Formation and dynamics of easy orientation axis in magnetic field on PVCN-F surface

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We describe the experiments on a magnetically-induced drift of the easy axis on a soft surface of photoaligning material fluoro-polyvinyl-cinnamate. We found unexpected partial relaxation of the drift of the easy axis after switching the magnetic field off. This relaxation cannot be explained in a framework of the existing models and requires additional assumptions about the drift process. We propose a model that explains the experimental data suggesting elastic-like behaviour of the polymer fragments during the drift of the easy axis.

Keywords: liquid crystal, easy axis, gliding, drift of easy axis, photoalignment.

1. Introduction

Traditional description of reorientation of a LC director in electric or magnetic field assumes a fixed position of the easy orientation axis $\vec{e}$ on the aligning surfaces of a cell [1]. At the same time, field-induced deviation of the director $\vec{d}$ near the surfaces from the direction $\vec{e}$ due to a finite anchoring may result in a gradual drift of the easy axis out of its initial position (so-called, gliding effect) [28]. The adsorption/desorption of LC molecules on/from the aligning surface and cooperative reorientation of polymer fragments and LC molecules are considered as possible mechanisms of a gliding effect. The adsorption/desorption (AD) mechanism was proposed by Vetter *et al*. [2] for description of the gliding effect on polyvinyl-alcohol surface (in our knowledge it was the first observation of the drift of an easy axis). According to Vetter, drift of the easy axis is caused by rotation of the symmetry axes of the distribution function of the adsorbed LC molecules under the influence of a reorientation torque. It is suggested that the adsorbed molecules are oriented preferably along the initial direction of director in the cell. Application of the torque reorients the director nearby the surface that leads to the adsorption of molecules along this new direction. As a consequence, the symmetry axes of the angular distribution function of the adsorbed molecules reorients as well as the associated easy axis.

The model of cooperative reorientation of the director and polymer fragments was proposed first by Kurioz *et al*. [5] for explanation of unexpectedly slow relaxation of the director in the zenithal plane after application of electric

field to the cell with a soft polymer surface. It was suggested that due to the weak anchoring, the electric field reorients the director on the polymer surface, which, in turn, drags the flexible polymer fragments. As a result, electric field orients both LC molecules and flexible fragments in the direction that results in a drift of the easy axis. Later on, Janossy [6] explained the drift of the easy axis in the azimuthal plane over a soft polymer surface in a similar way. His interpretation of the azimuthal gliding is based on the assumption that the polymer main chains can undergo conformational transitions under the influence of the anisotropic potential of the liquid crystal. The change of the director position at the surface initiates conformational changes in the polymer and as a result, the easy axis rotates towards the director. This rotation decreases the anchoring torque and the director can rotate further towards the external field, resulting in the drift of the easy axis. The cooperative model is supported by the fact that the drift of the easy axis speeds up when the temperature of glass-like transition in the polymer is approached.

The microscopic description of the gliding effect in the terms of the rotation of the angular distribution function of the LC molecules adsorbed on the surface was developed in Refs. 7 and 8. It should be noted that both, the model of the adsorption/desorption and the cooperative model are described by the same equations in the approach of Refs. 7 and 8 and the difference is just in the physical meaning of these equations and values of microscopic parameters. The situation gets even more complicated since a drift of the easy axis can be observed both on rigid inorganic surfaces [4] with no flexible surface fragments and on soft polymer surfaces. One can suggest that the only adsorption/desorption mechanism governs the drift of the easy axis on the

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rigid surface and both mechanisms contribute to the gliding effect on a soft polymer surface.

In the present paper we describe the experiments on a magnetically-induced drift of the easy axis on a soft surface of photoaligning material fluoro-polyvinyl-cinnamate. We found unexpected partial relaxation of the drift of the easy axis after switching the magnetic field off. This relaxation cannot be explained in a framework of the existing models and requires additional assumptions about the drift process. We propose a model that explains the experimental data suggesting elastic-like behaviour of the polymer fragments during the drift of the easy axis.

