

Surface Director Sliding in LC Cell with Light-Controlled Chirality

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In this paper we study a surface reorientation of an LC director of the nematic-chiral mixture. The mixture's exposure to the actinic light changes the concentration of chiral agent which leads to the expansion of the pitch, inducing elastic deformation. This causes long range forces of the LC to compete with forces of the rotational viscosity of the easy axis and the anchoring. We study the dynamics of this process experimentally and develop a theoretical model that describes the director distribution in a bulk constrained by asymmetric boundaries. The experimental results are found to be in good agreement with the developed theory.

Keywords: anchoring; chiral agent; liquid crystal director; photochemistry; rotational viscosity; surface reorientation

INTRODUCTION

Adding chiral molecules into nematic matrices substantially changes the properties of the latter. A very small amount of the chiral agent introduced into the nematic matrix leads not only to the change of optical Friedericksz transition threshold but also to the appearance

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of a double-threshold feature possessing a hysteretic loop [1,2]. A substantial shift of the wavelength of the Bragg selective reflection band of induced chiral nematic liquid crystal (CLC) is caused by a decrease of the twisting ability of the chiral agent with a step-like dependence of maximum wavelength against exposure time [3,4]. The light-controlled rotation of the light polarisation plane was observed in a cell of weakly twisted nematic with a planar orientation [5]. A more detailed study of such a system is reported in this paper, which also explains the so called "dark" reorientation of CLC director in the cell with asymmetric boundary conditions is also presented.

EXPERIMENT

Cell Preparation

In the experiments presented here the frame of the cell comprised the two parallel glass substrates separated by 20–25 μm , using teflon spacers. Both substrates had a size of 2×3 cm and differed by the virtue of aligning working surfaces. The surface of one substrate consisted of the rubbed polyimide (PI) and provided a strong planar anchoring of LC director with the planar orientation along the rubbing direction. The surface of another substrate was treated with parpolyvinyl-cinnamate (PVCN) polymer and provided a degenerated planar orientation allowing for in-plane rotation of the LC director [6]. The latter was prepared by coating a glass substrate with the photopolymer film that was homogeneously distributed across the substrate. The thickness of the film was around 0.1 μm [7]. The detailed description of this process follows.

The glass substrate was washed with pure alcohol then immersed in the ultrasound basin of acetone for 30 minutes. After this the substrate was rinsed with distilled water. The remaining water was removed with a help of pressurised nitrogen and the substrate was further annealed at 200°C for 1.5 hours. Then the photopolymer, dissolved in the equal solution of chlorobenzene and dichloroethane, was distributed on the substrate by spin-coating. The concentration of the polymer was 10 g/l and the rotation speed of the spin was 7000 rpm for a length of 10 sec. Finally, the coated substrates were baked at 80°C for 1.2 hours in order to eliminate any residual solvent left in the film.

In the next stage of preparation the polymer coated substrates were exposed to depolarized light of mercury lamp for 10 sec. The integral intensity of the lamp in UV spectral region was 0.7 ± 0.05 mW/cm². Such irradiation causes a photochemical reaction of cross-linking

between double carbon bonds in side groups of the polymer and consequently prevents the polymer dissolving in a LC compound [8].

We now go on to describe the working mixture of the nematic LC and the chiral agent used in the experiment. The mixture was composed of 5CB liquid crystal (K15, Merck) and 0.07–0.1 wt.% of the chiral agent, *l*-ariliden-menthanone [3,9] (Institute for Single Crystals, NASU, Ukraine). Molecules of the chiral agent are known to undergo irreversible E-Z photo-induced transformation, which reduces the twisting effect of the agent, from around $\beta_E = 35 \mu\text{m}^{-1}\text{mol}^{-1}$ in E-conformation to $\beta_Z < 10 \mu\text{m}^{-1}\text{mol}^{-1}$ in Z-conformation [9], for concentrations similar to those used in the experiment. We simply note that in its initial E-form, the chiral agent in the investigated mixture imposed on the LC a helical pitch of $P_0 = 40 \mu\text{m}$. Note that the both isomers are known to be stable, as their partial concentrations in the illuminated mixture are unchanged after the exposure to the actinic light [9].

