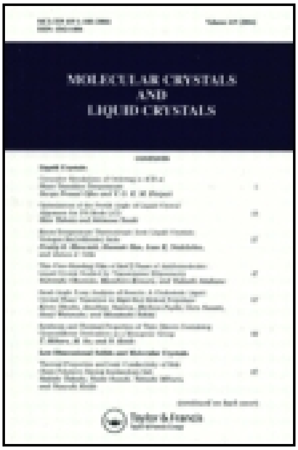

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Light-induced Anchoring Evolution in Nematic Phase of Liquid Crystal Doped with Azo-dye

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We report an experimental study of light-induced anchoring evolution of azo-dye-doped liquid crystal (LC) in nematic phase and present a model of this effect. To describe the experimental results we considered the gliding effect as a result of light-induced anisotropic adsorption/desorption of dye molecules on/from the boundary polymer aligning layer in the presence of light-induced bulk torque due to ordering of absorbing dye molecules. Our model qualitatively describes the observed drift of the light-induced easy axis.

Keywords: drift of the easy axis; dye-doped liquid crystal; light-induced adsorption and desorption; light-induced anchoring; nematic

1. INTRODUCTION

Known since 1995, light-induced anchoring of liquid crystals (LC) [1] still attracts close attention of scientists [2–7] due to fascinating science and potential applications. It was found that irradiation of a planar cell with the nematic LC 5CB doped with azo-dye Methyl Red (MR) produced an easy orientation axis on a non-photosensitive aligning surface at illumination with polarized light in the absorption band of MR. Voloshchenko *et al.* [1] suggested that photo-excited dye

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molecules adsorb onto the aligning surface preferably along the actinic light polarization due to absorption dichroism that results in producing of easy orientation axis and homogeneous alignment of LC in irradiated area. The later experiments on irradiation of the dye-doped LC in the isotropic phase showed that the effect of light-induced anchoring is governed by competition between light-induced desorption of azo-dye from spontaneously adsorbed layer of MR molecules and adsorption of MR molecules from LC bulk on the aligning surface [2,3]. The light-induced desorption of MR molecules resulted in the easy axis perpendicular to the polarization of the pump light, $\vec{E}_{pump}$, and the light-induced adsorption caused the easy axis parallel to $\vec{E}_{pump}$. At low light irradiation doses desorption prevails and light-induced adsorption dominates at high irradiation doses.

Majority of studies of light-induced anchoring were focused on investigations of stationary properties of LC orientation caused by adsorption/desorption (AD) of MR-molecules, and only few reports about dynamic of LC reorientation due to producing of the light-induced easy axis were published [8,9]. It was found that when the irradiation started, the effective sliding of LC director [10] over initially isotropic surface occurred followed by very slow director reorientation. The sliding effect was suggested to be due to light-induced bulk torque, and slow director reorientation was associated with producing of an easy orientation axis due to light-induced AD-processes. Competition between these processes results in a complex dynamic of the director reorientation in a nematic LC cell that is evolution of light-induced anchoring of NLC.

Here we present experimental studies of evolution and relaxation of light-induced anchoring in LC 5CB doped with azo-dye MR and propose a model where the light-induced director reorientation is associated with development and modification of the angular distribution function of MR molecules on the aligning surface caused by AD-processes and light-induced bulk torque. These processes result in a light-induced drift of the easy axis which direction depends on a mechanism that prevails at a current exposure dose.

2. EXPERIMENTS

We studied light-induced anchoring in nematic LC pentylcyanobiphenyl 5CB from Merck (clearing point $T_c = 34.5°\mathrm{C}$) doped with the azo-dye Methyl Red (MR) from Aldrich. At room temperature the majority of MR molecules are in a trans-form and they absorb light in the blue-green region of visible spectra. Light-induced trans-cis isomerisation [11,12] as well as light-induced adsorption [5,13] are characteristic features of this dye. To decrease possible interaction of MR molecules, a dilute weight concentration of MR $c = 0.5\%$ was chosen.

We used combined LC cell consisted of reference and tested substrates. Reference substrate was covered with rubbed polyimide layer providing strong unidirectional planar alignment of LC director in the cell. The tested surface was formed by isotropic layer of fluorinated polyvinilcinnamate (PVCN-F) that was irradiated by unpolarized UV light during 15 min. The UV irradiation made the PVCN-F film stable against dissolving in LC. Since using non-polarized UV light, the resulting layer provided degenerate planar alignment of LC.