2. Material and experiment technique

We studied a drift of the easy orientation axis of the liquid crystal pentyl-ciano-bephenyl (5CB, Merk) in a symmetric cell with the thickness $L = 50$ μm. The cells were made from two glass substrates which inner surfaces were covered with photoaligning material fluoro-polyvinyl-cinnamate (PVCN-F) [9]. Irradiation of this material by UV light results in cross-linking of the cinnamoile side fragments of the polymer chain [10] that prevents a swelling of the polymer layer due to penetration of LC molecules [11]. The PVCN-F film was irradiated with no-polarized UV light from a Hg-lamp ($I_{UV} \approx 10$ mW/cm^2) with different exposure time, $t_{exp} = 0.5$–3 min. The cells were filled with the LC by capillarity at the elevated temperature $t \sim 60°C$ in isotropic phase and then was cooled down to the room temperature in a magnetic field, $H = 0.3$ Tl. Since the PVCN-F surface produces very small but not-zero pretilt of LC we slightly tilted the cell with respect to the $\vec{H}$-field during the cooling. The angle between $\vec{H}$-field and plane of the cell was about $\beta \approx 10°$ during the cell cooling. The tilted orientation of the cell during the cooling removed the degeneracy between parallel and anti-parallel director distribution in the cell and results in a parallel director distribution. The magnetic treatment resulted in a good quality homogeneous planar alignment of LC along the projection of the H-field on the plane of the cell (pretilt angle, $\theta_0 < 1°$). The homogeneous easy axis orientation after the cooling of the cell in the magnetic field is due to the adsorption of the LC molecules on the PVCN surface [8]. Orientation of the LC molecules by the field during the cooling of the cell results in anisotropic angular distribution of the adsorbed molecules with the maximum parallel to the projection of the H-field on the cell plane. This anisotropically oriented adsorbed layer serves as aligning coating and control the easy orientation axis. To get the equilibrium alignment, we kept the cell during 60 min between the magnetic poles as it is. After that the cell was tilted to set the angle $\beta = 0°$ and then the cell was rotated for $\varphi_0 = 45°$ around normal from $\vec{H}$. In this geometry the elastic torque causes the reorientation of the director $\vec{d}$ both in the LC bulk and near the aligning surfaces toward to the magnetic field. To measure the reorientation of the director in the cell, we placed two
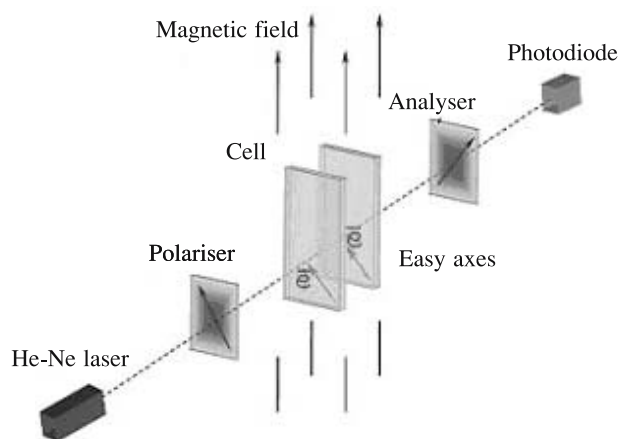

Fig. 1. Setup of the experiment.

polarizers on each side of the cell and probed the direction of the director on both substrates by circularly polarized He-Ne laser beam rotating the polarizers (Fig. 1). Since the Mauguin regime was valid in our case, the position of the director on the substrates can be determined by rotation of the polarizers till the blackpoint.

