

Sticking of liquid crystal on photosensitive polymer layers

I. GERUS¹, A. GLUSHCHENKO², YU. KURIOZ^{*3}, YU. REZNIKOV³,
and O. TERESHCHENKO³

¹Institute of Bioorganic Chemistry and Petrochemistry,
1 Murmanskaya Str., 03-039 Kiev, Ukraine

²Liquid Crystal Institute, Kent State University, Kent, 44240 OH, USA

³Institute of Physics, 46 Nauki Ave., 03-039 Kiev, Ukraine

The sticking effect on photoaligning surfaces was investigated. We demonstrated that additional irradiation of photoaligning polymers with cinnamoyl side groups with not-polarized UV-light strongly decreases their sticking parameter. We associate this effect with cross-linking of the flexible side-groups by UV light and, as a consequence, with light-induced strengthening of the photoaligning surface. Restriction of mobility of the flexible groups on the photoaligning surface (surface strengthening) resulted in depressing the sticking effect. The method of the decrease of the sticking effect by the light-induced strengthening is rather general, and it can be applied for any photoaligning materials undergoing a light-induced cross-linking of polymer fragments. For poly(vinyl 4-fluorocinnamate) the light-induced strengthening allowed us to get the record value of the sticking parameter, $S_0 = 0.2\%$, which is better than traditional rubbed polyimide surfaces provide. Such a value of the sticking parameter along with other aligning characteristics allows considering poly(vinyl 4-fluorocinnamate) as very prospective material for modern liquid crystal display technologies.

Keywords: liquid crystal, photoalignment, sticking effect.

1. Introduction

Appearance of a residual image of the previous frame at liquid crystal display (LCD) screen is called the sticking effect. In the case of the rubbed polyimide films, sticking effect is mainly caused by accumulation of electric charges near the oriented surfaces. In this case the anchoring energy of LC on the oriented surfaces is strong ($W > 10^{-2}$ erg/cm²) 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. In contrary, photoaligning polymers possess “soft” surface, containing flexible groups and typically provide low anchoring energy ($W < 10^{-2}$ erg/cm²) [3–6]. It can result in another origin 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 [7]. It results in a change of both easy axis and anchoring energy during the application of the field to the LC cell. The time of recovering of initial anchoring parameters can achieve tens of minutes that results in a sticking effect.

Thus, in accordance with the results of Ref. 7, the main contribution to the sticking effect comes from the modifi-

cation of the aligning surface due to the surface director re-orientation in the electric field. To overcome the sticking effect means to find a way to strengthen the photoaligning surface that restricts the mobility of the flexible groups on it. Here we propose a method of the surface strengthening based on irradiation of the photoaligning surface by an unpolarized light.

2. Materials and experimental procedure

The chemical structures of the photoaligning polymers used in our experiments are presented in Fig. 1. Poly(vinyl-4 fluorocinnamate) [PVCN-F, Fig. 1(a)] consists of a poly(vinyl alcohol) main chain and photosensitive side groups on the base of 4-fluorocinnamic acid. This material provides an excellent homogeneous alignment of most commercial LCs and LC mixtures for TN mode in the temperature range of mesophase. Overheating of the LC cell with PVCN-F aligning layers above the clear point T_c , usually results in appearance of surface defects after cooling back to the mesophase. PVCN-F is characterized by UV exposure controllable anchoring energy in the range 10^{-4} – 10^{-3} erg/cm² and the pretilt angle which value of 0–15° also depends on the exposure and geometry of UV irradiation [8,9]. Cellulose 4-pentyloxycinnamate [PG, Fig. 1(b), Ref. 10] is a thermostable analogue of PVCN-F. Enough long UV exposure allows getting a strong anchoring energy (up to 10^{-2} erg/cm²) a pretilt angle in the range