The prepared LC mixture was then forced into the glass frame by the capillary effect forming a working cell with a twisted LC structure. After being filled with LC substance, the cell was sealed around the perimeter with an epoxy adhesive, in order to prevent any leakage of the substance and an influence of the ambient moisture and oxygen.

LC director on the surface of PI-covered substrate of the cell was aligned along the rubbing direction of that surface. The orientation of the director at PVCN-covered, isotropic, surface was then determined by the helical pitch of the chiral nematic LC in the bulk and satisfied the unperturbed director distribution (Fig. 1). We would like to point out, however, that isotropic properties of PVCN-covered surface are not permanent. After short while the surface appears to acquire an easy orientation axis, due to the memory effect [10], which we will discuss later.

Experimental Set Up

The stimulation the E-Z photo-transformation of the chiral agents was performed using He-Cd laser ($\lambda_{\text{actinic}} = 440 \text{ nm}$, $E_{\text{actinic}} = 10 \text{ mW}$). A second laser, He-Ne ($\lambda_{\text{test}} = 633 \text{ nm}$, $E_{\text{test}} = 2 \text{ mW}$), was used to determine the orientation of LC director on the isotropic surface (Fig. 2). The actinic beam of He-Cd laser was circularly polarised (using the pair polarizer **P3** and $\lambda/4$ -plate) in order to reduce the anisotropic absorption. Polarizer **A1**, placed just after the light source, was used for the light intensity attenuation. The beam from He-Ne laser was split by mirror **M1** into the reference and the testing beams. The direction of an excitation radiation was adjusted with the mirror **M2** to be almost parallel to the testing beam. The diameter of the spot on the investigating

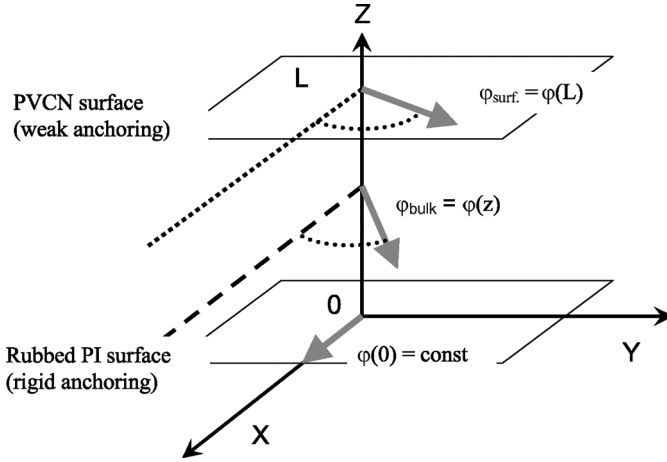


FIGURE 1 Geometry of the experiment and LC director distribution in a cell.

cell, projected by the latter, was sufficiently smaller than that of the excitation beam for the tested region to be considered uniform.

The cell with the liquid crystal mixture is positioned so that the testing beam passes along the normal to the cell facing first the anisotropic substrate, covered with rubbed PI. The polarisation of the testing beam was adjusted with polarizer **P1** so that the former is parallel to the direction of rubbing on the anisotropic substrate and, therefore, parallel to the director of LC on the PI surface. The helical pitch of the LC mixture ($P_0 = 40 \mu\text{m}$) was big enough to satisfy the Mauguin

