PHYSICAL REVIEW E **73**, 031701 (2006)

Evolution of light-induced anchoring in dye-doped nematics: Experiment and model

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(Received 18 October 2005; published 2 March 2006)

A series of experiments was carried out to describe the evolution of light-induced anchoring in dye-doped nematic liquid crystals (LCs) at irradiation with polarized light. The experiments included cells filled with a pure pentyl-cyanobiphenyl (5CB) and containing a layer of azo dye deposited on an aligning film, as well as cells filled with azo dye doped 5CB, which allowed us to distinguish the role of "surface" and "bulk" dye molecules in the evolution of light-induced anchoring. Modifications of the spectra of spontaneously adsorbed dye molecules under illumination enabled us to assert that light-induced desorption is a mechanism responsible for producing an easy orientation axis in a dark-adsorbed layer. We found that the evolution of light-induced anchoring involves a competition between light-induced desorption and adsorption of the dye molecules on the aligning surface, and the final anchoring is determined by the total light irradiation dose. These data allowed introducing a theoretical model of light-induced anchoring of dye-doped nematic LCs that quantitatively described the experimental results and portrayed the whole evolution of the dye-doped LC cell at irradiation.

DOI: 10.1103/PhysRevE.73.031701 PACS number(s): 61.30.Hn, 68.43.Mn, 78.20.−e

I. INTRODUCTION

Light-induced surface-mediated effects in liquid crystals (LCs) have been intensively studied for the past decade because of intriguing science and promising applications. Classical examples of these effects are photoalignment and photoreorientation of LCs arising from light-induced anisotropy on a polymer aligning surface [1–3]. Usually the anisotropy axis appears from the absorption of polarized light by the aligning layer that initiates photochemical processes in the polymer and the LC patterns on the light-induced anisotropy axis. More exotic effects can be observed when the LC plays a guiding role in the development of the anisotropy of the aligning surface. This kind of photoaligning effect is known as *light-induced anchoring*, which is caused by light absorption in liquid crystal. Light-induced anchoring was discovered by Voloshchenko *et al.* in dye-doped nematic LC [4]. It was found that irradiation of a planar cell with the LC 5CB doped with azo dye Methyl Red (MR) under illumination with polarized light in the absorption band of MR produced an easy orientation axis on a nonphotosensitive aligning surface. Light-induced adsorption of the phototransformed MR molecules onto the surface was suggested to be a cause of the effect. Further studies confirmed this hypothesis and demonstrated the important role of the orientation of MR molecules in effective adsorption [5]. In addition, a crucial link between a layer of azo-dye molecules, which initially spontaneously adsorbed on the aligning surface ("dark-adsorbed layer" further), and the final direction of the easy axis was demonstrated [6,7]. These studies led to a model that describes the evolution of the easy orientation axis as a competition between light-induced adsorption of the azo-dye molecules from the bulk and light-induced desorption of the dye molecules from a dark-adsorbed layer. Adsorption of the azo dye led to an easy axis parallel to light polarization, while azo-dye desorption resulted in an easy axis perpendicular to light polarization. It was suggested that the result of this competition is due to differing dependencies of the adsorption/desorption processes on light intensity (nonlinear and linear, respectively) that caused different directions of the easy axis in high- and low-intensity regimes [6].

Even though obtained results to date support the model, some points require additional clarification. The mechanism of light-induced desorption from a dark-adsorbed layer is still under discussion since photodegradation of the dark-adsorbed molecules may also lead to these observations. Postulated proportionality of the concentration of adsorbed/desorbed molecules to the light intensity was not grounded enough and experimentally checked. At the same time, these data are crucial for validating the microscopic model of light-induced anchoring and its evolution. In addition, Lee *et al.* [8] recently reported on producing a ripple morphology structure of light-adsorbed azo-dye molecules on an ITO surface that was observed to affect the evolution of anchoring.

Here we report on the study of light-induced anchoring that has allowed us to distinguish the roles of "surface" and "bulk" dye molecules in the evolution of light-induced anchoring. Modifications of the spectra of spontaneously adsorbed dye molecules under illumination indicates that light-induced desorption is a mechanism of producing an easy orientation axis in a dark-adsorbed layer. We have found that the evolution of light-induced anchoring is governed by a competition between light-induced desorption and adsorption of dye molecules on an aligning surface, while the final anchoring is determined by the light irradiation dose—not the intensity. These data suggest a theoretical model involving light-induced anchoring of dye-doped nematic LCs that we show quantitatively describes the experimental results as well as the evolution of LC cell under irradiation.

