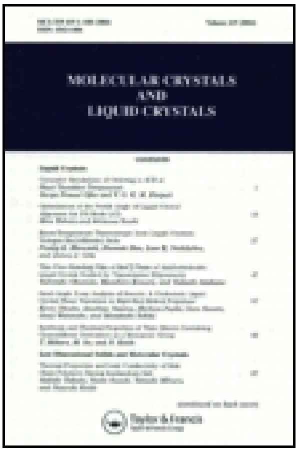

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Orientation of a Liquid Crystal on a Soft Photoaligning Surface

Yu. Kurioz [a] , V. Reshetniak [b] & Yu. Reznikov [a]

[a] Institute of Physics, National Academy of Sciences, Prospect Nauki 46, Kyiv, 03039, Ukraine

[b] Physics Faculty, Kiev Taras Shevchenko University, prospect Glushkova 6, Kiev, 03680, Ukraine

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Orientation of a Liquid Crystal on a Soft Photoaligning Surface

YU. KURIOZ[a], V. RESHETNIAK[b] and YU. REZNIKOV[a]

[a]*Institute of Physics, National Academy of Sciences, Prospect Nauki 46,*
Kyiv 03039 Ukraine and
[b]*Physics Faculty, Kiev Taras Shevchenko*
University, prospect Glushkova 6, Kiev 03680 Ukraine

In this paper, we present experimental and theoretical results dealing with soft anchoring i.e. anchoring that can be changed due to the influence of the adjacent LC bulk reoriented by strong external field. Such a change means that the magnitude forces responsible for the structure of the surface (easy axis) are less than or equal to forces of the interaction between LC molecules.

Keywords: liquid crystal; photoalignment; tilt.

INTRODUCTION

Orientation of a liquid crystal on an aligning surface is characterized by the direction of the easy axis, $\vec{e}$, and anchoring energy, W. Traditional rubbed aligning layers have a rigid surface and strong anchoring of LC ($W > 10^{-2}$ erg cm^{-2})[1,2]. Therefore, magnetic or electric field usually does not reorient director on the aligning surface, and easy axis and surface energy remain constant during the application of the field to the LC cell.

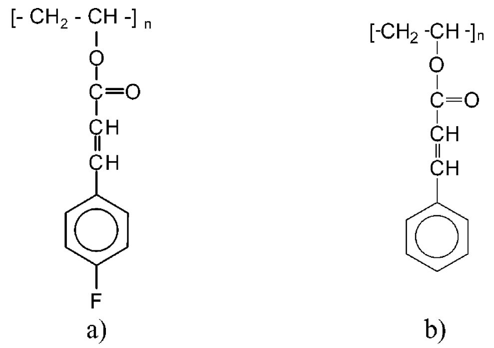
Novel aligning materials, such as photoaligning and brush-like polymers possess very soft surface, containing flexible groups and usually provide much less anchoring energy ($W < 10^{-2}$ erg cm^{-2})[3-5]. In this case the reorientation of the director on the aligning surface may be essential. Surface director reorientation can result in modification of the aligning surface, for example in realignment of flexible fragments of the polymer. Therefore, both easy axis and anchoring energy on a soft aligning layer can be changed during the application of the field to the LC cell.

In this paper we study aligning properties of a soft photosensitive surfaces of well-known photoaligning materials containing flexible side fragments. We found effect of electrically induced tilt of the director of LC on these surfaces and investigated the relaxation of the tilt after switching off external field.

MATERIALS AND EXPERIMENT

We studied aligning properties of nonfluorinated polyvinyl-cinnamate (PVCN) and para-fluorinated PVCN-F[6,7] (Fig.1). These materials consist of a polyvinyl-alcohol main chain and photosensitive side groups on the base of fluoride cinnamic acid. The appearance of an easy axis for liquid crystal alignment is due to the photo-induced crosslinking reaction between side groups under the influence of polarized UV light. Polymer films were produced by spin coating (velocity 7000 r.p.m.) of polymer solution in dichloretane (weight concentration 20 g/liter) on a glass substrate covered with ITO electrodes. The surfaces of PVCN and PVCN-F layers contain flexible cinnamoil fragments. The obtained films were annealing at 80° C for one hour to remove the solvent. After that the films were exposed with linearly polarized UV light from a Hg-lamp normally to their surfaces. The intensity of UV in the plane of the polymer film was about 60W/m^2. The exposure time t_{exp} was 5 minutes. The direction of the light-induced easy axes was perpendicular to the polarization of UV light. The anchoring energy value corresponding to this irradiation time was estimated as $W \leq 10^{-2}$ erg cm^{-2} [8].

