

# New Developments in Liquid Crystal Photo-Aligning by Azo-Dyes

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*Invited Paper*

**Abstract**—Liquid crystal (LC) photo-alignment using azo-dyes is reviewed. This alignment method is very different from previously reported ones, which are due to mechanisms such as photo-crosslinking, photo degradation, and photo-isomerization. We present the basic physical mechanisms of the photo-induced orientational order in various photo-aligning materials and in azo-dye layers in particular. This method is based on rotational diffusion in a potential created by the light field as well as intermolecular forces. It will be shown that this photo-aligning method can provide a controllable pretilt angle and strong anchoring energy of the LC cell, as well as having high thermal and ultraviolet (UV) stability. The application of this method to the alignment and fabrication of various types of LC displays is also discussed.

**Index Terms**—Liquid crystal display (LCD), order parameter, photo-alignment, rotational diffusion, UV light.

## I. INTRODUCTION

PHOTO-ALIGNMENT (PA) has been pursued rigorously for manufacturing liquid crystal displays (LCDs). This technique has the potential advantage of cleanliness as well as large area application when rubbing becomes inadequate. The field of liquid crystal (LC) photo-alignment is very rapidly developing and a vast amount of the new materials, techniques and LCD prototypes based on photo-alignment technology have appeared recently [1]–[9]. However, despite these potential advantages, the application of PA to LCD production is still limited to the laboratory. Large-scale deployment of PA is hampered by the lack of a good material and by long term stability, not to mention the lack of suitable mass production scale equipment.

The effect of LC photoalignment is a direct consequence of the appearance of the photo-induced optical anisotropy and dichroic absorption in thin amorphous films, formed by molecular units with anisotropic absorption properties [1]. The first publication on LC photo-alignment appeared in 1988, which discussed the application of a reversible cis-trans isomerization

of the azo-benzene molecular layers [2]. The optical control of LC alignment was made by changing the wavelength of the nonpolarized 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 polarized light [3]. LC molecules in contact with the illuminated area were homogeneously aligned perpendicular to the direction of the laser polarization and remained aligned in the absence of the laser light. Subsequently, LC photo-alignment was also achieved using cinnamoyl side-chain polymers [4], [5] and polyimide aligning agents [6]. More recently, a new class of azo-dyes have also been studied recently by with excellent results [10], [11].

The basic criteria for a good alignment material are simple. The material should be very clean so that the voltage holding ratio (VHR) is large. The material should also have low charge trapping so that the residual DC charge (RDC) is low. As well, the polar as well as azimuthal anchoring energies should be comparable to conventional rubbed polyimide (PI). Finally the ultraviolet light dosage needed should be low so that the LCD processing time is not compromised. Typically, the entire sheet of mother glass should be optically aligned in about the same time as mechanical rubbing. Considering that the UV light source is probably limited to 100 W in UV optical power and the processing time is 5 s, that sensitivity requirements translate to about 70 mJ/cm<sup>2</sup> for a Gen 3 system, and assuming 50% optical system efficiency. This is a far cry from the typical required dosage of 1–10 J/cm<sup>2</sup> for most PA materials reported so far.

We have recently investigated a class of PA material that fulfills these stringent requirements of large VHR, low RDC, and low light dosage [1]–[3]. These are the azo-dyes SD1, SD2, and their various derivatives. In this paper, we shall review the physical mechanism of this alignment process and report some new results related to the processing conditions using these azo-dyes. In particular, we discuss the conditions where the light dosage is greatly reduced, to less than 50 mJ/cm<sup>2</sup>. Applications of this new PA material to various types of LCD will also be reviewed.

## II. PHOTO-INDUCED REORIENTATION

Photo-alignment can generally be classified into four categories according to their mechanism. They are: 1) photochemically reversible cis-trans isomerization in azo-dye containing polymers, monolayers, and pure dye films [12], [13]; 2) photochemical crosslinking in preferred directions of polymer precursors, such as cinnamoyl side-chain polymers

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[4], [5]; 3) photodegradation and orientational bond breaking in polyimide materials [14], [15]; and 4) pure reorientation of the azo-dye chromophore molecules or azo-dye molecular solvates due to the diffusion under the action of polarized light [10], [11]. Recently the method of repeated cis-trans photoisomerization reaction resulting in the reorientation of the backbone structure of polyamic acid contained azobenzene units was reported [16], [17]. The subsequent imidization stabilized the polyimide structure. The LC alignment was thermally and optically stable and no decomposition was involved.

Processes 1) and 4) involving azo-dyes present reversible transformations, while the other two processes require irreversible photo-chemical changes. For these latter processes, since chemical changes occur, it is difficult to maintain the purity of the alignment layer. Thus the VHR and RDC are compromised. For cis-trans isomerization the change of the absorption spectra is observed after illumination [12], [13], which is not the case for the photochemical stable azo-dye molecules, involved in a reorientation and solvate formation process under the action of polarized light [10], [11]. These two processes can have good VHR and RDC. However there is a significant difference in their anchoring energies. The anchoring energy is also very strong (near  $10^{-3}$  J/m<sup>2</sup>) for the UV light induced pure reorientation process. Our recent results also show that the photosensitivity can be reduced to 50 mJ/cm<sup>2</sup> for the alignment of the LC layer. Thus, of all the PA processes, we believe that (iv) with pure diffusion reorientation of the the azo-dye chromophore molecules or azo-dye molecular solvates is the most promising one for large scale applications.