Standard "pump-probe" experimental setup was applied in our studies [10]. The linear polarized *He-Cd* laser beam at $\lambda = 441\,\text{nm}$ was used as a pump that irradiated the cell from the side of the tested surface. The laser beam was focused with the lens $f_1 = 0.5\,\text{m}$ to the spot with the halfwidth $d = 0.22\,\text{mm}$. The polarization of the pump beam, $\vec{E}_{pump}$, made an angle $\varphi_0 = 45^\circ$ to the rubbing direction of the polyimide layer. Power density in the spot was about $10\,\text{W/cm}^2$. The linearly polarized probe beam of *He-Ne* laser ($\lambda = 632\,\text{nm}$) was focused with the lens $f_2 = 0.05\,\text{m}$ into the center of the irradiated spot from the side of the reference surface. The polarization of the probe beam was parallel to the rubbing direction of the polyimide layer. The thickness of the cell was about $30\,\mu\text{m}$ and adiabatic propagation of the probe beam (Maugine regime) was realized. In this case probe beam polarization followed the director over the cell thickness, and on the tested surface it was parallel to the director position on the tested substrate, $\vec{n}_{test}$. It allowed us to follow reorientation of the director on the tested surface by measuring the intensity of the probe behind the analyzer.

Irradiation of the cell with the pump resulted in reorientation of the LC director from its initial position $\vec{n}_0$, parallel to the rubbing direction on the tested surface. The typical director reorientation dynamic is presented on the Figure 1. Negative values of the angle φ_{test} between $\vec{n}_{test}$ and $\vec{n}_0$ correspond to the director reorientation *away from* light polarization vector $\vec{E}_{pump}$, and positive values φ_{test} correspond to the reorientation *toward* $\vec{E}_{pump}$. On can see that the dependence $\varphi_{test}(t)$ consists of parts: initial fast director turn away from $\vec{E}_{pump}$ with the characteristic times order of 10 ms, much slow director reorientation in the same direction, and finally slow reorientation toward the pump polarization.

We suggested that slow director reorientation (2nd and 3rd parts of the curve) is connected with light-induced anchoring development due to AD-processes of MR molecules on the tested surface as in isotropic phase [2]. The process evoking the fast director reorientation over the

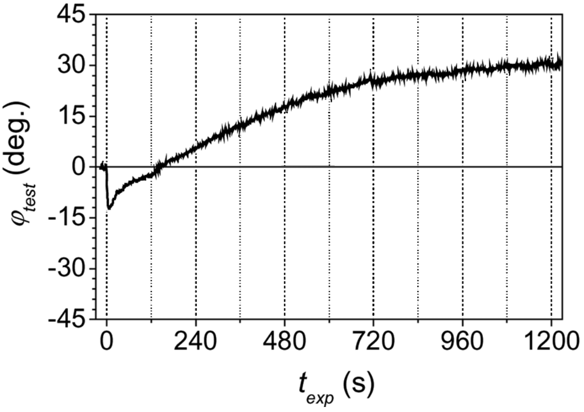

FIGURE 1 Dynamic of director reorientation of azo-dye-doped LC in nematic phase. $I = 10\,\mathrm{W/cm^2}$.

tested surface is associated with the sliding effect caused by light-induced bulk reorientation [10].

The relaxation of the director after the switching off the pump is rather complicated and strongly depends on the time of the previous exposure t_{exp} (Fig. 2). Switching off the pump just after several

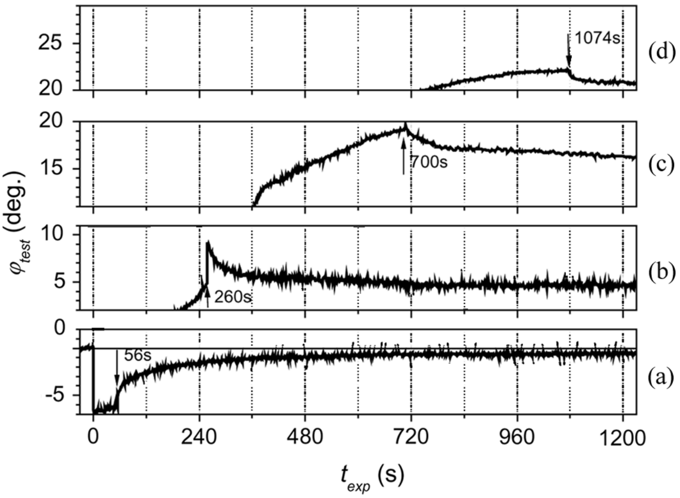

FIGURE 2 Dependence of relaxation of light-induced director reorientation at switching-off light on exposure time. Arrows mark instants of time of the pump switch-off.

