/m^2, the same as the anchoring of the rubbed polyimide (PI) layer. In photo-polymerized azodye layers the azimuthal and polar anchoring energy was about $1.5 \cdot 10^{-5}$ J/m^2 and $3 \cdot 10^{-4}$ J/m^2 for the exposure dose less than 1 J/cm^2. The values of the anchoring energy for azo-dye layers are the highest possible ones, obtained by the known photo-aligning materials [15]. The anchoring energy increases with the thickness of the azo-dye layer d_{AL} and comes to the saturation, when $d_{AL} > 12$nm. In this case a uniform and smooth azo-dye photo-alignment layer is formed on the glass or plastic substrate (Fig.4).
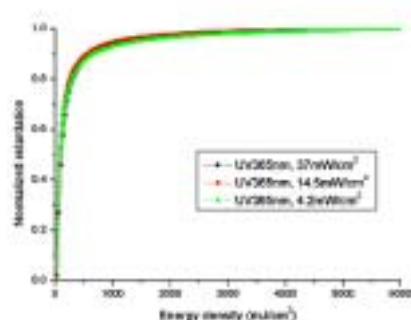
Figure 4. AFM picture of the azo-dye layer (SD-1) on the glass substrate.

The value of Voltage Holding Ratio (VHR), measured for the photo-aligned LC cell (>99% at 80^{0}C) and residual DC voltage (<50mV) was found to be even better, than for rubbed PI layer, which enables the azo-dye applications as aligning layers in active matrix liquid crystal displays (AM-LCDs). The thermal stability of the photo-aligned azo-dye layers was sufficiently high (up to 200^{0}C), while UV-stability was also improved by polymerization. The quality of a photo-aligned TN cell is shown in Fig. 5.

Figure 5. Polarized microscope photograph of LC alignment on photoaligned polymerized azo-dye film [15].

The size of the picture is 1mm^2. Both homogeneous and twist LC alignment looks perfect between crossed polarizers.

Our latest results show, that polymerized azodye layers can tolerate the temperature up to 250^0 C for two hours, while non-polymerized azodye layers exhibit the irreversible degradation of LC orientation. The dose of UV irradiation of 175 MJ/m^2 from Xe lamp does not destroy LC alignment on polymerized azodye layers. At the same time non-polarized azodyes cannot keep the stable LC alignment in this case.

2.2 LCDs based on azo-dye photo-aligning technology

A remarkable property of azodye aligning layers gives a good chance to provide a high photoalignment quality of *ferroelectric liquid crystal display (FLCD)* using the azodye layer. The photo-aligned FLC cell appeared to be better than prepared by buffing, if the UV-irradiation time of the azodye layer is high enough [16]. The bistability switching was perfect and steady, bistability degradation was not observed. Moreover, the multiplexing ability, which is necessary for a passively addressed FLCD cell operation was also observed, due to existence of a certain threshold of FLC switching, $V_{th} \approx 0.6$ V. The FLCD row addressing response time of $\tau \approx 100$ µs at the voltage pulse amplitude of U= ±15V was demonstrated [16]. Large FLC cell gaps of 5 µm and 7 µm increase the FLC steadiness in bistable and multistable switching and are easy in manufacturing. Perfect electrooptical performance of the photo-aligned FLC display was obtained after optimization in multiplexing driving regime, including high contrast ratio, low *N/S* ratio and memorized gray scale. A prototype of passively addressed 64×64
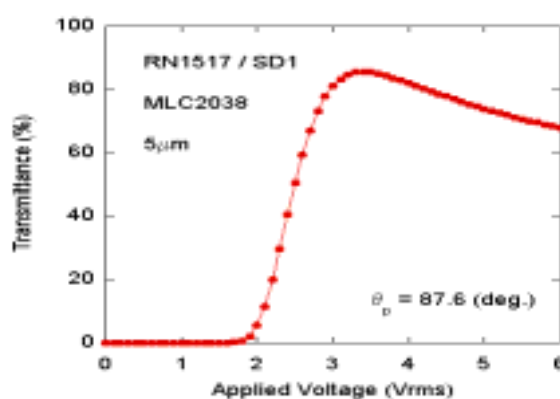
FLC display based on the photo-alignment technique has been developed with bistable switching in the multiplex driving regime [17]. The display matrix has dimensions of $33 \times 33 mm^2$, and the FLC layer thickness is (5.2 ± 0.2) μm. The display device operates with the frame frequency 30 Hz (at $V_{row} = \pm 18V$, $V_{col} = \pm 9V$, $T = 23°C$) generating a continuous gray scale, which can be memorized for more than 10 days after the driving voltage is switched off (Fig.6).