The mechanism of the photo-orientation process is quite interesting. The UV light induces an asymmetric potential field under which the stable configuration is characterized by the dye absorption oscillator perpendicular to the induced light polarization. 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  $\theta$  is the angle between the absorption oscillator of the azo-dye molecules and the polarization direction of the light is as shown in Fig. 1 [18]. Therefore, the azo-dye molecules, which have their absorption oscillators (chromophores) parallel to the light polarization, will most probably get an increase in internal energy, which results in more energetic rotational motion through internal energy transfer (electronic to rotation energy). Vibrational motions will probably occur, but that does not affect the PA mechanism.

The increased rotational motion of the excited dye molecules is damped resulting in a new orientation for the azo-dye. This absorption-rotation process will keep repeating itself until the chromophores have their absorption dipole oscillators perpendicular to the polarization of the input light. In that case there will be no absorption. The molecules will be at rest. Once all or most of the molecules are oriented this way, inter-molecular interaction will lock their positions in place and prevent rediffusion and randomization even if the input light is turned off. This is a heuristic picture of the photo-physical alignment process in these azo-dyes.

We have studied this UV light induced reorientation effect carefully. In our case the chromophore is parallel to the long molecular axis of the azo-dye (see Fig. 1), i.e., azo-dye

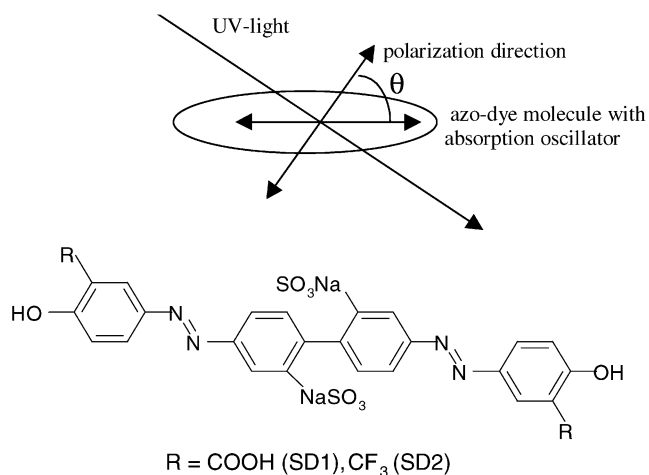


Fig. 1. Photo-induced order in photochemical stable azo-dye films. The structure of azo-dye molecule (sulfonic dyes, SD1, SD2) is also shown [10].

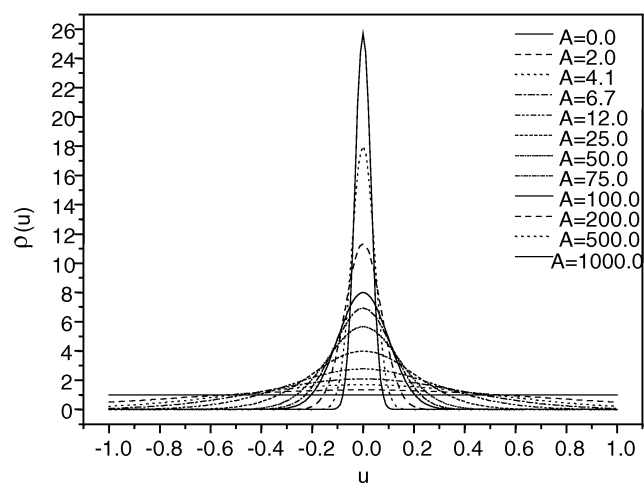


Fig. 2. The distribution function  $\rho(u) = 4\pi f(u)$ ,  $u = \cos \theta$  of the azodye molecules for various values of the parameter A (2), proportional to the intensity of the activated light [18].

molecules are tending to align their long axes perpendicular to the UV-light polarization. The statistical distribution of orientation of the molecules is described by the function  $f(\theta)$  where  $\theta$  is the angle between the molecular axis and the direction of the light polarization (Fig. 1). Obviously, the normalized  $f = 1/4\pi$  in the initial state, and the final desired state with total orientation is given by  $f = \delta(\theta - \pi/2)$ . The situation is shown in Fig. 2, [18]. At any light dosage, an intermediate distribution in thermodynamic equilibrium in the new oriented state will be established. Obviously this distribution can be related to the anisotropic dichroism or birefringence of the PA film. This dichroism can be measured and is related to the order parameter and related to  $f(\theta)$ . We shall make use of the induced order parameter as a measure of this effect of photo-orientation in the azo-dyes.

The physics describing the rotational diffusion process is given by the diffusion equation [18]

$$\frac{\partial^2 f}{\partial \theta^2} + \frac{\partial}{\partial \theta} \left( f \frac{\partial \Phi}{\partial \theta} \right) = \frac{1}{D} \frac{\partial f}{\partial t} \quad (1)$$