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1539-3755/2006/73(3)/031701(8)/$23.00

II. MATERIALS AND EXPERIMENTS

We studied light-induced anchoring in the LC pentylcyanobiphenyl (5CB, clearing point $T_c = 34.5$ °C) from Merck that was doped with the azo dye Methyl Red (MR) from Aldrich. MR absorbs light in the blue-green region of visible spectra, and trans-cis isomerization [9,10] as well as light-induced adsorption [5,11,12] are characteristic features of this azo dye. To decrease the likely mutual interaction of MR molecules, a dilute weight concentration of MR $c = 0.5\%$ was chosen. For light irradiation we used a polarized Gaussian beam from a He-Cd laser (wavelength $\lambda = 0.44$ μm, power $P < 4$ mW).

There are a number of possible processes governing the evolution of light-induced anchoring. They can be light-induced adsorption of the azo-dye molecules, phototransformation of the azo dye in a dark-adsorbed layer, light-induced desorption of dye molecules from the dark-adsorbed layer, light-induced bulk reorientation of LC, easy axis gliding, LC sliding, etc. This diversity of mechanisms makes light-induced anchoring a rather complex phenomenon, whose understanding requires experiments where the various processes are controlled. In our first experiment, we excluded bulk effects (light-induced adsorption of MR, director bulk reorientation, gliding of the easy axis, etc.), studying only the process located in the dark-adsorbed layer of MR molecules.

A. Anchoring due to light-induced anisotropy in a dark-adsorbed layer

To study light-induced anchoring due to photoprocesses in a dark-adsorbed dye layer only, we prepared a specific combined LC cell where a dark-adsorbed layer of MR molecules existed whereas "bulk" dye molecules were absent. As in Refs. [7,13], the cell consisted of reference and tested substrates separated by cylindrical polymer spacers (cell thickness 30 μm). The reference substrate was covered with rubbed polyimide and provided strong uniform anchoring of the dye-doped LC with a small pretilt angle ($\sim 1-2°$). The tested substrate was covered with an isotropic layer of fluorinated polyvinylcinnamate (PVCN-F). The polymer was irradiated with unpolarized UV light of 10 mW power for 15 min in order to prevent dissolution by the LC [14]. The treated PVCN-F provided for a degenerate planar alignment of the LC. The cell was filled in two steps. First, the cell was filled with dye-doped LC in the isotropic phase ($T = 50$ °C) and maintained at constant temperature on a hot stage for 3 h. As we described previously [7], this duration is sufficient to form a dark-adsorbed layer of MR molecules on an aligning surface. Second, we extruded doped LC out of the cell by absorbing it from the cell edge with cloth followed by filling the cell again with pure LC being at $T = 50$ °C. Thus, we obtained the cell filled with pure 5CB between aligning substrates covered with layers of spontaneously adsorbed MR molecules. One can expect that the adsorbed MR layer is angularly isotropic on the PVCN-F surface.

While in the hot stage at $T = 50$ °C, the cell was irradiated from the side of the tested surface with a Gaussian beam from a He-Cd laser at various intensities P and exposure times t. The intensity distribution of the beam cross section in the plane of the cell was described by $I = I_0 \exp[-(r/R)^2]$, where $I_0 = P/(\pi R^2)$, P was power of the beam, and $R = 110$ μm the beam radius. The angle ϕ between the initial direction of the director $\vec{n}_0 = \vec{n}_{rub}$ and light polarization vector $\vec{E}$ was set at 45°.

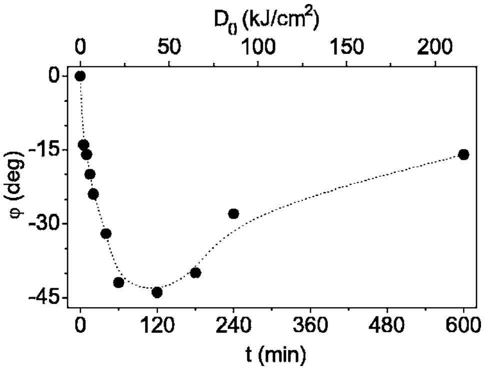


FIG. 1. The dependence of the twist angle φ due to the anisotropy in dark-adsorbed MR layer on exposure time. Light intensity $I_0 = 6$ W/cm^2.

After irradiation the cell was cooled down to the room temperature and the light-induced textures were examined with a polarizing microscope. A somewhat inhomogeneous planar alignment of the dye-doped LC preferably parallel to the rubbing direction on the reference surface was observed in the unirradiated area. In the irradiated areas we observed stable twist structures. Analysis of these structures indicated that the director was parallel to the rubbing direction on the reference surface, $\vec{n}_0$, and made an angle φ with $\vec{n}_0$ on the tested surface. This indicates a light-induced easy axis on the tested surface, $\vec{e}_{test}$, not parallel to $\vec{n}_0$. The dependence of the maximum value of the twist angle $\varphi(t)$ on the exposure time at $I_0 = 6$ W/cm^2 is presented in Fig. 1. One can see that the director always turns away from the light polarization vector $\vec{E}$, that is, the sign of the twist deformation is negative. The dependence of $\varphi(t)$ is not monotonic in t; it was observed the maximum of director reorientation occurs at $t \approx 120$ min followed by a slow decrease. In order to obtain the same twist angle the light intensity increase was needed to be accompanied with proportional decrease of the exposure time, that is, the effect is determined by the light irradiation dose $D_0 = I_0 t$, that is total irradiation in a certain exposure time.