seconds of the illumination results in the recovery of the initial orientation of the director with the close characteristic time as the initial fast director reorientation one. Longer pump exposure results in appearance of slow component of the director relaxation (Fig. 2), which contribution increases with the pump exposure. The later the switching-off occurs, the slower relaxation time and lower relaxation amplitude are. The direction of the slow director relaxation also depends on the time of the previous exposure. The director relaxed toward $\vec{E}_{pump}$ in the second part of the dependence $\varphi_{test}\ (t_{exp})$ (Fig. 2a) and turned away from $\vec{E}_{pump}$ in the third part of $\varphi_{test}\ (t_{exp})$ (Fig. 2b,c,d). Increase of the pump exposure leads to longer relaxation of the director, and smaller amplitude. The characteristic time of slow relaxation component is $t_{sl}^{rel} \approx 10^2\,\mathrm{s}$ at $t_{exp} \approx 60\,\mathrm{s}$, then $t_{sl}^{rel} \geqslant 10^4\,\mathrm{s}$ at $t_{exp} \approx 1000\,\mathrm{s}$. Besides, one can suggest that not-reversible component of director reorientation appears at long pump irradiation (this fact needs additional checking).

3. MODEL AND DISCUSSION

There are two main processes initiated by polarized light in the studied system. The first one is light-induced adsorption/desorption of MR molecules. These processes are rather slow (characteristic times 10^2–10^3 s) and were studied in details in recent publications [2,3]. The second one is reorientation of the LC director due to light-induced bulk torque [14,15]. This effect is common for azo-dye-doped LCs and usually is associated with consequent trans-cis-trans-... isomerisation of azo-dye. The characteristic times of the LC response to the light-induced bulk torque $t_{bulk} = 0.01 - 1\,\mathrm{s}$ depending on the cell thickness. Our experimental data can be qualitatively described involving the mentioned effects, namely, light-induced drift of the easy orientation axis caused by AD-processes in presence of light-induced bulk director torque.

First, let us consider a state of the LC cell before light irradiation. As it was shown in Ref. 3;5, after filling of the cell MR molecules were adsorbed on the polymer surface creating a “dark-adsorbed” layer. Since MR molecules exist preferably in a trans-form at a room temperature, the “dark-adsorbed” layer consists of trans-isomers. During cooling, just after transition from the isotropic phase to the mesophase, molecules in the LC bulk are preferably oriented along the director given by the strongly anchoring reference substrate. In this case the adsorbed MR molecules are distributed accordingly to the angular distribution of the LC molecules in the bulk. The angular distribution of the long axes of the adsorbed molecules $F_S(\varphi_S)$ is determined with projection of the bulk distribution $F_V(\Omega_V)$ onto the surface.

Therefore, the “dark-adsorbed” layer has the anisotropic angular distribution of dye molecules with the maximum parallel to $\vec{n}_0$, and the “dark-adsorbed” layer serves an aligning layer with the easy axis $\vec{e}_{test} \,||\, \vec{n}_0$. The anchoring energy of LC with this layer is determined with a width of the angular distribution of the adsorbed trans-isomers of MR molecules and their concentration [16].