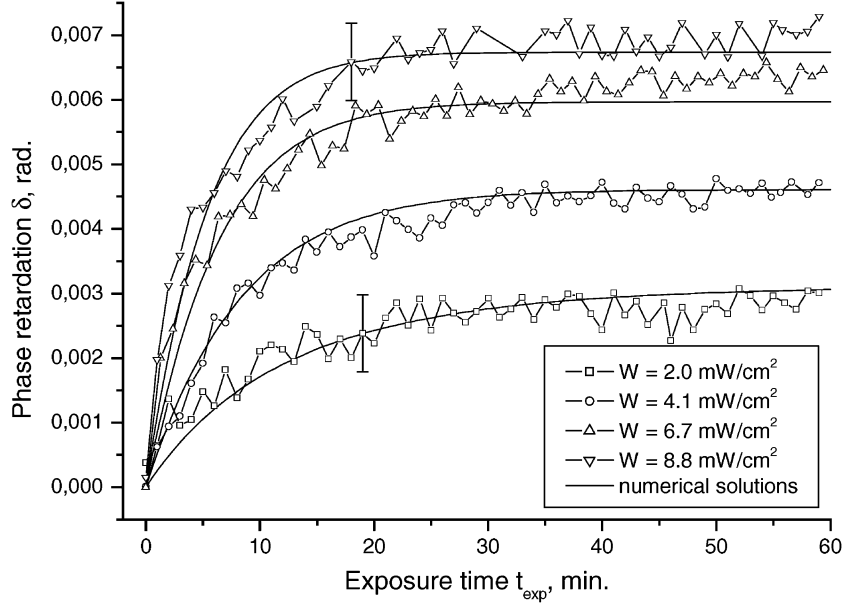


Fig. 3. The photo-induced birefringence  $\delta$  of the azodye SD-1, as a function of the exposure time for different exposure powers. The experimental data is in agreement with the calculations according to the model of Brownian rotatory diffusion of azo-dye molecules under the action of polarized light (solid lines) [18].

where  $D$  is the diffusion coefficient and  $\Phi$  is the light-molecule interaction potential given by

$$\Phi = \frac{I\alpha V_M \tau}{2kT} \cos^2 \theta = A \cos^2 \theta \quad (2)$$

where  $I$  ( $\text{W}/\text{cm}^2$ ) is the light power,  $\alpha$  ( $1/\text{cm}$ )—the absorption coefficient,  $V_M$ —the molecular volume,  $T$ —absolute temperature and  $k$ —Boltzmann constant. The parameter  $\tau$  is the relaxation time—the time of “cooling” of azo-dye molecule and its surroundings. During this time  $\tau$  the azo-dye molecule absorbs the energy of light, overcomes the potential barrier between two orientational states when it interacts with its surroundings, and then “cooled down” to the new state [18].

The order parameter is determined as the thermodynamic average  $\langle P_2 \rangle$

$$\langle P_2 \rangle = \int_0^\pi P_2(\theta) f(\theta, t) \sin \theta d\theta \quad (3)$$

where

$$P_2(\theta) = \frac{1}{2}(3 \cos^2 \theta - 1). \quad (4)$$

This model has been verified by several experiments. Fig. 3 shows the measured retardation of the PA film as a function of exposure time together with the theoretical fits. Since the retardation of the film is directly proportional to the order parameter  $P_2$ , this results directly confirms the diffusion model, and gives the diffusion coefficient at the same time.

One immediate question about the diffusion model is that if the alignment of the azo-dye molecules is induced by the linearly polarized light, will the alignment be randomized by thermal motion after the light is taken off? The answer is actually quite intriguing. It turns out that one should include intermolecular interaction in the diffusion (1).

Physically, one can imagine that if the molecules are all lined up, it is quite difficult for them to randomize again. This is similar to the case of amorphous crystal structure versus a perfect crystal structure (e.g., a-Si and c-Si). The perfect crystalline state is actually more stable. It takes energy or additional entropy to randomize the crystalline structure. Mathematically, this effect is taken care of by introducing an additional intermolecular potential, which is proportional to the order parameter. The total potential energy of the dye molecule is now given by

$$\Phi = \frac{1}{2kT} I \alpha V_M \tau \cos^2 \theta + a \langle P_2 \rangle P_2(\theta) \quad (5)$$

The parameter  $a$  in (5) is a phenomenological coefficient, which characterizes the molecular interaction within the azo-dye layer.

By solving the diffusion equation with this new potential, one can calculate the behavior of the order parameter after the light field is turned off. The behavior of the order parameter is given in Fig. 4. The UV light is turned off at different times. It can be seen that the retardation of the alignment film or the order parameter first drops slightly, and then remains constant. The final value of the order parameter depends on the exposure time. The solid lines in Fig. 4 are theoretical fits to the data points, which were experimentally measured. It can be seen that the theory works very well.

Experimentally, we can only measure the photo-induced birefringence  $\delta$  of the dye film. We argue that  $\delta$  is proportional to the order parameter  $S$  via  $\delta = kS$ , where  $k$  is a fixed constant [9]. The value of  $\delta$  versus exposure time  $t_{\text{exp}}$ , is measured with the high accuracy with the help of the photo-elastic modulator (PEM). The rate of the order parameter increase with the exposure time becomes higher for the higher values of the illumination power, which is in agreement with a model of Brownian rotatory diffusion of azo-dye molecules under the action of polarized light. The diffusion model of the light induced reorientation

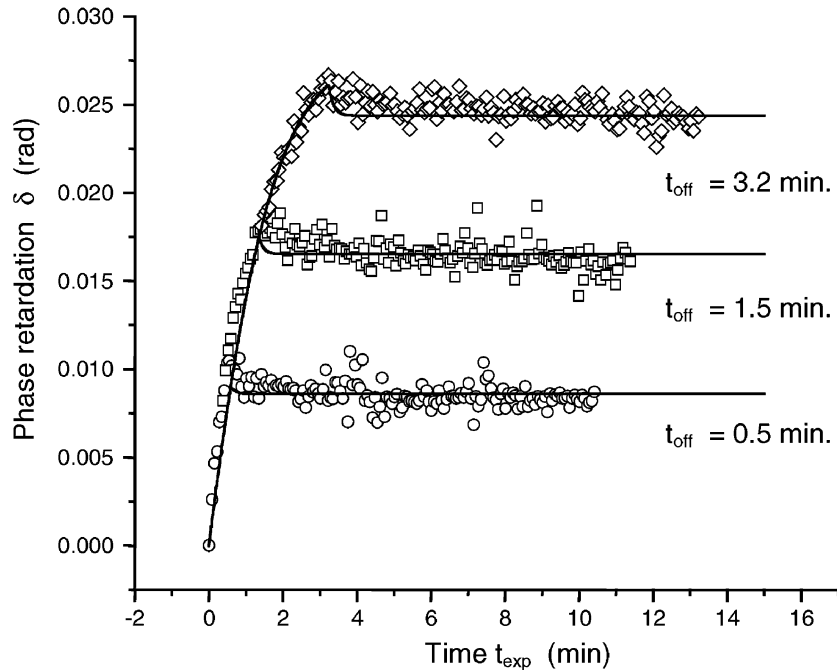


Fig. 4. The relaxation of azo-dye layer birefringence, proportional to order parameter after switching off the activated light for different exposure times  $t_{\text{off}}$  shown in Figure. The modified potential in diffusion model includes the effect of molecular interaction [18].