3. Experimental results and a model

Application of the magnetic field resulted in reorientation of the director on the both substrates for the same angle $\varphi_{S1,2}(t)$. The dependence of the reorientation angle $\varphi_S(t)$ on time is presented in Fig. 2 by squares. We found a quick director reorientation on the surfaces after turning the magnetic field on. We associate this fast director response with a bulk magneto-induced torque that reorients the director on the surface due to a weak anchoring energy. The characteristic time of this process t_v is shorter than the characteristic time of the setting time t_H of the magnetic field, $t_H \sim 5$ s. During the time t_v, equilibrium between the bulk torque of
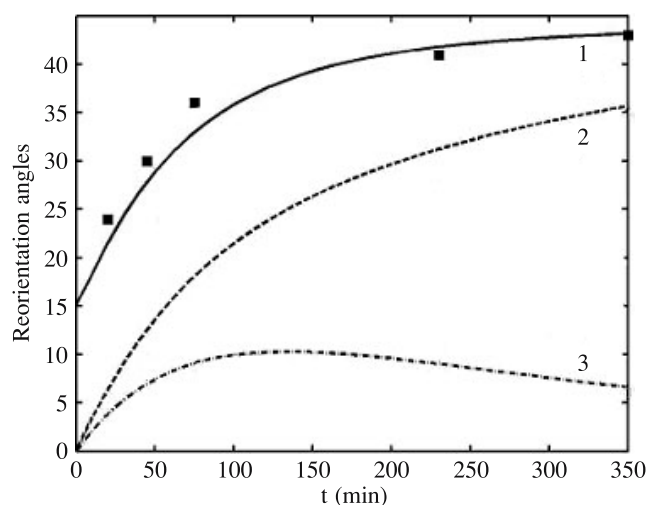

Fig. 2. (1) Experimental data for the reorientation angle (square dots) and theoretical curve $\varphi_S(t)$, (2) theoretical curve $\varphi_{a/d}(t)$, and (3) theoretical curve $\varphi_f(t)$.

the magneto-induced elastic deformation of LC and the surface anchoring torque is established. The time t_v of this reorientation is much shorter than the characteristic time of the drift of the easy axis. The amplitude of the "fast component" is changed during the drift of the easy axis since the angle between the easy axis and H-field is changed. The dependence of this amplitude on time after application of the magnetic field $\varphi_S^{fast}(t)$ is depicted in Fig. 3.

Fast surface reorientation is followed by a much slower rotation of the director toward $\vec{H}$. After hundreds of minutes director finally was set almost parallel to the direction of the magnetic field. Switching the field off during reorientation showed that the director did not return to its initial position but relaxed to an intermediate direction between the current values $\varphi_S(t)$ and $\varphi_S(t = 0)$. Since this position corresponds to the easy orientation axis, one can state that the long-term action of the magnetic field results in the azimuth drift of the easy orientation axis, which finally is directed parallel to the magnetic field.

The relaxation of the director consisted of the fast (few seconds) component due to relaxation of the bulk director deformation and the slow component with characteristic times increasing from minutes at small φ_S till several hours at φ_S close to 45°. The relaxation of the director after applying the memorization magnetic field for 350 min is presented in Fig. 4. The characteristic time of this relaxation was about 30 min.