The alignment of LC 4-4'-penthyl-cianobephenyl (5CB, EMI) was tested in a combined cells made from reference and tested surfaces and LC in between. Calibrated polymer stripes set the cell thickness L = 65 μm. The reference surface was covered with rubbed polyimide (PI) layer provided a strong planar anchoring with known pretilt angle $\theta_{ref} \approx$ 0.5°. The test surface was covered with the studied materials. The substrates with the reference and the tested surfaces were assembled so that the projections of the easy axes on the aligning surfaces were parallel. The LC-cells were filled with the liquid crystal in isotropic phase and cooled to room temperature in magnetic field 6 kGs.



a) b)

FIGURE 1. Chemical formula PCVN-F a) and PVCN b).

The cell rotation method was applied to measure the tilt of the LC on the polymer surface[9]. In this method, cell is adjusted between crossed polarizers so that the director made an angle of 45° to both their axes. The cell is rotated around the axis perpendicular to the director and the dependence of the system transparency $T(\varphi)$ of tested laser beam on the angle φ between the beam and the cell normal is measured.

The tilt angle value θ averaged over the cell thickness is estimated by the expression

$$\theta \approx \frac{\theta_{ref} + \theta_{test}}{2} \approx \frac{\Delta\varphi}{n_e + n_o} \qquad (1)$$

Here θ_{ref} and θ_{test} are the pretilt angles on the reference and test surfaces, $\Delta\varphi$ is the shift of the symmetry axis of the curve $T(\varphi)$ about the point $T(\varphi = 0)$, n_o and $n_{\hat{a}}$ are the refractive indexes of 5CB for ordinary and extraordinary light waves, respectively. The knowledge of the values of θ and θ_{ref} enables us to calculate the value of pretilt angle near the test surface.

The tilt angle θ_{test} was measured after a day after the cell filling. The first measurement was carried out without electric field applied and zero tilt was obtained. Then we applied the electric field (10 V, 100 Hz) to the cell during 30 minute. After that we switched the field off and measured the tilt each 2 minutes. The every measurement took up about 1 min.

The results are depicted in Fig.2. They show that the electric field produces the tilted alignment of the LC on both PVCN ($\theta_{test} \geq 2^{o}$)

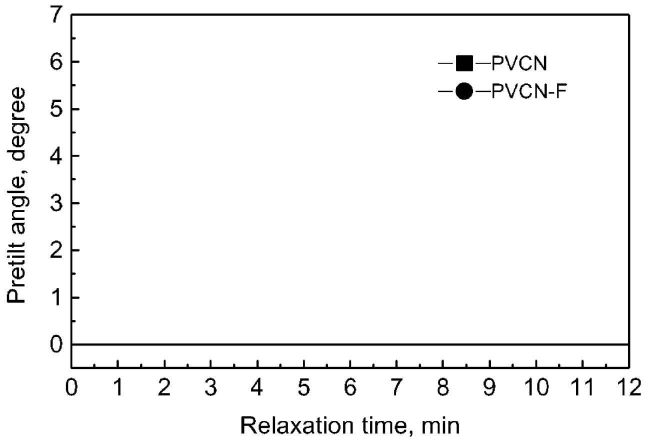


FIGURE 2. Tilt angle *vs* time after electric field application.

and PVCN-F ($\theta_{test} \geq 6^{o}$). The measurements in the symmetric cell with two PI surfaces did not show any changes in the initial value $\theta_{test} \approx 0.5^{o}$ after the electric field application[*]. Electrically induced tilt on PVCN-F surface $\theta_s = 6.5^{o}$ relaxed to the initial zero value within $\tau_s \approx 10$ min. PVCN surface revealed less tilt ($\theta_s = 1.5^{o}$) that after $\tau_s \approx 2$ minutes also relaxed to zero.