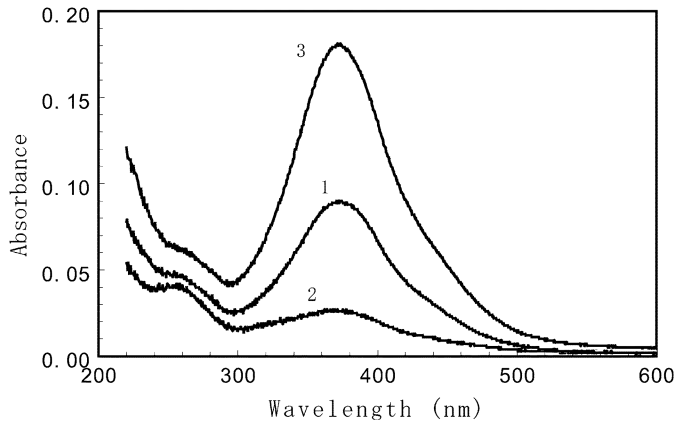


Fig. 5. Absorption spectra of SD-1 layer before the polarized UV exposure (curve 1). Curves 2 and 3 show the polarized absorption spectra after the exposure by a polarized UV light in the direction parallel ( $D_{\parallel}$ ) and perpendicular ( $D_{\perp}$ ) to the activating light polarization accordingly [10].

of azo-dye molecules is in a good agreement with experimental data as shown in Figs. 3 and 4.

Fig. 5 shows the polarized absorption spectra (absorbance or optical density) before (curve 1) and after (curves 2 and 3) the UV irradiation. 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. 5) while that one with orthogonal polarization direction ( $D_{\perp}$ ) increases (curve 3, Fig. 5). The evolution of the polarized absorption spectra after UV-illumination does not reveal any noticeable contribution of photochemical reactions [10], as the average absorption

$$D_{\text{ave}} = (D_{\parallel} + 2D_{\perp})/3 \quad (6)$$

remains the same for any fixed value of the exposure time, Fig. 5. The order parameter  $S$  of the azo-dye chromophores can be expressed as [9]

$$S = (D_{\parallel} - D_{\perp})/(D_{\parallel} + 2D_{\perp}) \quad (7)$$

where  $D_{\parallel}$  and  $D_{\perp}$  are absorption (optical density) of parallel and orthogonal polarized light to the polarization of the activated UV light. The order parameter  $S$  of SD1 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.

### III. LC SURFACE INTERACTION IN A PHOTO-ALIGNED CELL

Usually the azimuthal anchoring energy of photo-aligning materials is rather small (about 1 to  $7 \times 10^{-6}$  J/m<sup>2</sup>), which is about an order of magnitude smaller than the value obtained by the rubbing method [19]–[23]. A perfect quality homogeneous alignment was obtained on polyimide films, but a relatively high energy of illumination ( $\approx 7$  J/cm<sup>2</sup>) was needed to get the required maximum order parameter [7]. If the illumination energy ( $\lambda = 257$  nm) exceeds 7 J/cm<sup>2</sup>, the alignment became loose and soon monodomain LC alignment was not induced in accordance with the origin of the photochemical mechanism of photo-alignment.

We studied the LC aligning properties of the azo-dyes. As mentioned above, the alignment mechanism is that of photo-induced orientational ordering. The light-induced alignment should lock in place due to intermolecular interaction even when the light is switched off, as shown in Fig. 4. In practice, however, it is more stable to use another polymer network to “fix” the dye molecules. Thus the best process is to employ SD1 dye mixed with some polymer precursors. After PA, a heat treatment is afforded to polymerize the backbone so that the