The observed dependence $\varphi(t)$ reflects the evolution of the light-induced anisotropy in the adsorbed layer of MR molecules; the anisotropy axis appears perpendicular to $\vec{E}$ with its strength increasing with time, peaking, and then diminishing. As it was noted above, dye reorientation due to cascade trans-cis isomerization [15,16], angular hole-burning due to irreversible trans-cis isomerization or photodegradation of azo dye [15,17], and photodesorption of dye molecules [6] are all possible mechanisms of the light-induced anisotropy in the dark-adsorbed MR layer. A mechanism of reversible reorientation would lead to a monotonic increase of the anisotropy and a stationary anisotropy axis perpendicular to $\vec{E}$ [15]. In opposite, after achieving of a maximum turn, a following decrease of reorientation angle was observed. Therefore, this mechanism can be excluded from the

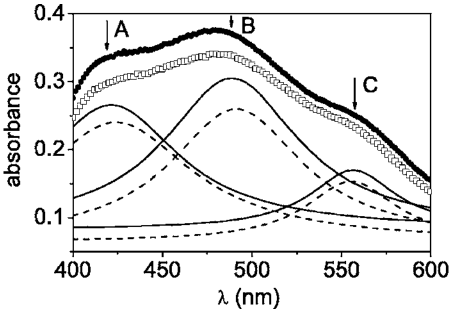


FIG. 2. The change of the absorbance spectra of a dark-adsorbed MR layer due to light irradiation in the visible band. Circles ●—initial absorption; open squares ☐—absorption after irradiation. Solid and dashed lines are the analysis of absorbance curve before and after irradiation, respectively. *A* band corresponds to the cis-form absorbance (n-π^* transition), $\lambda_{\max}=417$ nm; *B* band corresponds to the trans-form absorbance (n-π^*), $\lambda_{\max}=465$ nm; *C* band corresponds to the zwitterions (or dye dimers), $\lambda_{\max}=560$ nm. Irradiation intensity $I_0=6$ W/cm^2, exposure time $t=60$ min.

consideration, and just angular hole burning, photodegradation, and photodesorption are left to be checked.

We studied the absorbance spectra of the dark-adsorbed MR layer both before and after irradiation. The change in the absorbance spectra of a dark-adsorbed MR-layer in the visible band is presented in Fig. 2. According to Ref. [18], the *A* band corresponds to n-π^* absorption of cis form ($\lambda_{\max}=417$ nm), whereas a *B* band is associated with n-π^* absorption of trans form ($\lambda_{\max}=465$ nm), and a *C* band corresponds to absorption of either zwitterionic form or dimers ($\lambda_{\max}=560$ nm). It is evident that there is no redistribution between the trans and cis absorption bands after irradiation, merely a decrease of the absorption in all three bands is observed. This excludes irreversible trans-cis isomerisation from consideration. Photodestruction of the MR molecules could result in increased absorption in the far UV part of spectra after the irradiation. However, measurements of the absorption spectra in the region including the UV only showed decreased absorption (Fig. 3). Therefore, one can conclude that light-induced desorption of the MR molecules is the mechanism responsible for the observed light-induced anisotropy in the dark-adsorbed layer.

