

## P-124: Properties of Azo-Dye Alignment Layer on Plastic Substrates

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### Abstract

The alignment properties of the azo dye photo-alignment material SD-1/SDA-2 on plastic substrates are investigated. Excellent alignment with high anchoring energy can be achieved with a polarized UV dose less than  $1.0 \text{ J/cm}^2$ . A reflective 6-digit flexible passive matrix driven TN-LCD for smart card applications showing excellent electro-optical properties is demonstrated.

### 1. Introduction

Today there is an increasing demand for flexible LCD's in many applications such as mobile phones, smart cards and integrated displays [1]. Compared to traditional glass LCD's, flexible displays manufactured with plastic substrates have the advantage of being thin, lightweight and more mechanically robust. They also offer a clear advantage in design, since it allows integration into devices of non-rectangular and curved nature. If the aimed application is smart cards, the display should withstand frequent bending. Two of the most challenging steps in the manufacturing of flexible displays are the low process temperature and the spacer technology required for the display to maintain a constant cellgap during bending.

The photo-alignment technology for the alignment of liquid crystal molecules has lately gathered much attention because of its advantages over the rubbing of polyimide coatings and several different approaches for the realization of photo-alignment have been presented [2, 3]. Common for all methods is that anisotropy in the alignment layer is provided by exposing linearly polarized UV light to a photosensitive material. Due to its non-contact nature, photo-alignment eliminates generation of dust and electrostatic charges. The possibility of multi-domain patterning for wide viewing angle LCD's is another advantage. From another point of view, it is also interesting because of its low process temperature and therefore suitable in the manufacturing of flexible LCD's with plastic substrates. The maximum temperature in the photo-alignment process is determined by the evaporation of the solvent used for the alignment material and eventual polymerization required of the molecules. This temperature is usually not more than  $150^\circ\text{C}$  and hence compatible with most plastic substrates and should be compared with the corresponding temperature required for the imidization of the traditional polyimide alignment layer, which is usually between  $180$  and  $240^\circ\text{C}$  and in many cases too high for plastic substrates.

It has previously been shown that azo dye films can be used as materials for photo-alignment [4]. In this study, we investigate the alignment properties of the SD-1/SDA-2 azo dye mixture and for the first time use it in conjugation with plastic substrates. The azo dye SD-1, which chemical structure is shown in Fig.1, is proved to be photochemically stable and having a pure reorientation of the molecular oscillator perpendicular to the polarization plane of the activating UV light, without any cis-trans isomerization process [5]. This response to polarized UV light of the azo dye

film can be described by the diffusion model [6]. When an azo dye molecule is pumped by a polarized beam of light, the probability of reorientation is proportional to the square of cosine  $\theta$ , the angle between the absorption oscillator of the azo dye molecules and the polarization direction of the UV light.

In order to improve the alignment stability and sensitivity to moisture, the SD-1 material is used together with its derivate SDA-2 with polymerizable terminal groups. The optimal UV exposure dose required for the SD-1/SDA-2 layer is determined by measuring both azimuthal and polar anchoring energy of the alignment layer-nematic liquid crystal interface as a function of the polarized UV dose. Results are achieved for both plastic and reference glass substrates. Also, the possibility to generate and control the pretilt angle by varying the exposure conditions is investigated. To demonstrate the SD-1/SDA-2 alignment layer on plastic substrates, a reflective 6-digit flexible passive matrix driven TN-LCD is manufactured. Its electro-optical properties, such as contrast ratio and switching times, are evaluated. This display can find several applications, for example as the display in smart cards.

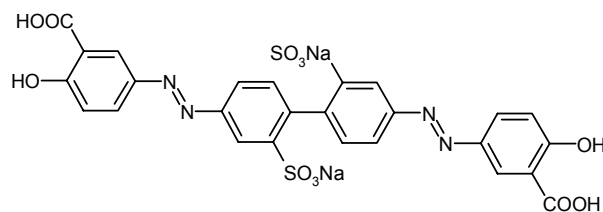


Figure 1. Chemical structure of SD-1.

### 2. Order parameter

A 40:60 mixture of SD-1/SDA-2 was dissolved in DMF to 1% together with the heat initiator V65 required for the polymerization process of the SDA-2. The amount of V65 was 2% in relation to SDA-2. To investigate the response of the polarized UV light exposure, a thin ( $\sim 10 \text{ nm}$ ) film of the mixture was spin-coated at 800 rpm for 5 seconds followed by 3000 rpm for 30 seconds to a quartz substrate and absorption spectra was recorded for light polarized parallel and perpendicular to the direction of the activating polarized UV light used to align the azo dye molecules, respectively. Before exposure, the azo dye layer is completely isotropic and the absorption of the film is independent of the polarization plane of the light used in the measurements, see Fig.2. After UV exposure, the absorption of light with its polarization plane parallel to the polarization of the activating UV

light decreases, while the corresponding absorption of perpendicular polarized light increases.