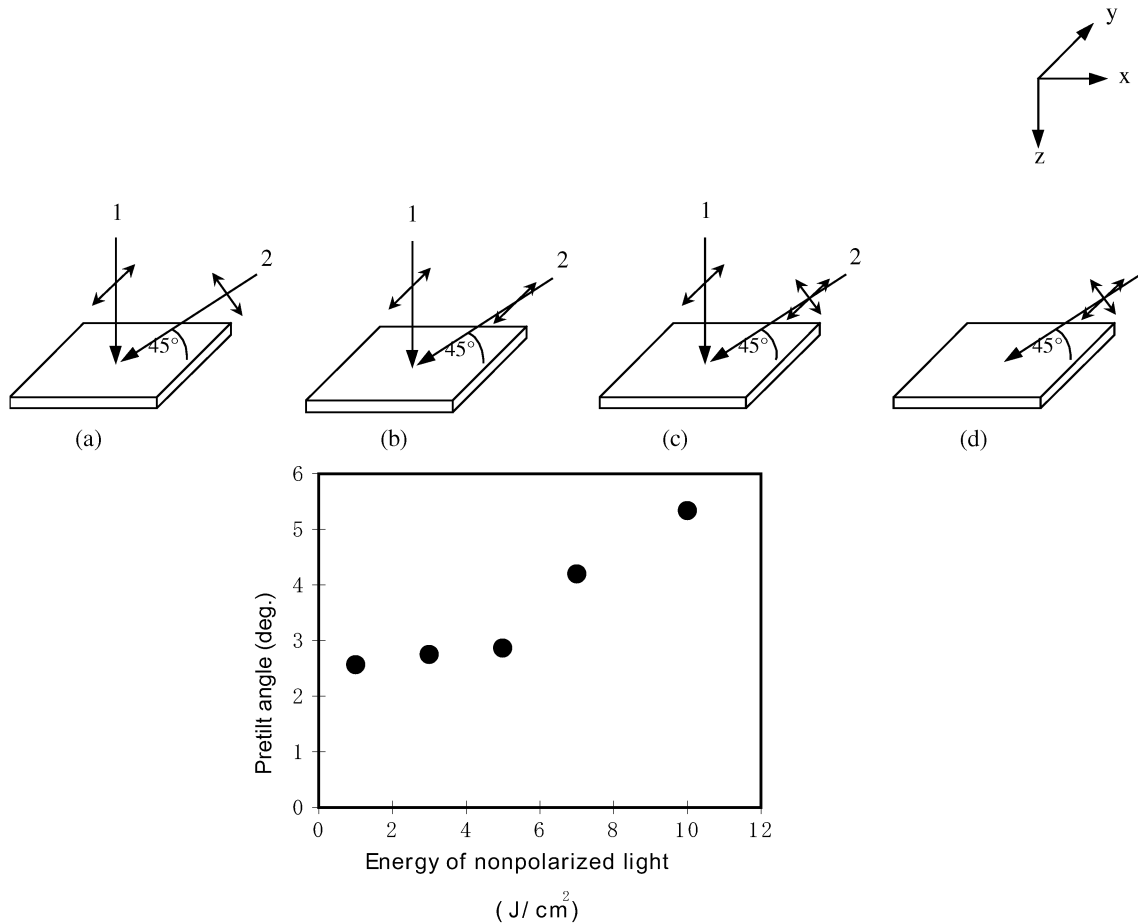


Fig. 6. (Top) Various methods of UV light irradiation to attain the pretilt angle of LC layer on the photo-aligned film. The activated UV light propagates in  $xz$  plane at an oblique angle with the substrate  $\theta = 45^\circ$ . (Bottom) Dependence of the pretilt angle on the energy density of the obliquely irradiated nonpolarized light after the irradiation of vertical polarized light (case c, above) with the energy density of  $10 \text{ J/cm}^2$  [10].

dye molecules are truly locked in place. The data to be reported here were obtained by this procedure.

We have measured various properties of the alignment film and the corresponding LC cells [10], [11], [22]. First, the temperature stability was checked. The temperature stable pretilt angle of  $5.3^\circ$  was obtained by a two-step exposure of azo-dye film using normally incident polarized light followed by oblique nonpolarized light (Fig. 6). The pretilt angle was temperature stable and does not change after heating the sample up to  $100^\circ\text{C}$  for 2 h.

The azimuthal anchoring energy  $W_\varphi$  of a photo-aligned substrate was measured [22]. It was found that the anchoring energy was very high and  $>10^{-4} \text{ J/m}^2$ , which is the same as the anchoring of the rubbed polyimide (PI) layer. As a comparison, in photo-polymerized azo-dye layers, the azimuthal and polar anchoring energies were about  $1.5 \cdot 10^{-5} \text{ J/m}^2$  and  $3 \cdot 10^{-4} \text{ J/m}^2$  for the exposure dose less than  $1 \text{ J/cm}^2$ . Thus the reorientation effect can provide very strong anchoring. This is probably due to the large order parameter that can be achieved with this process. Most of the dye molecules participate in this alignment process, versus perhaps a small fraction in photo-polymerization.

The value of VHR was also measured. The measured values for the photo-aligned LC cell ( $>99\%$  at  $80^\circ\text{C}$ ) and residual DC voltage ( $<50 \text{ mV}$ ) was found to be even better than those for rubbed PI layers. This implies that the azo-dyes studied can be

applied as aligning layers in active matrix liquid crystal displays (AM-LCDs). The thermal stability of the photo-aligned azo-dye layers is sufficiently high (up to  $200^\circ\text{C}$ ), while UV-stability is also improved by polymerization. The quality of a photo-aligned TN cell and the corresponding temperature dependence of transmission-voltage characteristics are shown by the cell in Figs. 7 and 8. Small difference in threshold voltages in Fig. 7 can be referred to the experimental errors. Our latest results show, that polymerized azo-dye layers can tolerate the temperature up to  $250^\circ\text{C}$  for 2 h, while nonpolymerized azo-dye layers exhibit the irreversible degradation of LC orientation. The dose of UV irradiation of  $175 \text{ MJ/m}^2$  from Xe lamp does not destroy LC alignment on polymerized azo-dye layers. At the same time nonpolarized azo-dyes cannot keep the stable LC alignment in this case.

#### IV. EFFECT OF PROCESSING CONDITIONS

One consequence of the diffusion nature of our PA material is that temperature and other environmental effects become quite important. We found that the sensitivity or the light dosage required for producing alignment can change by an order of magnitude by varying the environmental conditions during the PA process. Table I summarizes the results for several processing conditions. It can be seen that the effect of humidity is quite strong.