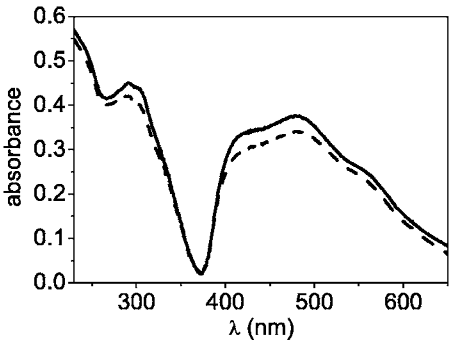


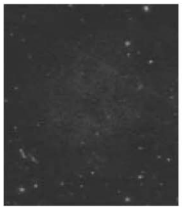
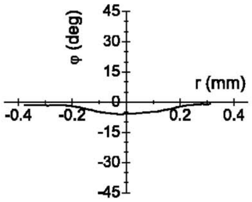
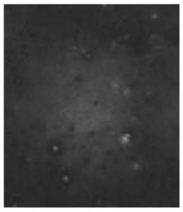
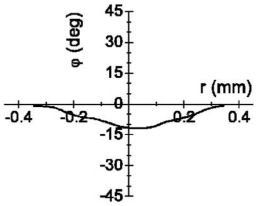
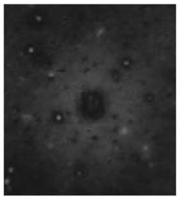
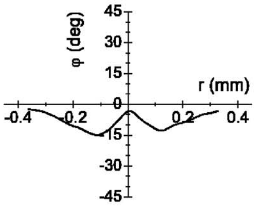
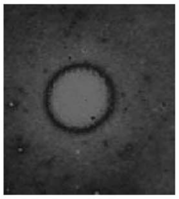
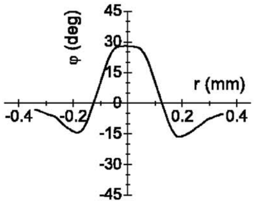
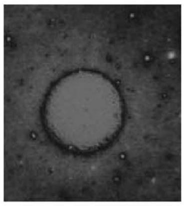
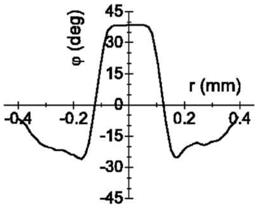
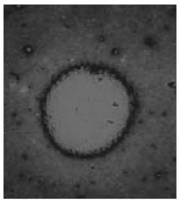
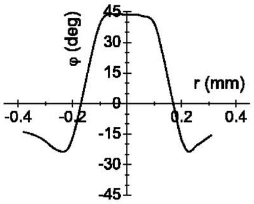
FIG. 3. The change of the absorbance spectra of dark-adsorbed MR layer due to light irradiation. Solid line, initial absorption; dashed line, absorbance after irradiation. Irradiation intensity $I_0=6$ W/cm^2, exposure time $t=60$ min.

B. Light-induced anchoring in the presence of MR molecules in the bulk

In the experiments described above, we oriented the LC using processes occurring in the dark-adsorbed layer only. Here we describe how MR molecules in the LC bulk affect the light-induced anchoring. To eliminate the effects of the bulk LC director reorientation during the evolution of the easy axis, we irradiated the cell in the isotropic phase of the LC. As in our previous study of hidden photoalignment of liquid crystals [6], we irradiated the combined cell with a mixture of 5CB and MR (0.5 wt. %) in the isotropic phase ($T=50$ °C). The geometry of the irradiation was the same as described above: the combined cell was irradiated from the tested surface by a Gaussian beam from a He-Cd laser, which polarization made an angle 45° to the rubbing direction on the reference surface. We investigated the twist structures in the irradiated areas after cooling the cell down to the room temperature. Analyses of the twist structures and their correlation with the distribution of the light intensity in the incident Gaussian beam allowed us to determine the intensity dependence of the twist angle $\varphi(r)$ in the irradiated area at various exposure times t.

We found that the dependence of $\varphi(r)$ measured at different exposure times drastically differed from those in the previous system. The evolution of light-induced twist structures in the irradiated areas is shown in Table I. The presence of the MR molecules in LC bulk resulted in a complicated anchoring evolution. Depending on the intensity and exposure time, the director reoriented either toward or away from the polarization of the incident light. Starting from a short exposure time, the director turned away from the polarization over the irradiated area (texture nos. 1 and 2). Then, the twist angle passed through zero (texture no. 3), and changed sign in the central part of the irradiated spot. Longer exposure time resulted in an extension of the region where the director reoriented toward $\vec{E}$ (texture nos. 4–6). Unlike previous measurements [6,7], there was an extended range of exposure times $t=(0-200)$ min and intensities $I_0=(0-6$ W/cm$^2)$. This allowed us to check whether the characteristics of light-induced anchoring depended on either the intensity or irradiation dose. In contradistinction to the conclusion of Ref. [6], which was made on a basis of a limited exposure range, we found that the value and the sign of the light-induced twist were determined by the light irradiation dose $D(r)=I(r)t$—not by the light intensity. In Table II one can see the light-induced twist structures obtained at maximal intensity $I_0=6$ W/cm^2 and minimal exposure time $t=9$ min, and vice versa $I_0=0.3$ W/cm^2, $t=180$ min, but at the same dose $D_0=3.2$ kJ/cm^2. Despite difference in the intensities and exposure times, the textures are identical. To observe the dependence of the light-induced twist angle on the light irradiation dose, we plotted the dependence of $\varphi(D(r))$ for textures obtained at various exposure times and $P=2.5$ mW on the common graph (Fig. 4). One can see that at a low light irradiation dose, the doped LC behaves in the same way as the pure LC on a layer of dark-adsorbed MR molecules: that is, light-induced desorption leads to an easy axis perpendicular to the polarization $\vec{E}$, and to a negative twist. At higher

TABLE I. Images of light-induced structures at different exposure times t. $I_0=6\ \mathrm{W/cm^2}$.