DISCUSSION

Our results clearly demonstrate a modification of the polyvinyl-cinnamate containing surfaces in electric field. Indeed, at the characteristic values of anchoring energy of these surfaces, $W \leq 5\ 10^{-4}$ - 10^{-2} erg cm^{-2} the anchoring parameter $\xi = WL/K$ is in the range 5-100 (L = 65 ìm, $K = 6.65{*}10^{-12}$ N). In this case the strong anchoring approximation is valid, and the relaxation time of the director should

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[*] Because the minute is required to measure the tilt, the data obtained correspond to some average value of the tilt, which could change during the measurements.

have been estimated by the formula $\tau_v \approx \frac{\gamma L^2}{\pi K} \approx 10^{-1}$ s (γ is orientational volume viscosity of LC). Huge discrepancy of this value with the observed values $\tau \approx 10$ min and $\tau \approx 2$ min can be explained if one suggests that electric field somehow changes the interaction between LC and aligning surface. Since we did not find a tilted alignment of LC after application of the field to the *empty cell* before filling with LC, it is very doubtful that direct action of the field can modify the polymer surface. At the same type reorientation of LC near aligning surface by electric or magnetic field can realign flexible fragments on the polymer[10]. Therefore, we suggest that the electrically induced tilt is a consequence of strong interaction between LC molecules and the flexible fragments of the soft polymer surface and the weak anchoring energy of the surface. Owing to the weak anchoring, the electric field reorients the director on the polymer surface, which in turn, rearranges the flexible fragments of the polymer surface. As a result, electric field orients both LC molecules and flexible fragments in the direction, which is determined by the anchoring parameter and LC – flexible fragments interaction.

The relaxation of the tilted LC to the initial planar state on the soft aligning surface should drastically differ from the relaxation of the tilt on the rigid surface. In opposite to the case of a rigid surface this process involves a collective reorientation both of LC molecules and flexible polymer groups. This collective behavior results in a decrease of the relaxation time and can be phenomenologically described by anomalously high surface viscosity of LC on a soft aligning surface.

Consider LC sandwiched between two aligning surfaces at distance L. Let LC anchoring with the reference surface be infinitely strong and easy axis makes angle $\theta_{ref,0}$ with the OX axis (OZ axis coincides with the normal to the cell walls). The anchoring energy and easy axis direction at the test plate are W and $\theta_{test,0}$ respectively. If the characteristic time of director relaxation in the cell volume, τ_v, is much shorter than characteristic time of the surface relaxation, the director in the volume follows its reorientation at the surface and the angle $\theta(z,t)$ satisfies the equation

$$\frac{d^2\theta}{dz^2} = 0 \qquad (2)$$

with the boundary conditions

$$\begin{aligned} &\theta(L)=\theta_{ref,0} \\ &-K\theta'(0,t)+W\left(\theta(0,t)-\theta_{test,0}\right)=\gamma_s\frac{\partial\theta(0,t)}{\partial t} \end{aligned} \qquad (3)$$

where γ_s is the surface viscosity[11].

The solution of (2) – (3) takes the form

$$\theta(z,t)=\theta_{ref,0}+\left(C\exp(-t/\tau_s)+\frac{\xi\left(\theta_{ref,0}-\theta_{test,0}\right)}{1+\xi}\right)\frac{z-L}{L}, \qquad (4)$$

where $\tau_s=\frac{\gamma_s L}{K(1+\xi)}$, constant C is determined by the director deviation θ_E at $t=0$, that is when the applied electric field was switched off, $C=\theta_{ref,0}-\theta_E-\frac{\xi\left(\theta_{ref,0}-\theta_{test,0}\right)}{1+\xi}$.

Tilt angle at the test surface is given by

$$\theta(0,t)=\theta_{ref,0}-\left(C\exp(-t/\tau_s)+\frac{\xi\left(\theta_{ref,0}-\theta_{test,0}\right)}{1+\xi}\right) \qquad (5)$$

Using our experimental data for $ô_s$, L, and K, and assuming that $\xi=1$ one can get $\gamma_s \approx 2.5\ 10^{-5}$ kg s^{-1} for PVCN-F, and the value γ_s for PVCN in one order less.

It should be noted that the interface layer of LC molecules and polymer flexible fragments could be rather stable. If it is, it is possible to suggest that the electrically induced tilted alignment is characterized by new direction of the easy axis and new value of the anchoring energy. It this case the origin of the slow relaxation of the tilt may be interpreted as a consequence of the time dependence of the anchoring on soft aligning surface.

CONCLUSIONS

To describe the director reorientation on the soft aligning surface we propose either to consider the interface containing LC molecules and flexible fragments of the aligning layer as a LC with effectively high orientation viscosity or to suppose time dependent anchoring energy and easy axis on the soft aligning surface. In the first case LC in cell with a soft aligning layers may be described as LC possessing anomaly high surface viscosity γ_s, anchoring energy and easy axis of the LC are supposed to be constant. Microscopic mechanism of soft alignment could be the same for both models and connected with collective reorientation both LC molecules and flexible polymer fragments in electric field.

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