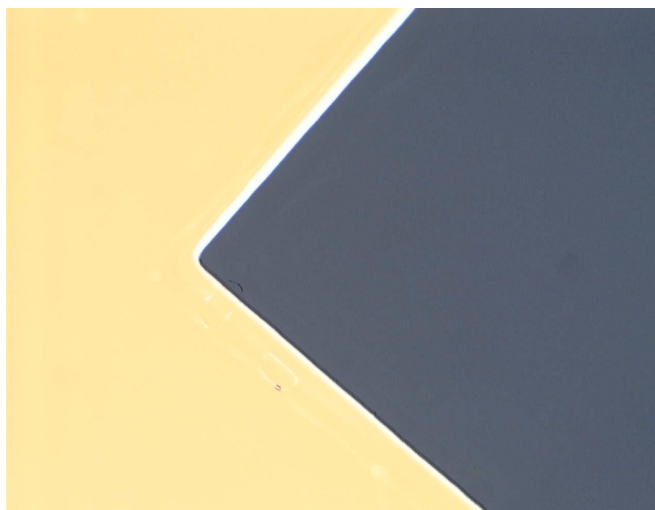


Fig. 7. Polarized microscope photograph of LC alignment on photoaligned polymerized azo-dye film [18]. The size of the picture is 1 mm<sup>2</sup>. Both homogeneous and twist LC alignment looks perfect between crossed polarizers as black and yellow regions. (Color version available online at <http://ieeexplore.ieee.org>.)

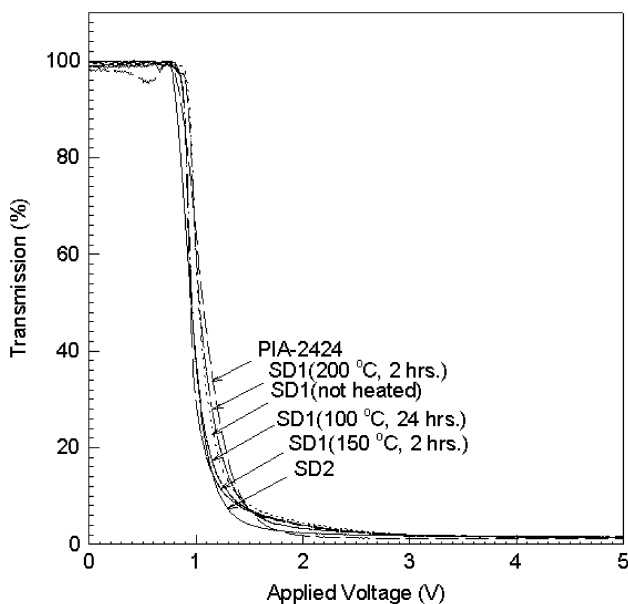


Fig. 8. Comparison of transmission—voltage curves for 90° twisted nematic LC cell (TN-LC) based on photo-aligned azo-dyes (SD1 and SD2 films) and rubbed polyimide PI 2424 layer. Heating the cell up to 100 °C, 150 °C, and 200 °C during 2 h does not have any effect to the transmission-voltage (TVC) curve. The contrast ratio remains considerably high (>70 : 1) [10], [18].

Physically, the result can be easily understood. The presence of foreign molecules inside the azo-dye film can affect greatly the ease of rotational diffusion during the PA process. In particular, moisture inside the solid film is detrimental to rotational reorientation due to the polar nature of water molecules. In the standard PA procedure, the alignment layer is first soft baked to drive out most, but not all of the solvents. SD1 is highly hygroscopic. It can thus absorb moisture, which will affect the PA process by providing much resistance to the rotational motion.

We also examined the effect of light intensity on the PA process. The idea is to see if there is any nonlinear effect so that a higher power light source will require less light dosage. Fig. 9 shows the results. It can be seen that the order parameter

TABLE I  
DEPENDENCE OF POLAR ANCHORING ENERGY OF SD1 ON DIFFERENT UV EXPOSURE ENVIRONMENT. TOTAL DOSAGE IS 50 mJ/cm<sup>2</sup> FOR ALL CASES

Exposure Environment	Alignment	Polar Anchoring Energy (J/m <sup>2</sup> )
Air (80% humidity)	Bad	NA
Air (50% humidity)	Good	3.5 × 10 <sup>-4</sup>
Nitrogen (0% humidity)	Good	3.8 × 10 <sup>-4</sup>
Vacuum (100 mTorr)	Good	3.6 × 10 <sup>-4</sup>

obtained is dependent only on the light dosage in J/cm<sup>2</sup>. In other words, it does not matter if the light intensity is high and the exposure time is short, or if the light intensity is low and the exposure time is long. Thus in actual applications, it is desirable to save processing time by having high intensity light sources. From Fig. 9, it can be seen that the order parameter is significant even at very low light dosages of less than 50 mJ/cm<sup>2</sup>. Experimentally, we found that indeed even with a light dosage of 50 mJ/cm, perfect alignment can be achieved in the LC cell. This is very important in applications since large sheets of glass have to be processed in a short time. As well, in roll to roll processing of retardation films, photo-alignment can also be applied using this method.

Another processing condition that we studied was the thickness of the alignment layer. The azo-dye can be used to align the LC even at very small thicknesses. We measured the anchoring energy of the PA layer as a function of the layer thickness. Fig. 10 shows the results. It was found that even a 1-nm thick layer (almost a monolayer) could produce alignment. However, the anchoring energy was reduced by a factor of two.

The results can be understood by noting that the film with a thickness of 1 nm may not be continuous. In fact it should be in the form of islands. Thus the coverage of the substrate is not perfect leading to weaker alignment effects. However, alignment of LC does not require a continuous film due to the tendency of the LC molecules to align themselves to minimize elastic deformation energy. The result is that there is still alignment of the LC by the discontinuous layer but the anchoring energy is reduced. Fig. 10 points to the fact that the alignment is a surface effect. Once a continuous film is obtained, LC alignment can be achieved with good anchoring properties. This is another supporting fact that the azo-dyes are good agents for PA.