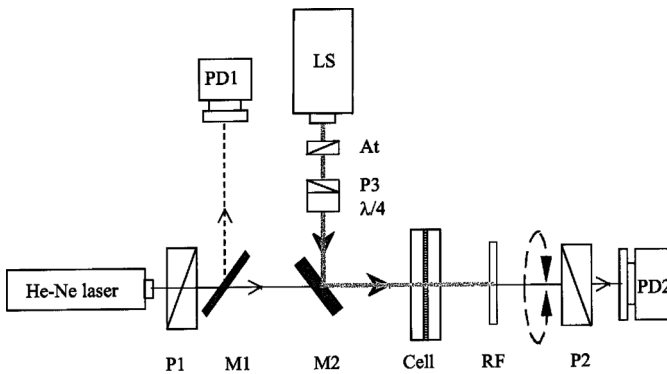


FIGURE 2 Experimental set up: **Cell**—liquid crystal cell, **LS**—light source (He-Cd laser), **P1-3**—polarisers, **At**—attenuator, $\lambda/4$ — quarter-wave plate, **PD1-2**—photodiodes, **M1-2**—mirrors, **RF**—red filter.

condition [11], in which $\lambda \ll (n_e - n_o)P$. This means that the polarisation of the testing beam could follow the local orientation of the director while propagating through the bulk and exiting the cell with the polarisation which is parallel to the orientation of the director on the isotropic, PVCN-covered, surface. Photodiodes **PD1** and **PD2** were then used to measure the intensities of the reference and the testing beams respectively. Red filter **R** was placed before photodiode **PD2** to reduce any interference from the excitation beam.

The initial orientation of the polarisation of the test beam upon its exit from the cell was deduced from the orientation of the polarizer **P2**. **P2** could be rotated into the position of the minimal intensity of the beam passed through onto photodiode **PD2**. The minimum signal on **PD2** corresponds to the polarisation of the test beam being perpendicular to the orientation of **P2**.

Thus all changes of the director orientation on the isotropic surface led to a signal increase on **PD2**, which was monitored by a computer equipped with a PC LabCard. The measured signal from **PD2** was then normalised by the reference signal from **PD1** in order to compensate for the temporal instability of the He-Ne laser. The resulting signal corresponds to the director orientation on the isotropic surface as:

$$I_{\text{sign}}(t) = I_{\text{test}} \cdot \sin^2(\varphi_o - \Delta\varphi(t)),$$

where $\Delta\varphi(t) = \varphi_o - \varphi(t)$ is the difference between the director orientation before and some time, t , after the exposure to the excitation beam. The recorded change of the signal on **PD2** in time is then translated into the dynamics of the LC director reorientation on the PVCN-covered surface.

Director Reorientation Under the Excitation Beam

The curves representing the typical reorientation behaviour of the director under the excitation are shown in Figure 3. Here, $I_0 = 500 \text{ mW/cm}^2$ is the highest actinic light intensity used in the experiment. The figure shows the dynamics of the reorientation and its saturation after several hundred seconds. The curves that represent the intensities I_0 and $0.6I_0$ appear to be very similar. This suggests that the time scale of the photo-induced processes is smaller than that of the director reorientation on the surface.

“Dark” Reorientation

A more interesting effect takes place when the excitation beam is cut off before the director rotation approaches its saturation. We continue

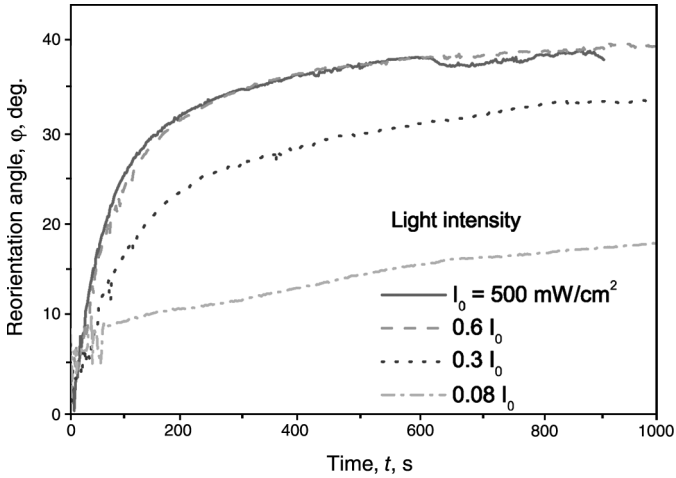


FIGURE 3 Time dependence of the director reorientation on the PVCN surface under irradiation with different light intensities.