No.	t, min	Texture in the irradiated area	Twist angle distribution
1	1		
2	3		
3	6		
4	10		
5	15		
6	20		

dose, an additional mechanism of light-induced anchoring starts dominating and causes the director to turn in the opposite direction, i.e., toward positive twist. This mechanism is proved to be light-induced adsorption of MR molecules from the LC bulk [12].

III. MODEL AND DISCUSSION

The experimental results together with the data obtained in Refs. [4,6,7,19–21] allows us to describe the production and evolution of light-induced anchoring. Cells filling with doped LC at $T>T_c$ results in the development of an isotropic layer of anisotropic 5CB and MR molecules on the aligning surface. The orientation of the MR molecules in the LC bulk is also isotropic. A majority of MR molecules are in the trans form in the LC bulk [16,18], suggesting that the spontaneously adsorbed MR molecules are trans isomers.

Irradiation of the cell with polarized light results in absorption of light by the MR molecules in the dark-adsorbed layer and the LC bulk. Electronic excitation of the MR molecules in the adsorbed layer causes their desorption from the surface. At the same time, the reverse spontaneous adsorption of MR molecules to the same location is very unlikely. Since the MR molecules predominantly absorb light with its polarization parallel to their long axes, the resulting anisotropic distribution of the remained adsorbed molecules has a maximum perpendicular to polarization $\vec{E}$. The flux of the desorbed molecules is proportional to the number of absorbed quanta (irradiation dose) and the number of dark-adsorbed molecules, which is limited. Therefore, the anisotropy of the light-induced distribution of dark-adsorbed MR molecules decreases at long exposure and this mechanism of light-induced anchoring depletes with time.

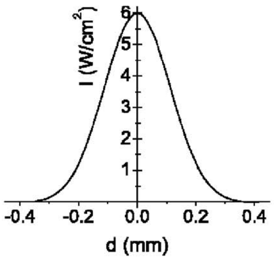
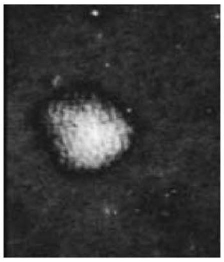
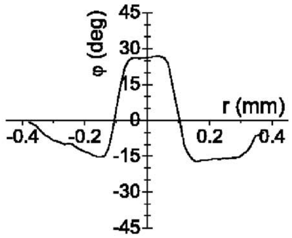
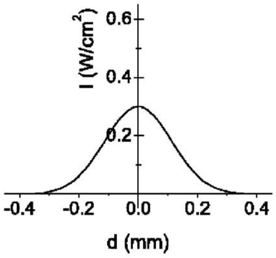
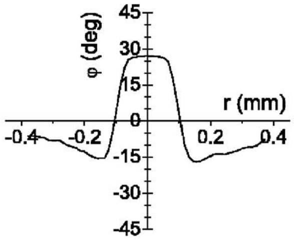
According to Refs. [4,12], absorption of polarized light by molecules in the bulk also contributes to light-induced anchoring owing to the light-induced adsorption of MR molecules. Microscopically, adsorption of azo compounds on the hydrophilic surface is enhanced by trans-cis isomerization [22], since the cis form possesses a larger dipole moment and polarity compared with trans form [23]. Due to a positive absorption dichroism of MR molecules, trans-cis isomerization is most effective for the molecules oriented parallel to $\vec{E}$. Therefore, an anisotropic distribution of adsorbed cis isomers on the aligning surface occurs parallel to the polarization $\vec{E}$. The adsorbed molecules can form H bonds with reactive fragments of the aligning polymer surface making desorption unlikely.

Thus, the observed angular distribution of MR molecules on the aligning surface is determined by the angular distribution of the light-desorbed and light-adsorbed MR molecules. The reservoir of light-induced adsorbing molecules from the LC bulk is almost infinite as compared to the reservoir of MR molecules in the dark-adsorbed dye layer. Therefore, anchoring due to light-induced adsorption of "bulk" MR molecules finally "wins" the anchoring due to light-induced desorption of "surface" MR molecules at high light irradiation dose.