Figure 6. Photo-aligned 64×64 FLC display in multiplexing driving regime, with a memorized gray scale.

Vertical aligned nematic (VAN) LCD cells prepared by photoaligning technique have not yet reached the appropriate quality (response time, contrast ratio) in comparison with conventional LCDs, prepared by rubbing technology [9]. The application of modern commercial VAN aligning agents with high resistivity to UV light in a combination with photo-aligned azo-dye materials [10,11] can help to overcome the above-mentioned problems. In experiment [18] the commercially available polyimide (PI) for homeotropic alignment was used in a combination with azo-dye for varying the pretilt angle from the homeotropic direction. The composition of 1% of azo-dye in solution with PI was prepared and the photo-aligning films were illuminated by a slantwise nonpolarized light. For comparison the aligning film of a pure PI was prepared by rubbing technique to align the LC molecules in a homeotropic state with some pretilt angle. The measured value of the pretilt angle was about 1.4°, which is higher than in photo-aligned VAN LC cell (0,53°). However the response time of the photo-aligned and conventional VAN LCD was almost the same $\tau_{on} + \tau_{off} = 7,8ms + 9$ ms and $\tau_{on} + \tau_{off} = 8,1$ ms + 8,9 ms accordingly. Probably this means that azo-dye as a dopant in PI has increased further the azimuthal anchoring strength in the photo-aligned VAN-LCD cells. The high values of VHR for the photo-aligned VAN-LCD using azo-dye/PI composition of 94 –96% (close to the

conventional rubbed VAN-LCD with VHR=88%) testify to the point. The measured value of the contrast ratio between "off" and "on" states in all the cases exceeds 1000:1 in the monochromatic light (λ=632.8nm). Recently a reliable pretilt angle of more than 1^0 from homeotropic LC alignment was obtained using the mixture of homeotropic PI and photopolymerized azo-dye SDA-2 [11]. Fig. 7 shows the transmission-voltage curve of the photo-aligned VAN LCD cell for the pretilt angle of 2.4^0 from the homeotropic orientation.

Figure 7. Transmission-voltage curve of the photo-aligned VAN LCD cell.

We fabricated truly bistable *π-BTN display*, based on photoaligning technology [19]. We found that the polar anchoring energy of photo-polymerized azo-dye SDA-1 (SDA-2) can be adjusted to 1.5-$2.8 \cdot 10^{-4}$ J/m^2 while azimuthal anchoring to 3.6-$5.6 \cdot 10^{-5}$ J/m^2 by changing the exposure time, which was suitable for obtaining π-BTN bistability by surface anchoring breaking. The π-BTN LCD was switched between -22.5^0 and 157.5^0 twisted states, exhibiting a high contrast ratio (CR>140) and wide viewing angle.

We have investigated also the properties of azo-dye alignment *on plastic substrates* [20]. Excellent alignment with a high anchoring energy was achieved with the exposure energy less than 1.5 J/cm^2, which corresponds to the azimuthal anchoring energy $> 10^{-4}$ J/m^2. The LC pretilt angle of about 5^0 on the plastic substrate was made by a double exposure method. To demonstrates the alignment quality on plastic substrates a 9-digit reflective passive matrix TN-LCD was fabricated. To maintain a uniform cell gap of 8 μm (second Mauguin minimum of MLC-6809-000 Merck LC mixture),

semi-dry adhesive spacers were chosen. The electrooptical performance of the photo-aligned plastic display was very similar to common TN-LCD fabricated for comparison by usual rubbing method on glass substrate (Fig.5).

Figure 5. Photo-aligned 9-digit reflective passive matrix TN-LCD on plastic substrates.

Recently a first *flexible π -BTN* with 1.8µm cell gap was fabricated using using azo-dye photo-alignment technology. The commercially available plastic substrates with the thickness of 200µm with LC mixture BN-104 provided by Nemoptic Company between them were used. This display has an unlimited memory in both display states and very stable to mechanical deformations.

3. Conclusion

In this original review we have briefly considered the physics of novel photo-aligning technology and its applications to LC displays. In particular we considered the progress the application of azo-dye aligning layers to produce temperature and UV-stable LC alignment with a sufficiently high pretilt angle and large VHR. The possibility to use photo-aligning for FLCD ,VAN-LCD, π-BTN LCD and TN-LCD on plastic substrates has been also demonstrated.

4. Acknowledgements

5. References

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