* e-mail: kurioz@iop.kiev.ua

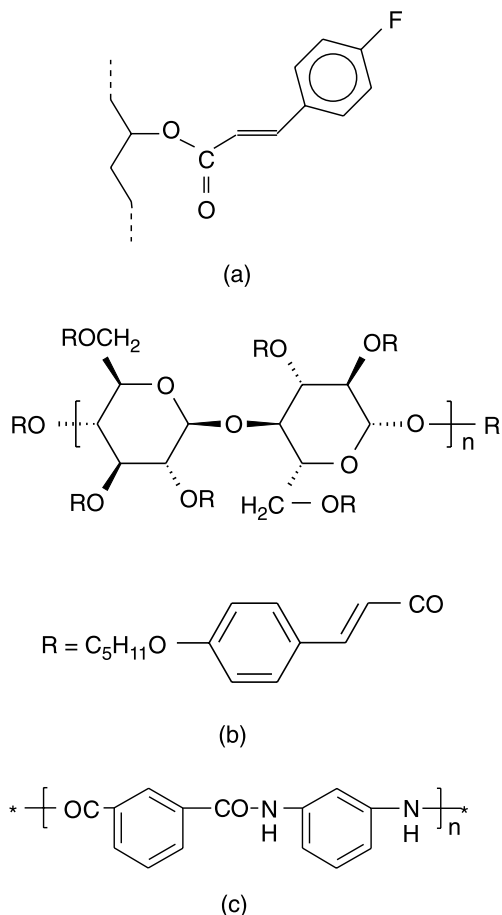


Fig. 1. Structure of photoaligning polymers: (a) PVCN-F, (b) PG, and (c) 3P.

0° – 5° . Unlike to PVCN-F, PG material not only provides an excellent alignment of commercial LC and LC mixtures in a mesophase but allows overheating of the LC above its clear point without any changes of the LC orientation after cooling back to the mesophase. Poly[N,N'-(1,3-phenylene)-isophthalamide] [3P, Fig. 1(c)] is a thermostable aligning material recently developed in our team. This material is characterized by strong anchoring energy (up to 10^{-2} erg/cm²) and provides rather small (0.8 – 1°) but very stable pretilt angle. 3P has no cross-linkable fragments and its aligning properties are provided by a photo-degradation of dichroic main polymer chains in analogue with light-induced deimidization of photoaligning polyimides [11].

The experiments were carried out with a standard 90° twist cells. The gap of the cells was adjusted by the spacer particles with diameter of 4.5 – 5 μm . The cell substrates were covered with the photoaligning layers by spin-coating of a solution of the materials spread onto glass substrates. 1,2-dichloroethane, chlorobenzene or dimethylformamide were used as solvents. The concentration of polymers were of 10 – 15 g/L. The spin-coating velocity was 7000 rpm and the spin-coating time was about 10 s that resulted in the film thickness of about 0.02 μm . After drying at (100 – 150) $^\circ\text{C}$ during 1 hour, the polymer films were illuminated by UV light of a Hg-lamp with the power of 500 W.

Homogeneous UV-light field was formed in the plane of the polymer film by a quartz condenser and a polarizing Glan-Thomson prism. The value of the light power density I_0 in the plane of polymer film was 30 mW/cm². We irradiated the films by UV light with different polarization state (*s*- and *p*-polarization or non-polarized light) at normal or oblique incidence.

The basic photochemical process resulting in aligning properties of the studied photoaligning materials is a cross-linking of flexible cinnamoyl side polymer groups [5]. Usually the cross-linking efficiency is small; less than 15% of cinnamoyl moieties undergo cross-linking during irradiation with polarized UV light. According to our model, the rest of flexible cinnamoyl groups provide main contribution to the sticking effect. To decrease a flexibility of these fragments, we used additional illumination with unpolarized light, which causes the cross-linking of remained cinnamoyl groups and in turns the strengthening of the photoaligning surface. Thus, we used 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° -twist cells with the photoaligning layers were filled LC MLC 6012 from Merck for TN-mode (optical anisotropy $\Delta n = n_e - n_o = 0.1$, $T_c = 86^\circ\text{C}$, and the dielectric anisotropy $\Delta\epsilon = 8.2$) in a 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 obtained and compared two TV-curves for the given cell [12] (see Fig. 2). The first, reference curve, $(TV)_{ref}$, was obtained after the 1 -min shortage of the cell with no field applied. The second curve, $(TV)_{30}$ was obtained after application, to the cell, the voltage