4. Calculations and discussion

Let us consider the processes of formation and reorientation of the easy axis correspondingly to the three stages of the experiment; formation of the easy axis at cooling of the cell in the magnetic field, easy axis drift in the magnetic field and relaxation of the easy axis after switching off the magnetic field.
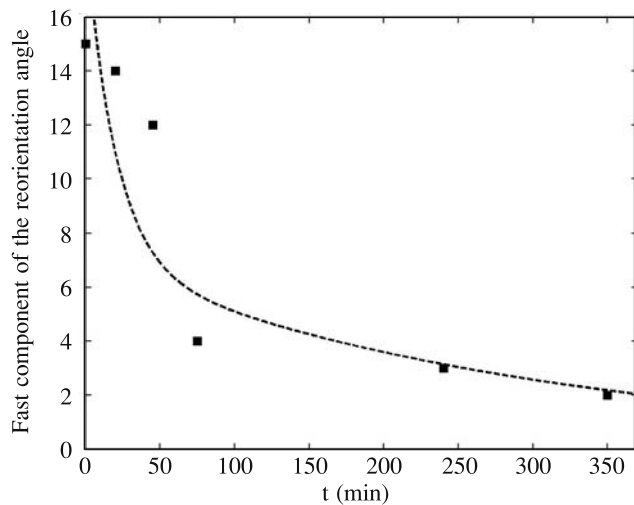
Fig. 3. Dependence of amplitude of the fast component of the reorientation angle on time after application of the magnetic field $\varphi_S^{fast}(t)$.
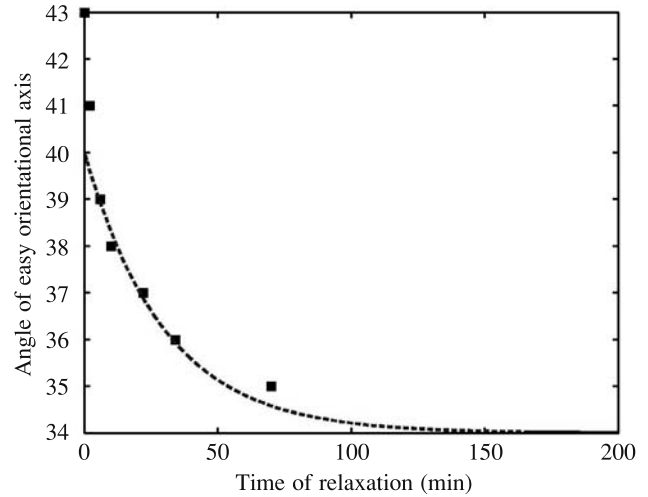
Fig. 4. Relaxation of easy orientation axis φ_e after the magnetic field was switched off. Points are experimental data, the dashed line shows experimental relaxation of φ_e, $t^* = 350$ min, $\varphi_S^* = 40°$, $\varphi_f^* = 6°$, $\varphi_{a/d}^* = 34°$, and s/k_f =30 min.

4.1. Formation of the easy axis

LC molecules in the bulk are oriented with the angular distribution function $F_V(\Omega_V)$ [1]

$$F_V(\Omega_V) = \frac{1}{N_V} \exp\left(\frac{\alpha S P_2\left(\vec{n}(\Omega_V), \vec{d}\right)}{k_B T} \right), \qquad (1)$$

where $\Omega_V = \Omega_V(\theta_V, \varphi_V)$ is a spatial angle in spherical reference frame, θ_V is the polar angle between the long axis of molecule and the normal to the substrate, φ_V is the azimuth angle between molecules and direction of $\vec{H}$, N_V is the concentration of LC molecules in a bulk, P_2 is the Legendre polynomial, α is the constant, S is the nematic order parameter, and $\vec{d}$ is the director of LC which direction coincides with the maximum of $F_V(\Omega_V)$. Cooling of the cell in the magnetic field results in the bulk distribution of the molecules $F_V(\Omega_V)$ with the director parallel to $\vec{H}$. One can suggest that the angular distribution of the long axes of the adsorbed molecules $F_S(\varphi_S^{mol})$ is given by a projection of the bulk distribution $F_V[\Omega_V(\theta_V, \varphi_V)]$ onto the surface [7–8], $F_{V\perp}$ where $\varphi_S^{mol} = \varphi_V$

$$F_{V\perp}(\varphi_S^{mol}) = \int_0^\pi F_V(\Omega_V) \sin\theta_V d\theta_V. \qquad (2)$$

The surface concentration of the adsorbed molecules on the substrate is determined by the kinetic equation [7]

$$\frac{dN_S}{dt} = A_+ N_{VS} - A_- N_S, \qquad (3)$$

where A_+ and A_- are the probabilities of the adsorption (A_+) and the desorption (A_-) of LC molecules, $N_{VS} = l_m N_V$,

l_m is the distance between the LC molecules in the bulk and N_v is the molecular bulk density. In the equilibrium $A_+N_V = A_-N_S$.

