

## Director gliding on photoaligning surfaces

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### Abstract

*Photoaligning polymers usually possess “soft” surface, containing flexible groups and provide relatively small anchoring energy ( $W < 10^{-2}$  erg  $cm^{-2}$ ). In this case field-induced reorientation of director on the aligning surface is essential. We have shown that surface director reorientation can modify the aligning surface and result in gliding of the axis of easy orientation of LC. This phenomena together with adsorption/desorption of ions in electric field cause strong sticking effect in LCDs photoaligning materials. We proposed a method of decreasing of the sticking effect based on irradiation of the photoaligning surface by an unpolarized light.*

### 1. Objectives and Background

Appearance of a residual image of the previous frame at LCD screen is called the sticking effect. In the case of regular rubbed polyimide films, the sticking effect is mainly caused by accumulation of electric charges near the orienting surfaces. In this case the anchoring energy of LC on the orienting surfaces is usually strong ( $W > 10^{-2}$  erg\* $cm^{-2}$ ) and the surface is “rigid” [1,2]. Therefore, electric field does not reorient director at the surface, and the anchoring (anchoring energy value,  $W$  and easy axis direction,  $\vec{e}$ ) remains constant during the application of the field to the cell. On the contrary, photoaligning polymers possess “soft” surface, containing flexible groups and typically provide low anchoring energy ( $W < 10^{-2}$  erg\* $cm^{-2}$ ) [3-6]. This may cause an appearance of the sticking effect at photoaligning surfaces. In our previous work, we

have shown that due to low anchoring energy the reorientation of the director on photoaligning surface is essential and causes realignment of flexible fragments of the polymer, i.e. the modification of the aligning surface [6]. It leads to the change of the easy axis orientation during the field application to the LC cell. The process of LC molecules surface adsorption/desorption was also shown to make a contribution into such an effect [7]. *The drift of an easy axis caused by external action is called an easy axis gliding.* The time of recovery of the initial anchoring parameters could last tens of minutes bringing out a sticking effect. Moreover, such a modification of a soft surface could even be an irreversible one, i.e. the final direction of the easy axis would differ from its initial orientation after the external field cut off. *Memory of liquid crystal alignment on external action is known as “memory effect”.*

Here we report on a study of gliding and memory effects in cinnamol-based photoaligning materials in respect to the sticking effect. We propose a method of essential decrease of the sticking effect based on irradiation of the photoaligning surface with an unpolarized light.

### 2. Results

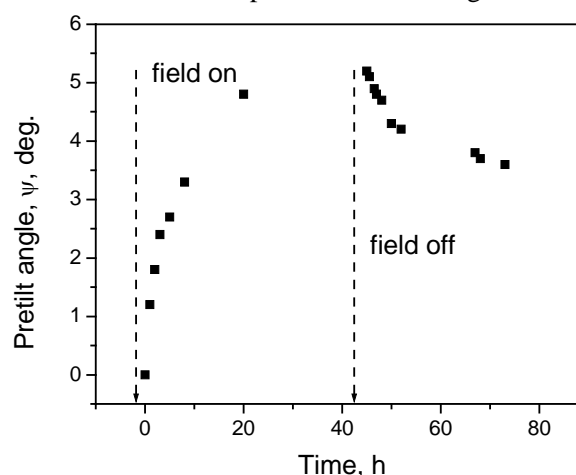
We have used cinnamoil-based photoaligning materials in our experiments. These materials consist of either polyvinylalcohol- or cellulose- main chains and photosensitive *flexible* side groups on a base of cinnamic acid. In particular, polyvinyl-4(fluorocinnamate) (PVCN-F), cellulose-4-

pentylloxycinnamate (PG<sup>1</sup>) and cellulose-3(4-propenyloxy)cinnamate (PG-1) were studied. The basic photochemical process resulting in aligning properties of these materials is a cross-linking of flexible cinnamoyl side polymer groups [8]. Due to a strong absorption dichroism of cinnamoyl groups, irradiation of the photoaligning polymer with polarized UV-light results in anisotropic angular distributions of the crossed-linked cinnamoyl groups and the remaining cinnamoyl fragments producing easy orientation axis. PVCN-F, PG and PG-1 provide excellent homogeneous alignment of most commercial LCs and LC mixtures for TN mode in the temperature range of a mesophase. PVCN-F is characterized by UV exposure controllable anchoring energy,  $W$ , in the range  $10^{-4} - 10^{-3} \text{ erg}\cdot\text{cm}^{-2}$ . PG and PG-1 are the thermostable analogs of PVCN-F, which keep their aligning properties up to (150 - 200) °C. These materials possess rather strong anchoring energy, which amounts to  $10^{-1} \text{ erg}\cdot\text{cm}^{-2}$ .