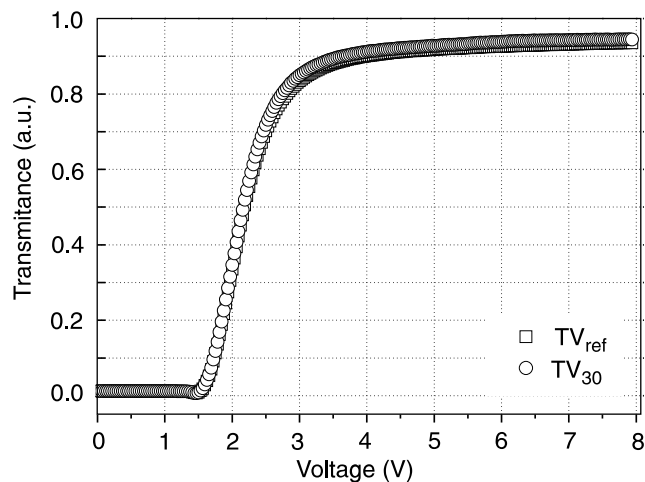


Fig. 2. Dependence of transmittance of twist cells on the applied voltage.

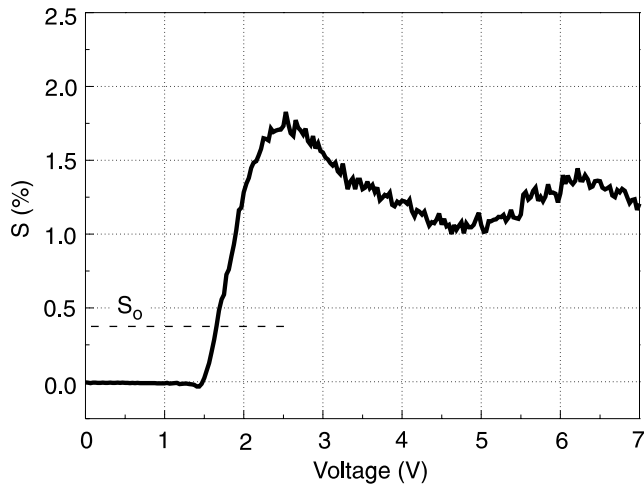


Fig. 3. Dependence of relative difference between the TV-curves on the applied voltage.

$U = 5$ V during 30 minutes. Before each measuring 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 the sticking parameter S_0 , which is equal to a maximum value of S (see Fig. 3).

3. Results and discussions

The characteristics of LC alignment in the cells with the PG-photoaligning substrates obtained at different values t_{exp2} and t_{exp1} , p -polarized light and oblique incidence (the angle between the substrates plane and the UV-beam was 45°) are presented in Table 1. The reproducibility of the results was about 80%. One can see that the additional exposure with nonpolarized light decreases a sticking parameter for all times of the second exposure with the polarized light. The worse aligning quality and the largest sticking parameter were obtained for traditional one-exposure technique. The best result (homogeneous alignment with the sticking parameter, $S_0 < 2\%$) was obtained for the first non-polarized exposure $t_{exp1} = 5$ min and the second oblique p -polarized irradiation during $t_{exp2} = 10$ min.

Table 1. Sticking parameter of the PG material at different exposures with polarized (t_{exp2}) and not-polarized (t_{exp1}) UV-light.

t_{exp2} (min)→ t_{exp1} (s) ↓	1	3	10	30
0	12%	9%	4–6–8%	8%
5	bad alignment	< 4%	< 2%	< 6%
10	bad alignment	7%	~4%	< 6%
15	bad alignment	bad alignment	bad alignment	bad alignment

In Table 2, the results of the light-induced strengthening to PVCN-F 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 in its thermostability can make this material a potential competitor of commercial polyimides.

Table 2. Sticking parameter of PVCN-F material at different exposures with polarized (t_{exp2}) and not-polarized (t_{exp1}) light.

t_{exp2} (min)→ t_{exp1} (s) ↓	1.5	3	10	30
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 alignment	0.5%	2.5%	0.2%
120	bad alignment	2.0%	1.0%	0.8%

The analogous measurements were carried out for new photoaligning material, 3P. This material has no cross-linkable fragments and its aligning properties are provided by a photo-degradation of main polymer chain. In this case the two-exposure technique is not applicable. Our results, presented in Table 3 confirm this suggestion. One can see that irradiation with not-polarized light does not decrease the sticking characteristic of 3P material.