To describe the evolution of light-induced anchoring in the cell, we need to determine the director profile across the cell thickness taking into account the angular distribution of MR molecules on the substrate. According to our model, the angular distribution functions $f_d(\theta,I,t)$ and $f_a(\theta,I,t)$ of dark-adsorbed MR molecules and light-adsorbed MR molecules on the aligning surface under illumination with polarized light is given by two kinetic equations,

$$\frac{\partial f_d(\theta,I,t)}{\partial t} = -\alpha_d I f_d(\theta,I,t)\cos^2(\theta-\phi), \tag{1}$$

TABLE II. Light-induced twist structures between crossed polarizers at the same light irradiation dose $D_0=3.2\ \mathrm{kJ/cm^2}$.

t, min	Intensity distribution in the pump beam	Texture of the irradiated area	Twist angle distribution
9			
180			

$$\frac{\partial f_a(\theta,I,t)}{\partial t}=\alpha_a I\cos^2(\theta-\phi). \tag{2}$$

Here θ is the azimuthal angle of the dye molecules' orientation with respect to rubbing direction, α_d is the efficiency of desorption, α_a is the efficiency of adsorption, and ϕ is the angle between the light polarization and rubbing direction at the reference substrate. In the initial state ($t=0$), the MR molecules in the dark-adsorbed layer are oriented isotropically and $f_d(t=0)=(N_d/2\pi)$, N_d is the initial surface concentration of MR molecules that can be desorbed in the irradiated area.

Solution of the differential Eqs. (1) and (2) describes the evolution of the angular distribution function of the dye due to light-induced desorption and adsorption processes,

$$f_d(\theta,I,t)=\left(\frac{N_d}{2\pi}\right)\exp[-\alpha_d It\cos^2(\theta-\phi)], \tag{3}$$

$$f_a(\theta,I,t)=\left(\frac{N_a}{2\pi}\right)\alpha_a It\cos^2(\theta-\phi). \tag{4}$$

where N_a is the initial surface density of MR molecules near the cell wall (i.e., number of molecules per unit area of the tested surface) initially dissolved in the LC cell in the irradiated area. One can see that the distribution functions $f_d(\theta,It)$, $f_a(\theta,It)$ depend on the product It, that is, the light irradiation dose D.

The evolution of the resulting distribution function $f_{sum}=f_d(\theta,It)+f_a(\theta,It)$ is shown in Fig. 5 for our experimental parameters $N_d=10^{18}\ \mathrm{m^{-2}}$; $N_a=3\times10^{20}\ \mathrm{m^{-2}}$ (similar values were estimated in Ref. [12]) and $\alpha_d=4\times10^{-4}\ \mathrm{cm^2/J}$; $\alpha_a=3.4\times10^{-7}\ \mathrm{cm^2/J}$. As one would expect from the model, light-induced desorption of MR molecules leads to an anisotropic angular distribution of MR molecules, which maximum is perpendicular to the polarization $\vec{E}$, whereas light-induced adsorption of MR molecules from the bulk results in anisotropic angular distribution, which maximum is parallel to $\vec{E}$.

Evolution of the director profile in the LC cell due to the transformation of the distribution function f_{sum} of MR molecules on the tested surface is determined by the minimum of the total free energy of the LC in the cell per unit surface area,

$$F=\frac{1}{2}K_{11}\int(\mathrm{div}\,\vec{n})^2dz+\frac{1}{2}K_{22}\int(\vec{n}\cdot\mathrm{curl}\,\vec{n})^2dz+\frac{1}{2}K_{33}\int(\vec{n}\times\mathrm{curl}\,\vec{n})^2dz+W_S, \tag{5}$$

where K_{11},K_{22},K_{33} are the splay, twist, and bend elastic constants, respectively, and W_S is the anchoring energy due to the anisotropic distribution of MR molecules at the tested substrate; the anchoring energy on the reference surface is supposed to be infinite, which corresponds to our experiment.

We assume that the director reorients in the plane of the cell and director orientation depends only on distance from the cell surface: $\vec{n}=[\sin\varphi(z),\cos\varphi(z),0]$, where φ is the angle between the director and the rubbing direction on the reference surface. In this case, the Euler-Lagrange equation and boundary conditions are

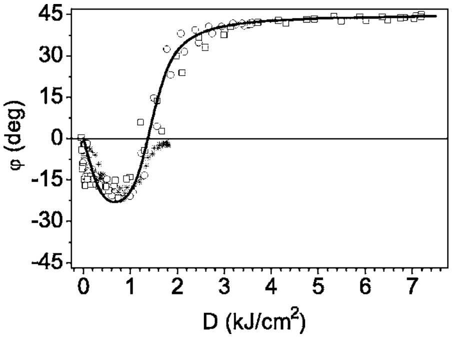


FIG. 4. The dependence of the twist angle φ of director reorientation on light irradiation dose D. The symbols denote our experimental results; asterisks $*$—$t=6$ min, open circles ○—$t=10$ min, open squares □—$t=20$ min. The solid line is the solution of Eq. (10) with parameters $w_{MR}^{dark}=2\times10^{-23}$ J/molecule; $w_{MR}^{light}=6\times10^{-23}$ J/molecule.

$$\frac{d^2\varphi}{dz^2}=0, \quad \varphi(z=0)=0, \quad \left(K_{22}\frac{d\varphi}{dz}-\frac{dW_S}{d\varphi}\right)_{z=L}=0. \quad (6)$$