to observe a substantial director reorientation in the “dark” with a further angle change of up to $10 \div 20$ deg. The magnitude of the change depended on the duration of the exposure of the cell to the excitation (Fig. 4). Dependences plotted in Figure 4 represent different exposure

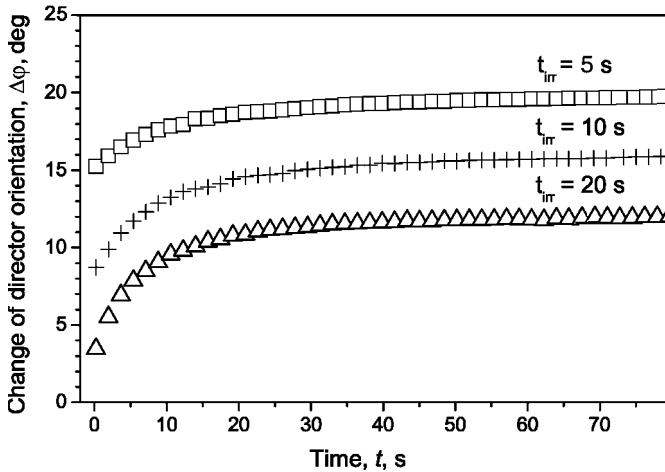


FIGURE 4 “Dark” reorientation of LC director for different exposure times to He-Cd laser beam ($I_0 = 500 \text{ mW/cm}^2$). The point $t = 0$ corresponds to the moment of the actinic light cut off for each experimental curve.

times of the cell to the He-Cd-laser radiation ($I = 500 \text{ mW/cm}^2$), namely 5, 10 and 20 seconds.

DISCUSSION

The process of the photo-transformation of chiral molecules occurs only under the irradiation with the actinic light [9]. Moreover, taking into account that the absorption of a visible light is very small (*i.e.*, light intensity within the cell is $I(z) \equiv \text{const}$), we consider the distribution of chiral molecules along the helical axis to be uniform for isomers with both high and low chirality. We also consider thermal diffusion to be negligible with the timescale of several orders of magnitude faster [12] than the process investigated. As to the process of the diffusion of molecules of the chiral agent parallel to the substrates, it should last tens of minutes as evaluated using standard figures [11]: for the diameter of a light spot $d = 1 \text{ mm}$ and self-diffusion coefficient $D \approx 4 \cdot 10^{-6} \text{ cm}^2/\text{s}$ the characteristic time is about $\tau_{\text{dif}} \sim d^2/D = 2.5 \cdot 10^3 \text{ s}$.

Thus, we can state that at the moment of the light cut off the intrinsic helical pitch of chiral nematic LC is the same across the illuminated part of the cell. However, the actual director distribution in the helix is more twisted than that corresponding to its equilibrium state. The difference between the actual and the desired pitch of the helix in the bulk causes substantial elastic deformation stimulating further relaxation of the helix. Owing to the asymmetric anchoring conditions the relaxation of the helix occurs in the form of reorientation the director on the PVCN-covered substrate with a weak anchoring. It is the mere elastic force that drives the helix relaxation, which, together with the competing viscous and the anchoring forces, governs the director reorientation process.

Kinetics of Director Distribution in an Asymmetric Cell

Let us consider a mixture of a nematic liquid crystal with a chiral dopant subjected to a light-induced transformation from the form with a high twisting power (*E*-isomer in our case) to the form with a much smaller chirality (*Z*-isomer). For simplicity, the latter is considered to be an achiral. We also assume the LC director, $\mathbf{n} = (\cos \phi, \sin \phi, 0)$, to be parallel to the both cell substrates. One of the substrates provides a rigid planar anchoring of LC on the surface whereas another substrate allows for an in-plane director reorientation and, in principle, provides a weak anchoring with an easy axis, $\mathbf{e} = (\cos \phi_0, \sin \phi_0, 0)$. The total elastic energy of the liquid crystal with the chiral dopant and the anchoring at the both cell surfaces has the form [11]