## V. APPLICATIONS

### A. Photo-Aligning of Ferroelectric LC

PA of ferroelectric LCD (FLC) is ideal since FLC is very sensitive to surface treatment conditions. PA is much better than rubbing as the latter will introduce RDC on the alignment layer. The first paper on FLC photo-alignment describes the polyvinyl-alcohol layer doped with azodye [24]. A hybrid of linearly photopolymerized photoalignment (LPP) with liquid

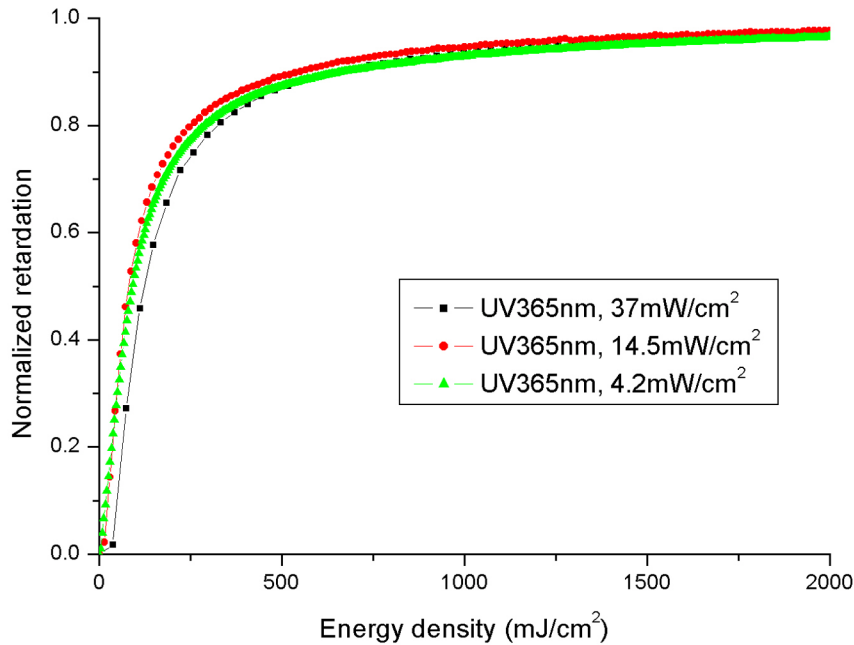


Fig. 9. Retardation of the alignment layer as a function of UV dosage, at various peak intensities. (Color version available online at <http://ieeexplore.ieee.org>.)

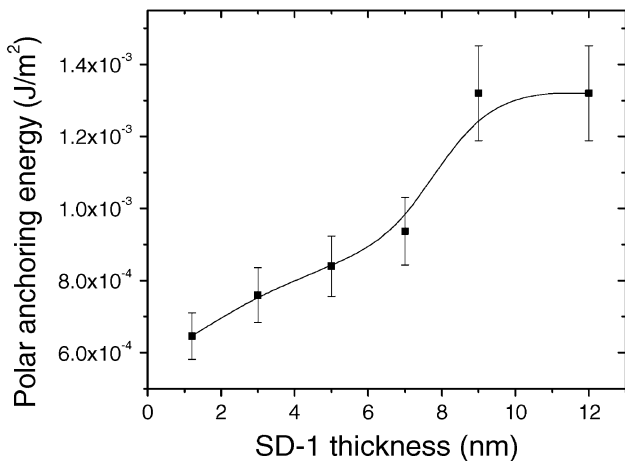


Fig. 10. LC polar anchoring energy as a function of the thickness of SD-1 photoaligning layer.

crystal polymer (LCP) layers provides a very good alignment of deformed helix ferroelectric (DHF) FLC with the contrast ratio more than 200:1 as well as the electrooptical response time less than 200  $\mu\text{s}$  [25]. PA proves to be useful also for Polymer-Stabilized V-Shape and Half-V-Shaped ferroelectric displays due to a low operation voltage and defect-free alignment [26].

A remarkable property of azo-dye aligning layers gives a good chance to provide a high photoalignment quality of FLC using the azo-dye layer. The photo-aligned FLC cell appeared to be better than prepared by buffing, if the UV-irradiation time of the azo-dye layer is high enough [27]. The bistability switching was perfect and steady, bistability degradation was not observed. Moreover, the multiplexing ability, which is necessary for a passively addressed FLC display cell operation was also observed, due to existence of a certain threshold of FLC switching,  $V_{\text{th}} \approx 0.6$  V. The FLC row addressing response time of  $\tau \approx 100$   $\mu\text{s}$  at the voltage pulse amplitude of

$U = \pm 15$  V was demonstrated [27], [28]. Large FLC cell gaps of 5  $\mu\text{m}$  and 7  $\mu\text{m}$  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 (Fig. 11). A prototype of passively addressed  $64 \times 64$  FLC display based on the PA technique has been developed with bistable switching in the multiplex driving regime [28].