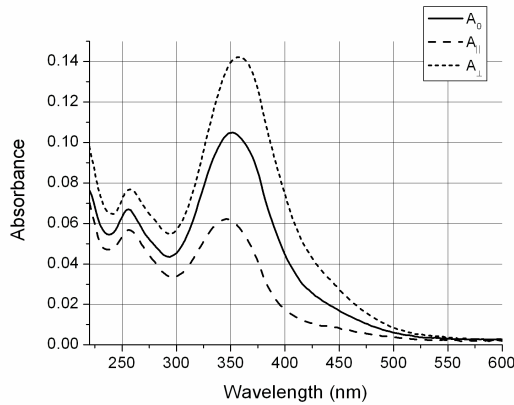


Figure 2. Absorption spectra of the SD-1/SDA-2 film before ( $A_0$ ) and after ( $A_{||}$  and  $A_{\perp}$ ) polarized UV exposure dose of  $7.5 \text{ J/cm}^2$ .

The order parameter  $S$  of the azo dye film is calculated according to [7]:

$$S = (A_{||} - A_{\perp}) / (A_{||} + 2A_{\perp}) \quad (1)$$

where  $A_{||}$  and  $A_{\perp}$  are the absorption parallel and perpendicular to the activating polarized UV light, respectively. The UV exposure dose was varied from 0 to  $20 \text{ J/cm}^2$  by varying the exposure time of an  $8.3 \text{ mW/cm}^2$  light source. The relation between the order parameter and the UV exposure dose is shown in Fig.3. It is found that the absolute value of the order parameter increases rapidly with increasing UV exposure dose and approaches saturation.

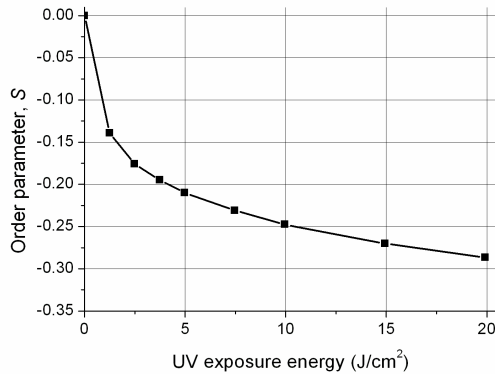


Figure 3. Order parameter of the SD-1/SDA-2 film as a function of the polarized UV exposure dose.

### 3. Anchoring energy

To investigate the relation between the order parameter and the alignment properties of nematic liquid crystals on the film, various LC-cells were fabricated. The ITO coated flexible PES substrates was washed in detergent in ultrasonic bath, dried and

then exposed to UV/O<sub>3</sub>. The 40:60 SD-1/SDA-2 mixture with V65 was spin-coated to the PES substrates at 800 rpm for 5 seconds followed by 3000 rpm for 30 seconds. The solvent was evaporated before the azo dye film was exposed, at normal incidence, to the polarized UV light source causing the reorientation of the azo dye molecules and the corresponding anisotropy in the film required for the alignment of liquid crystals. After the exposure, the film was polymerized in nitrogen environment at  $150^\circ\text{C}$  for 1 hour.

The azimuthal anchoring energy  $W_a$  of the azo dye film-nematic liquid crystal interface was measured by assembling two substrates with the exposure directions  $80^\circ$  to each other. The cells were filled with the commercial active matrix nematic liquid crystal mixture MLC-9000-100 (Merck), which material parameters are shown in table 1.

Table 1. Material parameters of liquid crystal mixture MLC-9000-100 (Merck).

$n_o$	1.4851	$K_{11}$	11.3
$n_e$	1.5988	$K_{22}$	6.1
$\epsilon_{\perp}$	4.2	$K_{33}$	14.3
$\epsilon_{  }$	12.4		

Only if the anchoring is sufficient strong will the resulting twist angle be equal to  $80^\circ$ . The twist angle of  $\sim 5 \mu\text{m}$  cells with various exposure doses was measured and the corresponding azimuthal anchoring energy was calculated from the torque balance equation for cells with symmetrical boundary conditions [8]:

$$W_a = \frac{2K_{22}\phi}{d \sin(\phi_0 - \phi)} \quad (2)$$

where  $K_{22}$  is the twist elastic constant of the liquid crystal material,  $d$  is the cellgap,  $\phi_0$  is the assumed ( $80^\circ$ ) and  $\phi$  is the measured twist angle. The dependence of azimuthal anchoring energy on the exposure dose is shown in Fig. 4. For exposure doses larger than  $1.0 \text{ J/cm}^2$ , the twist angle was measured close to  $79^\circ$ , corresponding to an anchoring energy of  $\sim 1.4 \cdot 10^{-4} \text{ J/m}^2$ . This value is fully comparable with the strong anchoring shown by rubbed polyimide alignment layers. For lower exposure doses, the anchoring energy drops and for doses less than  $0.25 \text{ J/cm}^2$  the quality of the alignment is insufficient.