Let us consider now what is happening with the angular distribution of MR molecules when the light irradiation starts. First, a fast director reorientation due to the light-induced bulk torque occurs. Since the anchoring on the tested surface is week, this torque causes the director reorientation not in the bulk only but on the tested surface also (see the jump of the director away from $\vec{E}_{pump}$ in Fig. 1). It results in rotation of the bulk distribution function $F_V(\Omega_V)$ outward initial position $\vec{n}_0$ and in mismatching of the director on the tested substrate, $\vec{n}_{test}$, with the easy axis $\vec{e}_{test}$. Since the maximum of the angular distribution function of the LC molecules in the bulk near the surface is parallel to the new orientation $\vec{n}_{test}$, permanent exchange with the molecules between the bulk and the surface specified by light-induced and spontaneous AD-processes leads modification of the surface angular distribution function $F_S(\varphi_s)$. Light-induced desorption of strongly dichroic MR molecules decreases the number of spontaneously adsorbed molecules oriented nearby $\vec{E}_{pump}$. Light-induced trans-cis isomerisation of MR molecules located nearby of the polymer surface substantially increases probability of their adsorption onto the surface due to larger dipole moment [17] and polarity [18] of cis-isomers. It causes light-induced adsorption of MR cis-isomers onto the polymer surface, preferably along $\vec{E}_{pump}$.

At the moment $t_{exp} = 0$ the adsorbed molecules distribution consists only of dark-adsorbed molecules. Therefore, changing of the surface distribution $F_S(\varphi_s)$ occurs substantially due to light-induced desorption of trans-isomers preferably oriented at $\varphi_0 = 45^\circ$. It leads to rotation of the $F_S(\varphi_s)$ maximum and of the easy axis outward $\vec{n}_0$. The reorientation angles both for the easy axis and the director (which are different) increase with exposure time due to continued desorption of MR molecules (the region from $t_{exp} \approx 0\,\mathrm{s}$ to $t_{exp} \approx 150\,\mathrm{s}$ in Fig. 1). Later, when the contribution of the light-induced adsorbed MR molecules becomes essential that results in a gradual rotation of $F_S(\varphi_s)$ and of the easy axis toward the polarization $\vec{E}_{pump}$ (the region from $t_{exp} \approx 150\,\mathrm{s}$ in Fig. 1). The anchoring energy associated with $\vec{e}_{test}$ increases with time due to increase of the concentration of adsorbed cis-isomers of MR molecules on the test substrate.

Switching-off the pump beam results in changing the cis-isomer of Methyl Red back into the trans-form, that is disappearance of the light-induced bulk torque and fast relaxation ($t_{bulk} \approx 1$ s) of the director toward a current position of the easy axis. Revising the isomer content in the LC mixture slightly decreases the anchoring energy but does not influence to the qualitative behavior of the system. At the beginning of irradiation the light-induced easy axis is not changed yet and director returns to the initial position completely. Longer exposure (part 2 of the dependence $\varphi_{test}(t_{exp})$) results in producing of the light-induced anisotropy axis perpendicular $\vec{E}_{pump}$ and drift of the easy axis $\vec{e}_{test}$ right away from $\vec{n}_0$. Therefore, switching off the pump leads to the fast relaxation of the director to the current position $\vec{e}_{test}$ rotated away from $\vec{E}_{pump}$. Then, the bulk torque from the reference surface causes slow drift of $\vec{e}_{test}$ toward $\vec{n}_0$. In the third part of the dependence $\varphi_{test}(t_{exp})$ the light-induced adsorption prevails. Switching-off the pump results in the fast relaxation of the director to the current position $\vec{e}_{test}$ now shifted toward $\vec{E}_{pump}$, but from $\vec{n}_0$, and following slow drift of the easy axis to $\vec{n}_0$. Increasing of exposure time leads to increase of the concentration of the light-induced adsorbed azo-dye molecules and the anchoring energy of LC on the tested surface. It causes rotation of the easy axis toward $\vec{E}_{pump}$ and decreases the mismatching angle between the easy axis $\vec{e}_{test}$ and the direction $\vec{n}_{test}$. The increase of the anchoring energy results in decrease of the amplitude of the fast component of relaxation and slowing down of the drift of the easy axis back to $\vec{n}_0$. If the anchoring energy is strong enough, the mismatching between $\vec{n}_{test}$ and $\vec{e}_{test}$ becomes so small that relaxation of the director after the switching-off the pump is negligible.

CONCLUSIONS

We report on experimental study of light-induced anchoring evolution of azo-dye-doped liquid crystal (LC) in nematic phase and present a model of this effect. To describe the experimental results we considered the gliding effect as a result of light-induced anisotropic adsorption/desorption of dye molecules on/from the boundary polymer aligning layer in the presence of light-induced bulk torque due to ordering of absorbing dye molecules. Our model qualitatively describes the observed drift of the light-induced easy axis.

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