The solution of this equation is $\varphi(z)=az$, $a=(1/K_{22})\times(dW_S/d\varphi)|_{z=L}$ with the director orientation at the tested substrate determined by the nonlinear equation

$$\varphi_{z=L}=\left.\frac{L}{K_{22}}\frac{dW_S}{d\varphi}\right|_{z=L}. \quad (7)$$

To connect the anchoring W_S with the angular distribution of MR molecules on the tested surface and light polarization, we assume that the potential energy has a Rapini-type form and is given by the distribution of MR molecules with respect to the director of LC,

$$W_S(\varphi,t)=\frac{1}{2}w_{MR}^{dark}\int_0^{2\pi}(\vec{n}\cdot\vec{e}_{MR})^2 f_d(\theta,t)d\theta + \frac{1}{2}w_{MR}^{light}\int_0^{2\pi}(\vec{n}\cdot\vec{e}_{MR})^2 f_a(\theta,t)d\theta. \quad (8)$$

Here w_{MR}^{dark}, w_{MR}^{light} are the parameters describing the interaction of the LC with dark-adsorbed MR molecule and light-adsorbed MR molecule, respectively; the unit vector $\vec{e}_{MR}=(\sin\theta,\cos\theta,0)$ describes the orientation of the long axis of MR molecules.

Substituting (3) and (4) to (8) one obtains,

$$W_S(\varphi,It) = \frac{N_d w_{MR}^{dark}}{4\pi}\int_0^{2\pi}\cos^2(\varphi-\theta)\exp[-\alpha_d It\cos^2(\theta-\phi)]d\theta + \frac{N_a w_{MR}^{light}}{4\pi}\alpha_a It\int_0^{2\pi}\cos^2(\varphi-\theta)\cos^2(\theta-\phi)d\theta, \quad (9)$$

and Eq. (7) finally reads

$$\varphi(It,L,\phi)=\frac{N_d w_{MR}^{dark}}{2\pi}\frac{L}{K_{22}}\int_0^{2\pi}\sin\{2[\varphi(It,L,\phi)-\theta]\}\times\exp[-\alpha_d It\cos^2(\theta-\phi)]d\theta + \frac{N_a w_{MR}^{light}}{2\pi}\frac{L}{K_{22}}\alpha_a It\int_0^{2\pi}\sin\{2[\varphi(It,L,\phi)-\theta]\}\cos^2(\theta-\phi)d\theta. \quad (10)$$

The nonlinear equation (10) describes the dependence of the twist angle φ on the light irradiation dose D. Numerical solutions for various values of w_{MR}^{dark} and w_{MR}^{light} are presented in Fig. 6. Depending on the values of w_{MR}^{dark} and w_{MR}^{light}, one can obtain qualitatively different solutions; the director can reorient toward $\vec{E}$ $(\varphi>0)$, away from $\vec{E}$ $(\varphi<0)$ with orientation transitions depending on dose. Varying the parameters w_{MR}^{dark} and w_{MR}^{light}, we obtained a very good fit with the experimental data presented in Fig. 4 where $w_{MR}^{dark}=2\times10^{-23}$ J/molecule and $w_{MR}^{light}=6\times10^{-23}$ J/molecule. Substituting these values into Eq. (9) and fitting with the Rapini potential $W_S=\frac{1}{2}W_0\sin^2\varphi$ the dependence of light-induced anchoring energy W_0 on the light irradiation dose (Fig. 7) is obtained. These calculated values $W_0\approx10^{-5}$ J/m^2 agree with experimental values obtained elsewhere [2,4,6–8]. The change of the sign of the value W_0 at low dose indicates a change in the direction of the easy axis from perpendicular to parallel to the polarization of the light.

Equation (10) also well describes the experimental data obtained in Ref. [21] in other geometries, namely, with the polarization of the incident light parallel and perpendicular to the initial orientation of the director in the cell. Calculated exposure dependencies of the twist angle φ for these geometries are presented in Fig. 8. One can see that at $\phi=0°$ the director reorients in a limited range of dose and always away