The interaction of the "bulk" molecules with the layer of the adsorbed "surface" molecules W_S is proportional to the concentration of the adsorbed molecules N_S, the molecular anchoring coefficient w_0, and depends on angular distribution of both the "bulk" and the "surface" LC molecules [8]

$$W_S = \frac{1}{2}w_0 N_S \int_{-\pi/2}^{\pi/2} d\varphi_V \int_{-\pi/2}^{\pi/2} d\varphi_S^{mol} F_S(\varphi_S^{mol})\cos^2(\varphi_V - \varphi_S^{mol})$$
$$\int_0^{\pi} F_V(\Omega_V)\sin^3\theta_V d\theta_V. \qquad (4)$$

As it will be shown below, the coefficient $w_0 N_S \sim 10^{-6}$ Jm^{-2}. Since the value $w_0 N_S$ is of the order of the macroscopic anchoring energy W_S, we can say that the anchoring produced by adsorption of LC molecules on the PVCN-surface is rather high and is of the order of the anchoring energy induced by UV light [8].

4.2. Drift of the easy axis

To describe the drift of the easy axis, we need to solve a problem about a change of the angular distribution of the adsorbed molecules in a magnetic field taking into account that the adsorbed molecules are located on flexible polymer fragments. For the geometry of the experiment, the free energy function per unit surface has the form

$$F = \frac{1}{2}\int_0^L \partial z \left\{ K_{22}\left[\frac{\partial\varphi_V(z,t)}{\partial z}\right]^2 - \chi_a H^2 \sin^2\varphi_V(z,t) \right\}, \quad (5)$$
$$- W_S(0,t) - W_S(L,t)$$

where $W_S(0,t)$ and $W_S(L,t)$ are the values of the anchoring energy on the two substrates at $z = 0$ and $z = L$, correspondingly, L is the thickness of the cell, K_{22} is the twist Frank's elastic constant and χ_a is anisotropy of the magnetic susceptibility.

Taking the variation of this functional, we get the following Euler-Lagrange equation

$$\varphi_V''(z) + \frac{1}{\xi_H^2}\sin\varphi_V(z)\cos\varphi_V(z) = 0, \qquad (6)$$

where $\xi_H = 1/H\sqrt{K_{22}/\chi_a}$ is the magnetic coherence length.

The boundary conditions are

$$\left[k_{22}\varphi_V'(z) - \frac{dW_S(\varphi_S^{mol})}{d\varphi_S}\right]_{\substack{z=0 \\ z=L}} = 0. \qquad (7)$$

The solution of Eq. (6) is

$$\sin\varphi_V(z) = k sn\left(\frac{z}{\xi_H} - \frac{L}{2\xi_H} + K(k),k\right), \qquad (8)$$

where $K(k)$ is the complete elliptic integral of the first kind and k is the parameter of elliptic functions.

Substituting Eq. (8) to the boundary conditions of Eq. (7) one can get the equation for unknown parameter k

$$\left[kcn\left(\frac{z}{\xi_H} - \frac{L}{2\xi_H} + K(k),k\right) - W'\frac{dw_S(\varphi_S^{mol})}{d\varphi_S}\right]_{\substack{z=0 \\ z=L}} = 0, \quad (9)$$

where

$$W' = \frac{w_0\xi_H}{K_{22}}N_S, \quad w_S = \frac{W_S}{w_0 N_S}.$$

Knowing derivative of the anchoring energy of Eq. (4) $dW_S/d\varphi_S$ it is possible to calculate the parameter k from Eq. (9) and to find the solution of Eq. (8) in explicit form.