#### B. Photo-Aligning of Vertical Aligned Nematic (VAN) Mode

VAN-LCD has become very popular for LCD TV applications because of the high contrast and wide viewing angle it affords. Vertical photo-alignment has been attempted. Photodegradation of the commercially available polyimide aligning materials [29] or crosslinking of photo-polymers [30] during the exposure of obliquely incident unpolarized light is believed to be the main processes responsible for vertical alignment. Recently, a high pretilt angle from homeotropic LC configuration was obtained by *in situ* photoalignment method [31]. However, notwithstanding the efforts the VAN-LCDs 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 drawbacks. In experiment [32] 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



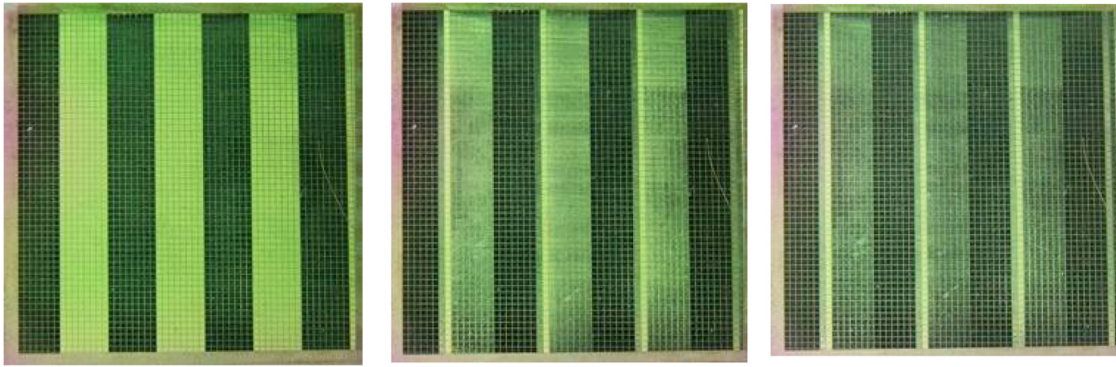


Fig. 11. Photo-aligned  $64 \times 64$  FLC display obtained after optimization in multiplexing driving regime, with a memorized gray scale. (Color version available online at <http://ieeexplore.ieee.org>.)



Fig. 12. Photo-aligned 9-digit reflective passive matrix TN-LCD on plastic substrates [37].

homeotropic state with some pretilt angle. The measured value of the pretilt angle from the homeotropic alignment was about  $1.4^\circ$ , which is higher than in other photo-aligned VAN LC cell ( $0.53^\circ$ ).

While the pretilt angle is adequate, the response time needs to be studied as well. The response times of photo-aligned and conventional rubbing VAN LCD were measured. The results indicate almost no change, with  $\tau_{\text{on}} + \tau_{\text{off}} = 7.8 \text{ ms} + 9 \text{ ms}$  for the former and  $\tau_{\text{on}} + \tau_{\text{off}} = 8.1 \text{ ms} + 8.9 \text{ ms}$  for the latter. 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  $\text{VHR} = 98\%$ ) testify to this point. The measured value of the contrast ratio between “off” and “on” states in all the cases exceeds 1000:1 in the monochromatic light ( $\lambda = 632.8 \text{ nm}$ ). Recently a reliable pretilt angle of more than  $1^\circ$  from homeotropic LC alignment was obtained using the mixture of homeotropic PI and photopolymerized azo-dye SDA-2 [11]. Thus it is concluded that azo-dyes are suitable for the alignment of VA-LCD.

### C. Photo-Aligned Bistable $\pi$ -BTN Display

The high pretilt angle, made by photo-aligning was demonstrated recently to enable bistable switching with inherent long term optical memory in  $2p$ -BTN (bistable twist nematic) cell [33]. Meanwhile, the bistability of  $p$ -BTN is based on asymmetric anchoring of the LC cell [34], [35]. Recently, we fabricated truly bistable  $p$ -BTN display, based on photoaligning technology [36]. The strong anchoring surface was achieved by the usual rubbed polyimide (PI) layer. Such PI layer provides a strong polar anchoring energy of  $1.5 \times 10^{-3} \text{ J/m}^2$ . We found that the polar anchoring energy of photo-polymerized azo-dye SDA-1 (SDA-2) can be adjusted to  $1.5\text{--}2.8 \cdot 10^{-4} \text{ J/m}^2$ , while

azimuthal anchoring to  $3.6\text{--}5.6 \cdot 10^{-5} \text{ J/m}^2$  by changing the exposure time, which was suitable for obtaining  $p$ -BTN bistability by surface anchoring breaking. The  $p$ -BTN LCD was switched between  $-22.5^\circ$  and  $157.5^\circ$ , exhibiting a high contrast ratio ( $\text{CR} > 140$ ) and wide viewing angle [36].

### D. Photo-Aligned Nematic Displays on Plastic Substrates

We have also investigated the properties of azo-dye alignment on plastic substrates [37]. Excellent alignment with a high anchoring energy was achieved with the exposure energy less than  $1.5 \text{ J/cm}^2$ , which corresponds to the azimuthal anchoring energy  $> 10^{-4} \text{ J/m}^2$ . The LC pretilt angle of about  $5^\circ$  on the plastic substrate was made by a double exposure method (Fig. 6). To demonstrate the alignment quality on plastic substrates a 9-digit reflective passive matrix TN-LCD was fabricated (Fig. 12). To maintain a uniform cell gap of  $8 \mu\text{m}$  (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.

## VI. CONCLUSION

In this paper, we have briefly reviewed a new photo-aligning technology based on photo-induced reorientation of dye molecules. We have shown that basic optical studies are consistent with the notion that the dye molecules reorient themselves in the potential field generated by the light and are held in place by their intermolecular potentials. We have also pointed out that the processing condition can be quite important, with a minimum sensitivity of  $50 \text{ mJ/cm}^2$  possible under the best conditions. This is highly desirable for manufacturing.

As well, we considered the temperature and UV-stability of such LC PA with a sufficiently high pretilt angle, large VHR and low RDC. The possibility to use this new photo-aligning layer for FLC, VAN-LCD,  $p$ -BTN LCD, and TN-LCD on plastic substrates has been also demonstrated.

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