$$F = \frac{1}{2} \int \{K_1(\operatorname{div} \mathbf{n})^2 + K_2(\mathbf{n} \cdot \operatorname{rot} \mathbf{n} + p)^2 + K_3(\mathbf{n} \times \operatorname{rot} \mathbf{n})^2\} dV - \frac{W}{2} \int (\mathbf{n} \cdot \mathbf{e})^2 dS \quad (1)$$

where K_i are the elastic constants of liquid crystal, p is the inverse pitch of twisted LC, and \mathbf{e} is the easy axis at the cell surface with energy W .

The next assumption is that the director reorientation in the bulk occurs only in the plane XOY and can, therefore, be described by a single angle, $\phi(z)$ (Fig. 1). Taking into account a strong anchoring at $z = 0$ and the easy orientation axis at $z = L$ (Fig. 1) the elastic energy of the system can be written as follows:

$$F = \frac{1}{2} K_2 \int_0^L \left(p(t) - \frac{\partial \phi}{\partial z} \right)^2 dz - \frac{W}{2} \int \cos^2(\phi - \phi_0) dS \quad (2)$$

The equation of the director reorientation is described in (11)

$$K_2 \frac{\partial^2 \phi(z, t)}{\partial z^2} = \gamma_1 \frac{\partial \phi(z, t)}{\partial t} \quad (3)$$

where γ_1 is the rotational viscosity.

The process of irreversible light-induced transformation of the chiral molecules can be noted as the dependence of the inverse pitch of nematic chiral mixture on time, $p(t)$, under the illumination of intensity I :

$$p(t) = p_1 + p_2 e^{-t/\tau}, \quad \tau = (\alpha I)^{-1}. \quad (4)$$

Here, $p(0) = p_1 + p_2$ is the initial value of the inverse pitch and α is the efficiency of E - Z photo-transformation.

By minimization of the functional (2), considering the energy dissipation at the surface $z = L$, we obtain the following boundary and initial conditions:

$$\begin{cases} \phi(0, t) = 0 \\ \frac{\partial \phi(L, t)}{\partial z} = p_1 + p_2 \cdot e^{-t/\tau} - \frac{\gamma_s}{K_2} \frac{\partial \phi(L, t)}{\partial t} - \frac{W}{2K_2} \sin[2(\phi(L, t) - \phi_0)] \\ \phi(z, 0) = (p_1 + p_2)z \end{cases} \quad (5)$$

where γ_s is a so called surface viscosity [13].

We also consider the angles of the director reorientation at the surface $z = L$ to be small enough to use a small angle approximation: $\sin[2(\phi - \phi_0)] \approx 2(\phi - \phi_0)$.

Thus, rewriting the basic equations using normalized and dimensionless variables and parameters we obtain a system of equations:

$$\begin{cases} \frac{\partial \phi(\eta, t)}{\partial t} = \frac{K_2}{\gamma_1 L^2} \frac{\partial^2 \phi(\eta, t)}{\partial \eta^2} \\ \phi(0, t) = 0 \\ \frac{\partial \phi}{\partial \eta}(1, t) + \Gamma \frac{\partial^2 \phi}{\partial \eta^2}(1, t) + \xi \phi(1, t) = q_1 + q_2 e^{-t/\tau} + \xi \phi_0 \\ \phi(\eta, 0) = (q_1 + q_2)\eta = \phi_0 \eta \end{cases} \quad (6)$$

where $\eta = z/L$, $\Gamma = \gamma_s/\gamma_1 L$, $\xi = WL/K_2$, $q_1 = p_1 L$, $q_2 = p_2 L$.