We have investigated the gliding and memory effect both in azimuthal and polar planes. The polar reorientation of the director was explored in a symmetrical cells with photoaligning polymer layers filled with a LC 5CB. To achieve a strong electric field, we used rather thin gap,  $L = 2.7 \mu\text{m}$ , between the substrates covered with photoaligning materials. We applied an *ac*-voltage ( $\nu = 20 \text{ kHz}$ ) with different amplitudes (5 V, 10 V and 20 V) to the cells during several tens of hours. The field was temporarily (for measuring period) switched off for about 5 minutes and the pretilt angle,  $\psi$ , of the LC director on the polymer surface was measured using an electro-optic technique [9]. This chosen time interval for measuring was much larger than the bulk relaxation time (a few milliseconds).

We have observed a very slow drift of an easy axis (gliding) under electric field action and its relaxation after the field removal. The amplitude of the gliding (the deviation,  $\Delta\psi$ , from the initial value  $\psi_0 = 0$ ) depended both on the applied voltage and the duration of treatment. The dependence of the easy axis gliding on time of the voltage treatment for  $U = 10 \text{ V}$  is presented in Figure 1. At  $U = 10 \text{ V}$  notable change of  $\psi_0$  appears after 1h of the voltage application and achieves a quasi-stationary value

$\Delta\psi = 5.5^\circ$  in 45 hours. The asymptotic value  $\Delta\psi$  increased with the amplitude of the curing field.



**Figure 1. The dependence of the easy axis polar gliding on time of voltage treatment for  $U = 10 \text{ V}$**

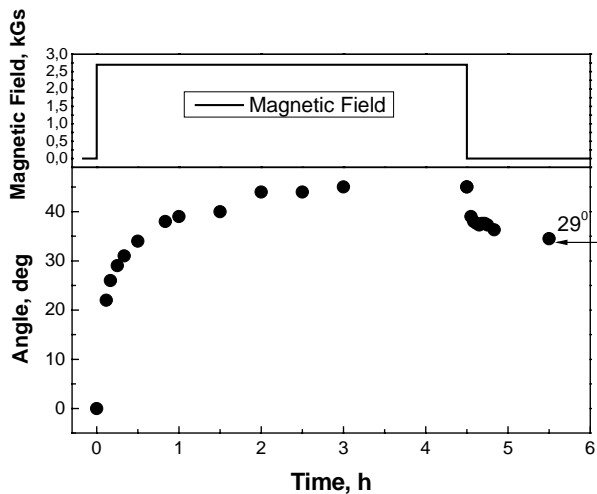
The switching off the voltage resulted in extremely slow relaxation of the easy axis toward its initial direction. We could not measure complete relaxation even after 40 days. This absence of a full recovery of the easy axis after the field switching off is related to the surface memory and is a characteristic of the memory effect.

As one can see, the typical gliding characteristic time is of the order of a few hours both in field on and off, six to eight orders of magnitude longer than the bulk or elastic reorientation times. We associate super-long characteristics times with a mutual interaction of the LC director with a soft photoaligning surface that results in a slow collective reorientation of both LC molecules and flexible polymer fragments in the electric field.

Analogous gliding of the easy axis and effective memory effect was observed during reorientation of the director in the azimuthal plane of the symmetrical cell with photoaligning polymer layers and LC 5CB. The cell ( $L = 50 \mu\text{m}$ ) was put between the poles of a magnet, which field  $H = 2.7 \text{ kGs}$  made an angle  $45^\circ$  with the director of LC. The dependence of the easy axis gliding in azimuthal plane on time of the magnetic treatment is presented in Figure 2. One can see that the characteristic times of the gliding are shorter than observed for director reorientation in the polar plane. We associate this difference with the differing values of the polar and

<sup>1</sup> Material was synthesized by I.Gerus.

anchoring energy on the photoaligning surface.



**Figure 2.** Dependence of the easy axis azimuthal gliding on time of magnetic treatment.

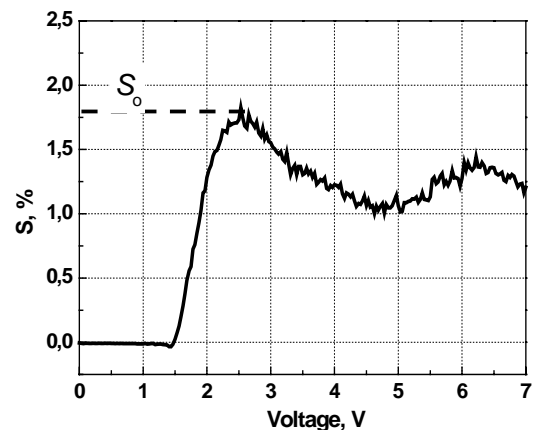
Thus, the described results demonstrate the evident gliding and memory effects in photoaligning materials. These effects result in modification of the aligning surface during the surface director reorientation and lead to a strong sticking. To overcome the sticking effect means to find a way to harden the photoaligning surface suppressing the mobility of the flexible groups on it. We proposed a method of the surface hardening based on irradiation of the photoaligning surface by an unpolarized light.