The system of Eqs. 8 and 9 determines the position of the director on the surface at the given $F_S(\varphi_S^{mol})$. Application of the magnetic field results in the reorientation of the director and consequently, in a change of the shape distribution function $F_S(\varphi_S^{mol})$. Adsorbed LC molecules are disposed on the polymer surface which contains isotropically distributed orientationally-movable cinnamoil fragments. It is reasonably to suggest that strong LC-polymer interaction causes a cooperative reorientation of the movable polymer fragments due to a volume reorientation torque. Considering the ensemble of the movable fragments as viscous-elastic medium, it is plausible to write the following equation for reorientation of the movable fragments on the polymer surface

$$s\frac{d\varphi_f}{dt} + k_f\varphi_f = \Gamma, \qquad (10)$$

where Γ is the torque from the bulk LC molecules which turn the flexible fragments together with the adsorbed molecules toward $\bar{H}$, k_f and s are the phenomenological coefficients of rigidity and viscosity of the ensemble, $\varphi_f = 0$ at $t = 0$. The torque Γ from the LC molecules is given by the first term in Eq. (9)

$$\Gamma = K_{22}\varphi'(z)|_{\substack{z=L \\ z=0}} = \frac{K_{22}k}{\xi_H}cn\left(\frac{L}{2\xi_H} + K(k),k\right). \quad (11)$$

The torque Γ results in a drift of the easy orientation axis toward the magnetic field. This torque also leads to a change of the distribution function of the adsorbed molecules.

The AD-process also contributes to the drift of the easy axis. Taking into account the reorientation of the movable fragments, Eq. (3) for density of the adsorbed molecules along φ_S^{mol} takes a form

$$\frac{\partial\left[F_S(\varphi_S^{mol} - \varphi_f)N_S\right]}{\partial t} = A_+F_{V\perp}(\varphi_S^{mpl})N_{VS} \qquad (12)$$
$$- A_-F_S(\varphi_S^{mol} - \varphi_f)N_S$$

The stationary form ($t \to \infty$, $t = 0$) of this equation reads

$$A_+F_{V\perp}(\varphi_S^{mol})N_{VS} - A_-F_S(\varphi_S^{mol} - \varphi_f)N_S = 0. \, (13)$$

Using Eqs. (10), (11), and (12) one can calculate the time-dependency of the distribution function $F_S(\varphi_S^{mol})$. Knowledge of the distribution $F_S(\varphi_S^{mol})$ allows, in turn, to find the solution of Eq. (8) for the reorientation angle $\varphi_S(t)$ in the explicit form, and to determine the value $w_0 N_S$, see Eq. (4), from the amplitude of the fast component of the director reorientation, φ_S^{fast}.

In our experiment, we obtain $\varphi_S^{fast}(t=0) \approx 15°$. Using this magnitude in Eqs. (8) and (9), as well as the values $K_{22} = 3.6 \times 10^{-12}$ N, $H = 3$ kGs, $L = 50$ µm, $\chi_a = 1.76 \times 10^{-7}$ we obtained the value $w_0 N_S \approx 4 \times 10^{-6}$ Jm^{-2}. The numerical calculations of the dependence $\varphi_S(t)$ at the same parameters and $A_- = A_+ = 1/45 \min^{-1}$, $s/k_f = 30$ min are depicted in Fig. 2 (curve 1), and it fits well to the experimental data.

4.3. Relaxation of easy orientation axis

As described above, switching the magnetic field off resulted in a fast reorientation of the director to the current position of the easy axis φ_e followed by a long time drift of the easy axis toward the initial position was observed. The AD-processes do not change the angle φ_e since LC molecules are absorbed by the surface preferably along φ_e. Therefore we associate the relaxation of the easy axis with an elasticity of the movable polymer fragments (relaxation of the angle φ_f). According to Eq. (10) we get at $\Gamma = 0$

$$\varphi_f = \varphi_f^* \left[1 - \exp\left(-\frac{k_f}{s} t \right) \right], \qquad (14)$$

where φ_f^* is the angle of reorientation of the fragments. Here and after the "star" points the time of the magnetic field switching off. Thus, the relaxation of the easy axis is described by an exponential law that corresponds to the experimental data (Fig. 4). The fitting of the experimental curve was done at $t^* = 350$ min, c, $\varphi_f^* = 6°$, $\varphi_{a/d}^* = 34°$, and $s/k_f = 30$ min.