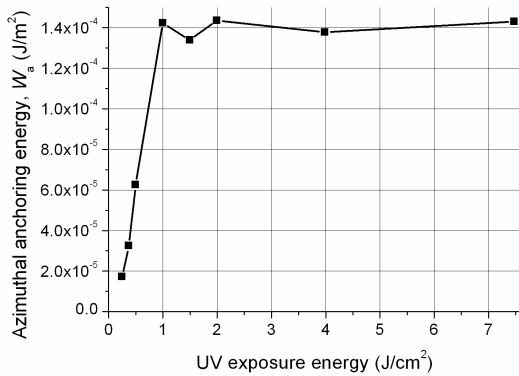


Figure 4. Azimuthal anchoring energy  $W_a$  as a function of the polarized UV exposure dose.

To measure the polar anchoring energy  $W_p$  of the alignment film-liquid crystal interface, the simplified high electric field technique (HEFT) was used [9]. Thick (~40 μm) antiparallel cells were fabricated and filled with MLC-9000-100. The optical retardation  $R$ , induced by the cell, inversely proportional to the applied voltage  $V$  (30 kHz AC), was measured and plotted as a function of the applied voltage inverted. Least square fitting was performed and the extrapolation length  $d_e$  is given from the intersection with the ordinate axis. The polar anchoring energy is then calculated from the extrapolation length according to:

$$W_p = \frac{K_{11} \sin^2 \theta_e + K_{33} \cos^2 \theta_e}{d_e} \quad (3)$$

where  $K_{11}$  and  $K_{33}$  are splay and bend elastic constant of the liquid crystal material, respectively and  $\theta_e$  is the pretilt angle. It was found that the behavior of the polar anchoring energy with respect to the UV exposure dose is similar to that of the azimuthal anchoring energy and saturation is reached at a value of  $\sim 8 \cdot 10^{-4}$  J/m<sup>2</sup>.

#### 4. Pretilt angle

When the substrates are illuminated at normal incidence, there is no pretilt angle defined. In order to generate a pretilt angle, oblique exposure is needed. Two different methods are studied. In the first one the substrate is illuminated with oblique S-polarized light at 45° angle of incidence. In the second, a two-step exposure is performed. First the substrates are exposed to polarized UV light at normal incidence, aligning the randomly oriented molecules, followed by a second oblique unpolarized exposure, causing the pretilt angle of the liquid crystal molecules. To investigate the pretilt angle generation, thick (~40 μm) anti-parallel cells, filled with the liquid crystal, with various exposure conditions were fabricated and the pretilt angle was measured using the conventional crystal rotation method [10]. The one-step exposure induced pretilt angles up to 1.4°, while the two-step method could give larger pretilt angles up to 2.4°, see Fig.5. The pretilt angle was temperature stable and did not change after heating the sample to 100°C for 10 minutes.

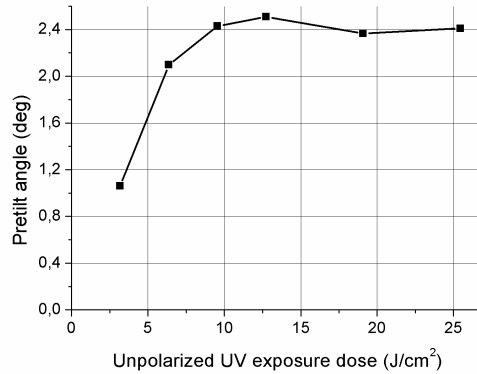


Figure 5. Pretilt angle as a function of the second, oblique unpolarized UV exposure dose.