As it was noted above, the basic photochemical process resulting in aligning properties of the studied photoaligning materials is a cross-linking of flexible cinnamoyl side polymer groups. Usually the cross-linking efficiency is small; less than 15% of cinnamoyl moieties undergo cross-linking during irradiation with polarized UV light. It is reasonable to suggest that the rest of flexible cinnamoyl groups provide main contribution to the gliding of the easy axis and the memory effect. To decrease a flexibility of these fragments, we used additional illumination of the photoaligning layer with unpolarized light, which caused the cross-linking of remained cinnamoyl groups and hardens in turn the photoaligning surface. Thus, we used a two-exposure technique: the first exposure was carried out with unpolarized light during the time,  $t_{exp1}$ , and the second exposure was carried out with polarized light during the time,  $t_{exp2}$ .

The  $90^\circ$  twist cells with the photoaligning layers

were filled with LC MLC 6012 (Merck for TN-mode,  $\Delta n = n_e - n_o = 0.1$ ,  $T_c = 86^\circ\text{C}$ , and the dielectric anisotropy  $\Delta\epsilon = 8.2$ ) in the nematic phase at room temperature due to capillary effect. The samples were placed between parallel polarizers and we measured the dependence of the intensity of a testing beam of He-Ne laser on the applied voltage ( $TV$ -curve for normally black-mode). The measurements were carried out at the field frequency  $\nu = 1$  kHz.

To characterize a sticking ability of the aligning surfaces we consequently measured and compared two  $TV$ -curves for the given cell [2]. The first, reference curve,  $(TV)_{ref}$ , was obtained after the 1-min electrical shortage of the cell with no field applied. The second curve,  $(TV)_{30}$  was obtained after application to the cell the voltage  $U = 5$  V during 30 minutes. Before each measuring cycle the sample was hold at a zero external field for one minute. The relative difference between the  $TV$ -curves,  $S = (\Delta T / T) 100\%$  was caused by a sticking effect that we characterized by sticking parameter  $S_0$ , which is equal to a maximum value of  $S$  (see Figure 3).



**Figure 3.** The dependence of relative difference between the  $TV$ -curves on the applied voltage.

The characteristics of LC alignment in the cells with the PG-photoaligning substrates obtained at different values of  $t_{exp1}$  and  $t_{exp2}$  are presented in Table 1. The reproducibility of the results was about 80%. One can see that the additional exposure with unpolarized light decreases a sticking parameter for all times of the second exposure with polarized light.

$t_{exp2}$ , min →	1	3	10	30
$t_{exp1}$ , s ↓				
0	12%	9%	4-6-8%	8%
5	bad align.	< 4%	<2%	<6%
10	bad align.	7%	~4%	<6%
15	bad align.	bad align.	bad align.	bad align.

**Table 1. Sticking parameter of PG material at different exposures with polarized ( $t_{exp2}$ ) and unpolarized ( $t_{exp1}$ ) UV-light.**

The worse aligning quality and the largest sticking parameter were obtained for the traditional one-exposure technique. The best result (homogeneous alignment with the sticking parameter,  $S_0 < 2\%$ ) was obtained for the first unpolarized exposure  $t_{exp1} = 5$  s and the second oblique  $p$ -polarized irradiation during  $t_{exp2} = 10$  min.

In the Table 2 the results of the light-induced strengthening of the PVCN-F aligning layers are presented. One can see that the extremely low sticking parameters ( $< 1\%$ ) can be achieved for this material by two-exposure technique. It should be noted that the value  $S_0 < 1\%$  is better than obtained on a rubbed polyimide materials. This result shows that PVCN-F based materials remain very promising for LCD applications and further improvement of its thermostability can make this material a potential competitor of commercial polyimides.

$t_{exp2}$ min →	1,5	5	10	15
$t_{exp1}$ , s ↓				
0	3.6%	2.3%	N/A	1.0%
10	N/A	2.5%	2.3%	1.5%
30	4.0%	7.8-2,5%	2.9%	N/A
60	bad align.	0.5%	2.5%	0.2%
120	bad align.	2.0%	1.0%	0.8%

**Table 2. Sticking parameter of PVCN-F material at different exposures with polarized ( $t_{exp2}$ ) and unpolarized ( $t_{exp1}$ ) light.**

#### 4. Conclusion

We have shown that surface director reorientation modifies the surface of photoaligning materials on a

base of cinnamoil acid. It results in the gliding of the axis of easy orientation of LC. This phenomena together with adsorption/desorption of ions in electric field causes strong sticking effect in LCDs photoaligning materials. We proposed a method to decrease the sticking effect based on irradiation of the photoaligning surface with unpolarized light.

#### 5. Acknowledgements

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