Table 3. Sticking parameter of 3P material at different exposures with polarized (t_{exp2}) and not-polarized (t_{exp1}) light.

t_{exp2} (min)→ t_{exp1} (s) ↓	15	20	25	30
0	N/A	3.0%	3.0%	3.9%
10	5.5%	4.0%	4–7.5%	N/A
30	2–3.0%	4.9%	5.0%	0.5–12%
60	9.0%	7–11%	4.0%	5.0%

4. Conclusions

On the example of PVCN-F and PG photoaligning materials we demonstrated that additional irradiation of these polymers with not-polarized UV-light strongly decreases their sticking parameter. We associate this effect with cross-linking of flexible side-groups by UV light and, as a consequence, with light-induced strengthening of the photoaligning surface. The method of the decrease in the sticking effect by the light-induced strengthening is rather

general one and can be applied for any photoaligning materials undergoing a light-induced cross-linking of polymer fragments. For PVCN-F photoaligning material the light-induced strengthening allowed us to get the record value of the sticking parameter, $S_o = 0.2\%$, which is better than traditional rubbed PI surfaces provide. Such a value of the sticking parameter along with other aligning characteristics allows considering the PVCN-F material as the most prospective for modern liquid crystal display technologies.

Acknowledgements

The authors are very thankful to S.B. Kwon, A. Dyadyusha and A. Iljin for useful discussions. The research was partially supported by the NATO Science Fellowships National Administration in Warsaw, Poland No OPI/KA/302/2002 and INTAS Grant No 01-170.

References

1. P. Chatelain "Orientation of liquid crystal", *Bull. Soc. Franc. Miner.* **66**, 105 (1943).
2. J. Cognard, "Alignment of nematic liquid crystals and their mixtures", *Mol. Cryst. Liq. Cryst.*, Supplement, 1982.
3. W.M. Gibbons, P.J. Shannon, S.T. Sun, and B.J. Swetlin, "Surface-mediated alignment of nematic liquid crystals with polarized laser light", *Nature* **351**, 49 (1991).
4. A.G. Dyadyusha, T.Ya. Marusii, V.Yu. Reshetnyak, Yu.A. Reznikov, and A.I. Khizhnyak "Orientational effect due to change in the anisotropy of the interaction between a liquid crystal and a bounding surface", *JETP Lett.* **56**, 17–21 (1992).
5. M. Schadt, K. Schmitt, V. Kozenkov, and V. Chigrinov "Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers", *Jpn. J. Appl. Phys.* **31**, 2135 (1992).
6. D. Andrienko, A. Dyadyusha, A. Iljin, Yu. Kurioz, and Yu. Reznikov, "Measurement of azimuthal anchoring energy of nematic liquid crystal on photoaligning polymer surface", *Mol. Cryst. Liq. Cryst.* **321**, 271–281 (1998).
7. Yu. Kurioz, V. Reshetnyak, and Yu. Reznikov, "Orientation of a liquid crystal on a soft photoaligning surface", *Mol. Cryst. Liq. Cryst.* **375**, 535–541 (2002).
8. D. Andrienko, A. Dyadyusha, Yu. Kurioz, Yu. Reznikov, F. Barbet, D. Bormann, M. Warengem, and B. Khelifa, "Photoalignment of pentyl-cyanobiphenyl on the fluorinated polyvinyl-cinnamates induced by UV and visible light", *Mol. Cryst. Liq. Cryst.* **329**, 219–226 (1999).
9. L. Bugayova, I. Gerus, A. Glushchenko, A. Dyadyusha, Yu. Kurioz, V. Reshetnyak, and Yu. Reznikov, "Non-monotonic exposure dependence of the pretilt angle and surface polarity of the photo-orientant F-PVCN", *Liq. Cryst.* **29**, 209–212 (2002).
10. S. Shiyanovskii, A. Glushchenko, and Yu. Reznikov, "Tensor and complex anchoring in liquid crystals", *Phys. Rev. E* **62**, (2000).
11. D. Andrienko, Yu. Kurioz, Yu. Reznikov, M. Nishikava, and J. West. "Control of the anchoring energy on polyimide layers by irradiation of depolarized UV-light", *Jpn. J. Appl. Phys.* **39**, 1217 (2000).
12. A. Lien, "Image sticking measurement of LCDs", *SID Digest*, 203 (1997).