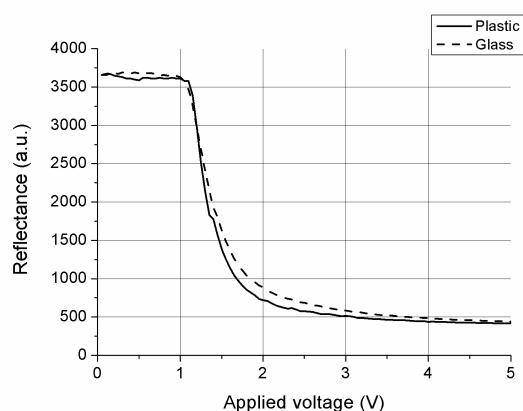
#### 5. Smart-card demonstrator

To demonstrate the alignment layer quality on plastic substrates, a 6-digit reflective passive matrix driven flexible TN-LCD was fabricated. To maintain a uniform cellgap during bending of the display, semi-dry adhesive spacers were chosen. The liquid crystal mixture MLC-6809-000 (Merck) was used in order to operate at the second Gooch & Tarry condition for an 8 μm cellgap. The display prototype was exposed to mechanical testing according to the ISO/IEC 10373-1:1998(E) standard, a test method for identification cards. After 1000 cycles of dynamic and torsional bending stress no noticeable change in the alignment quality or cell gap of the tested displays could be observed, hence the prototypes have the same performance after the mechanical bending tests required for smart cards. Figure 6 shows the display mounted into a smart card prototype.

The reflectance as a function of applied voltage was measured for both the plastic cell and glass reference cell, see Fig.7. The curves are similar and show good reflective contrast (8:1) at normal incidence. This is a consequence of the extremely good LC alignment achieved on both plastic and glass substrates.

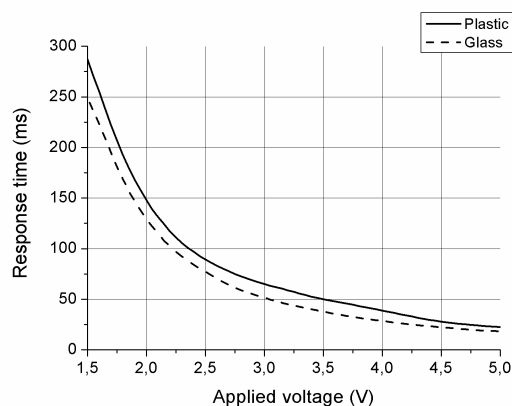


Figure 6. Reflective flexible TN-LCD with SD-1/SDA-2 alignment layer mounted in smart card prototype.

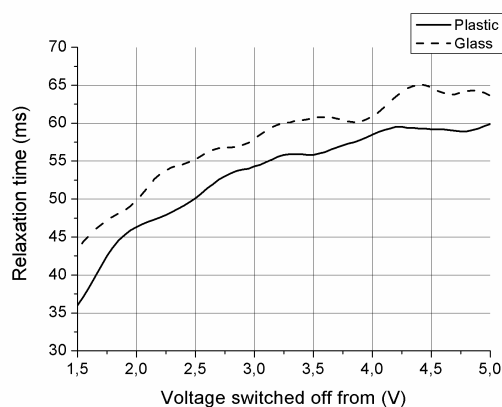


**Figure 7. Comparison of reflectance-voltage curves for the flexible demonstrator and a glass reference, respectively.**

The corresponding switching times were also studied and the results are shown in Figs.8 and 9, respectively.



**Figure 8. Response time as a function of applied voltage for the flexible demonstrator and a glass reference, respectively.**



**Figure 9. Relaxation time as a function of the voltage switched off from for the flexible demonstrator and a glass reference, respectively.**

## 6. Conclusions

In this study we have investigated the alignment properties of the azo dye SD-1/SDA-2 mixture on both plastic PES and conventional glass substrates. The results on plastic substrates are in agreement of those achieved using the glass substrates. It has been shown that excellent alignment properties can be achieved with a UV exposure of  $1.0 \text{ J/cm}^2$ , corresponding to a 2 minute exposure on the  $8.3 \text{ W/cm}^2$  lamp system used. The corresponding azimuthal anchoring energy was measured to  $\sim 1.4 \cdot 10^{-4} \text{ J/m}^2$ , fully comparable to anchoring strengths of rubbed polyimide. The polar anchoring energy for the same UV dose was found to be  $\sim 8 \cdot 10^{-4} \text{ J/m}^2$ . It was deduced that the anchoring strength reaches saturation before the saturation of the order parameter of the film occurs. Hence long exposure times are not needed in order achieved good alignment. Pretilt angles up to  $2.4^\circ$  could be generated by using a two-step exposure in which the normally incident polarized UV light is followed by a second oblique unpolarized exposure. By varying the dose and the angle of incidence of the unpolarized light, the value of the pretilt angle could be controlled. Cells fabricated with the SD-1/SDA-2 alignment layer shows excellent alignment quality and electro-optical properties, both on plastic and glass substrates. In conclusion, by manufacturing the flexible TN-LCD we have demonstrated that the SD-1/SDA-2 alignment layer is a most suitable choice of alignment material when working with plastic substrates.

## 7. Acknowledgements

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## 8. References

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