The experimental data on the dynamics of the drift of the director in the magnetic field (Fig. 2) and the easy axis relaxation (Fig. 4) allow us to distinguish the contributions of the AD-process and the rotation of the movable fragments to the easy axis drift. To do this, we measured first the angle φ_e^* by the switching $\vec{H}$ off. Then, we followed for the relaxation of the drift of the easy axis $\varphi_e(t)$ till the steady residual angle $\varphi_e = \varphi_{a/d}^*$ was achieved. Finally, we calculated the value $\varphi_f^* = \varphi_e^* - \varphi_{a/d}^*$. In Fig. 2, the dependencies $\varphi_f^*(t)$ and $\varphi_{a/d}^*(t)$ calculated by this procedure are plotted. In these calculations we used the same parameters as ones were used at the calculations of $\varphi_S(t)$.

5. Conclusions

We have studied the time evolution of the director orientation in a cell under the influence of an external magnetic field and further relaxation after the field switching off in the case of time-dependent boundary conditions. Boundary conditions change due to a combination of adsorbtion/desorbtion processes of LC molecules and of flexible fragments reorientation of the polymer substrates. We get numerical fitting of dependencies of the director angle, the flexible fragments reorientation and the easy axis angle of the adsorbed molecules versus the memorization time of the cell in the magnetic field. We obtain these fitting in a good accordance with the experimental data.

Acknowledgements

References

1. P.G. De Gennes and J. Proust, *The Physics of Liquid Crystals*, Oxford, Clarendon Press, 1993.
2. P. Vetter, Y. Ohmura, and T. Uchida, "Study of memory alignment of nematic liquid crystals on polyvinyl alcohol coatings", *Jpn. J. Appl. Phys.* **32**, L1239–L1241 (1993).
3. V.P. Vorflusev, H.S. Kitzerow, and V.G. Chigrinov, "Azimuthal surface gliding of a nematic liquid crystal", *Appl. Phys. Lett.* **70**, 3359 (1997).
4. S. Faetti, M. Nobili, and I. Raggi, "Surface reorientation dynamics of nematic liquid crystals", *Eur. Phys. J.* **B11**, 445 (1999).
5. Yu. Kurioz, V. Reshetnyak, and Y. Reznikov, "Orientation of a liquid crystal on a soft photoaligning surface", *Mol. Cryst. Liq. Cryst.* **375**, 535 (2002).
6. I. Jànossy and T.I. Kóssa, "Gliding of liquid crystals on soft polymer surfaces", *Phys. Rev.* **E70**, 052701 (2004).
7. A. Romanenko, I. Pinkevich, V. Reshetnyak, I. Dozov, and D. Stoenescu, "Director reorientation in a cell with time-dependent anchoring due to adsorption/desorption of LC molecules", *Mol. Cryst. Liq. Cryst.* **422**, 173 (2004).
8. A. Romanenko, V. Reshetnyak, I. Pinkevich, I. Dozov, and S. Faetti, "Magnetic field induced director reorientation in the nematic cell with time-dependent anchoring due to adsorption/desorption of LC molecules", *Mol. Cryst. Liq. Cryst.* **439**, 1867 (2005).
9. O. Buluy, A. Iljin, E. Ouskova, Y. Reznikov, C. Blanc, M. Nobili, and K. Antonova, "Anchoring and gliding of easy axis of 5CB on photoaligning PVCN-F surface", *Journ. SID* – accepted for publication (2006).
10. O. Buluy, I. Gerus, K.R. Ha, D.S. Kim, and Y. Reznikov, "Mechanisms of photoalignment of liquid crystals on polyvinylfluorocinnamate", *Proc. IMID'06*, accepted for publication.
11. E. Ouskova, Y. Reznikov, S.V. Shiyanovskii, L. Su, J.L. West, O.V. Kuksenok, O. Francescangeli, and F. Simoni, "Photo-orientation of liquid crystals due to light-induced desorption and adsorption of dye molecules on an aligning surface", *Phys. Rev.* **E64**, 051709 (2001).