The solution to the above problem reads:

$$\phi(\eta, t) = \frac{q_1 + \xi \phi_0}{1 + \xi} \eta + B e^{-t/\tau} \sin(\sqrt{\chi} \eta) + \sum_n a_n e^{-(K_2/\gamma_1 L^2) \nu_n^2 t} \sin(\nu_n \eta) \quad (7)$$

where $B = q_2/(\sqrt{\chi} \cos(\sqrt{\chi}) + (\xi - \Gamma \chi) \sin(\sqrt{\chi}))$, $\chi = \gamma_1 L^2/K_2 \tau$.

Applying this solution to the boundary condition at the surface $z = L$, we have a transcendent eigenvalue equation:

$$\cot(\nu_n) = \Gamma \nu_n - \frac{\xi}{\nu_n}. \quad (8)$$

The characteristic times of the relaxation modes are:

$$\tau_n = \frac{\gamma_1 L^2}{K_2 \nu_n^2}. \quad (9)$$

Now we consider the initial conditions of the problem (6). Taking into account that the differential operator in Eqs. (3) and (5) is not self-adjoint and the fact that the Fourier expansion is inapplicable in this case, we can deduce coefficients a_n by minimizing the following functional

$$\Phi(\{a_n\}) = \int_0^1 \left(\sum_n a_n \sin(\nu_n \eta) - w(\eta, 0) \right)^2 d\eta. \quad (10)$$

We obtain the following system of equations

$$\int_0^1 \left(\sum_m a_m \sin(\nu_m \eta) - A \eta + B \sin(\sqrt{\chi} \eta) \right) \sin(\nu_n \eta) d\eta = 0 \quad (11)$$

where $A = q_2/(1 + \xi)$. After integration we finally get the following system of linear equations for the amplitudes a_n

$$\sum_m I_{nm} a_m = \zeta_n \quad (12)$$

where $I_{nm} = \int_0^1 \sin(\nu_n \eta) \sin(\nu_m \eta) d\eta$, $\zeta_n = A \int_0^1 \eta \sin(\nu_n \eta) d\eta - B \int_0^1 \sin(\sqrt{\lambda} \eta) \times \sin(\nu_n \eta) d\eta$.

Thus far, we obtained a complete exact solution, which takes into account the effect of photo-transformation in chiral molecules and experimental data. For the director orientation at the surface $z = L$ we have the following expression:

$$\phi_{\text{fin}} = \phi(1, \infty) = \frac{q_1 + \zeta \phi_0}{1 + \zeta}, \quad t_{\text{irr}} \rightarrow \infty. \quad (13)$$

In the case of the “dark” reorientation (the excitation beam is turned off at time t_{irr}), the solution for the director relaxation reads

$$\tilde{\phi}(\eta, t) = \frac{q_1 + q_2 e^{-t_{\text{irr}}/\tau} + \zeta \phi_0}{1 + \zeta} \eta + \sum_n b_n e^{-(K_2/\gamma_1 L^2) \nu_n^2 (t - t_{\text{irr}})} \sin(\nu_n \eta), \quad t > t_{\text{irr}} \quad (14)$$

where amplitudes b_n are determined as follows:

$$\sum_m I_{nm} b_m = \tilde{\zeta}_n, \quad (15)$$

with $\tilde{\zeta}_n = -(q_2 e^{-t_{\text{irr}}/\tau} / 1 + \zeta) \int_0^1 \eta \sin(\nu_n \eta) d\eta + B e^{-t_{\text{irr}}/\tau} \int_0^1 \sin(\sqrt{\lambda} \eta) \times \sin(\nu_n \eta) d\eta + \sum_m a_m e^{-(K_2/\gamma_1 L^2) \nu_m^2 t_{\text{irr}}} I_{nm}$.

For the saturated director orientation at cell surface $z = L$ we have similar expression, differing from the previous case by virtue of the value of the intrinsic helical pitch, which depends on the exposure time ($\tilde{q}_1 = q_1 + q_2 e^{-t_{\text{irr}}/\tau}$):

$$\tilde{\phi}_{\text{fin}} = \tilde{\phi}(1, \infty) = \frac{q_1 + q_2 e^{-t_{\text{irr}}/\tau} + \zeta \phi_0}{1 + \zeta}, \quad t_{\text{irr}} - \text{finite}. \quad (16)$$

Therefore, we presented a full description of both experimental cases of the director reorientation, namely under continuous illumination with actinic light and during the “dark reorientation”.

It is possible now to estimate unknown parameters q_1 , q_2 , ζ and τ in Eqs. (13) and (16) from the experimental data (Figs. 3 and 4), such as different exposure conditions, saturation angles, *etc.* On the other hand, applying the analytical fit to the experimental data yields the values of surface rotational viscosity γ_s . Using Eqs. (7) and (14) we were able to construct the best fit for the director orientation angles on surface $z = L$ during and after the exposure, Figure 5 (solid lines). Note, that fitting of these parameters was performed using numerical methods. The following parameters from the experiment were used for the fitting: $L = 2 \cdot 10^{-5}$ m, $K_2 = 3 \cdot 10^{-12}$ N, $\gamma_1 = 0.8 P$, $\phi_0 = \pi$. Average

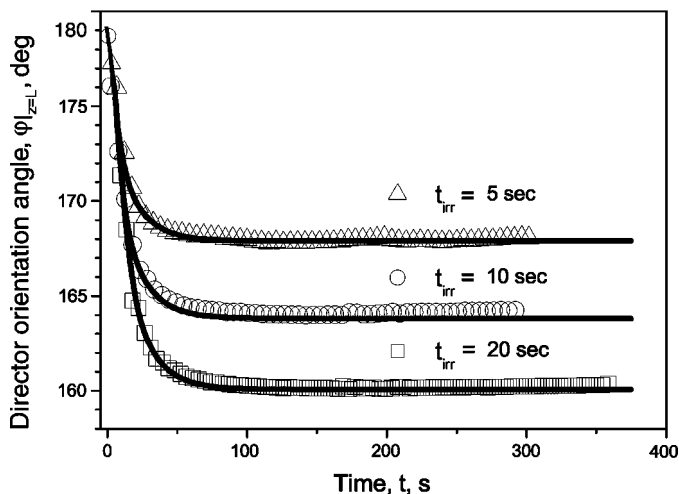


FIGURE 5 Time dependences of the angle of LC director orientation at the PVCN-covered surface for different times of exposure to He-Cd laser beam ($I_0 = 500 \text{ mW/cm}^2$); solid lines represent the fitting of the Eqs. (7) and (14) taking into account experimental data and material properties.

parameter values that satisfied the best fit, were determined as $\xi = 4.6$, $q_1 = 1.1$ and $\tau = 6.4 \text{ s}$. Finally, the estimated value of the surface rotational viscosity was found to be $\gamma_s = 3.25 \cdot 10^{-6} \text{ P} \cdot \text{m}$. The standard deviation was 0.007.

CONCLUSIONS

We studied the effect of the rotation of the LC-director on the surface, which is believed to be solely due to the force associated with a twist elastic deformation. The director reorientation occurs as a result of the light-induced discrepancy between the apparent and the desired distribution of helical pitch in the bulk. A substantial “dark” reorientation of the director, the magnitude of which depended on the exposure, was observed. Owing to the time scale of the phototransformation of chiral molecules being much faster than that of the director redistribution, the unstable state of intrinsic helical pitch (diverged from the apparent director distribution) geared the process of reorientation. Rather long characteristic times of this effect were explained as the influence of the surface rotational viscosity of liquid crystal.

Since the differential operator of the problem was not self-adjointed, the solution of the problem required some special efforts to resolve the

non-orthogonal set of eigen-functions. The obtained complete solution provides a full description of all experimental cases of the director relaxation in both cases; under continuous illumination with actinic light and during the “dark reorientation” after the light cut off. Theoretical results were in a very good agreement with the experiment. The developed method allows for a value of the surface director viscosity to be determined from the experimental data and known properties of the material. However, the study of this effect in the paper is far from exhaustive and requires further detailed studies, as the processes discussed here appear to be very interesting.

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