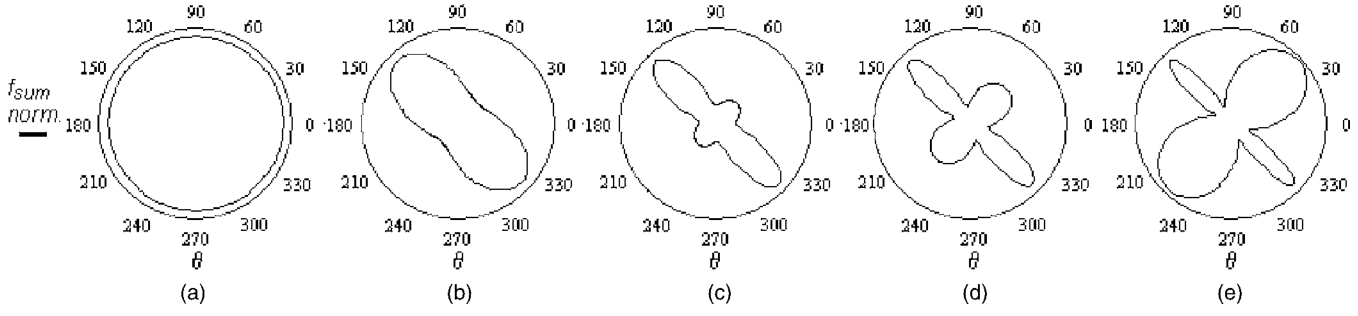


FIG. 5. Dependence of the normalized distribution function of MR molecules on the surface on light irradiation dose. (a) $D=0$; (b) $D=0.36$ kJ/cm^2; (c) $D=1.44$ kJ/cm^2; (d) $D=2.52$ kJ/cm^2; (e) $D=4.68$ kJ/cm^2.

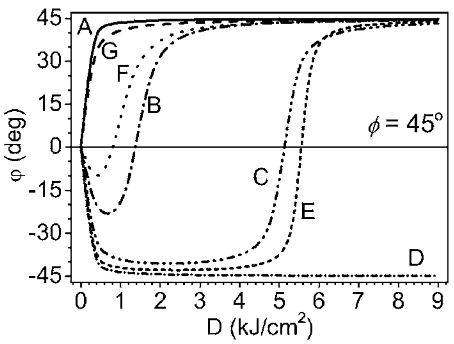


FIG. 6. Calculated dependence of the twist angle φ on light irradiation dose D at $\phi=45°$ and various parameters $w_{MR}^{dark}=x \times 10^{-23}$ J/molecule; $w_{MR}^{light}=y \times 10^{-23}$ J/molecule. (*A*) ($x=2$; $y=20$); (*B*) (2, 6), (*C*) (2, 3.2), (*D*) (8, 6), (*E*) (4, 6), (*F*) (1.2, 6), (*G*) (0.4, 6). The cell thickness $L=30$ μm; elastic constant $K_{22}=3.6$ pN.

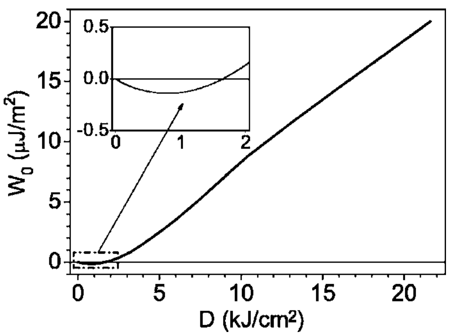


FIG. 7. Calculated dependence of the anchoring energy W_0 on the light irradiation dose D corresponding to the best fit to the experimental data given in Fig. 4; $w_{MR}^{dark}=2 \times 10^{-23}$ J/molecule; $w_{MR}^{light}=6 \times 10^{-23}$ J/molecule. The inset depicts the behavior at low dose.

from the light polarization. At $\phi=90°$ the director begins to reorient at a definite dose, always toward the light polarization. This exact behavior was observed in Ref. [21].

IV. CONCLUSIONS

The main experimental results can be summarized as follows:

(i) Light irradiation of a layer of MR molecules deposited on a PVCN-F surface produces twist textures in cells filled with pure 5CB. The director in the twist structures is reoriented *away from* the polarization of the light over a range of the light irradiation dose.

(ii) Light irradiation of the same LC cells filled with MR-doped LC 5CB results in twist textures, in which the director is reoriented *away from* the polarization of the light at low dose and *toward* the light polarization at high dose.

(iii) The value of the light-induced reorientation angle in both cases above is determined by the light irradiation dose, i.e., by the product of the light intensity and exposure time.

(iv) The irradiation of the layer of MR molecules deposited on the PVCN-F substrate results in a decreased absorbance of the MR layer in the UV-visible range of the spectra and producing an anisotropy axis.

Our experimental results allowed us to develop a model of a light-induced anchoring. According to the model, irradiation of the dye-doped LC results in light-induced desorption of molecules from the layer of spontaneously adsorbed MR molecules, and in light-induced adsorption of MR molecules from LC bulk near the aligning surface. The light-induced desorption results in an anisotropic angular distribution of the remaining molecules with maximum in perpendicular direction to the polarization $\vec{E}$, while maximum of angular distribution of light-induced adsorbed MR molecules is parallel to polarization $\vec{E}$. The flux of desorbed molecules is proportional to the irradiation dose and to the number of dark-adsorbed molecules, which is limited. Therefore, the anisotropy of the light-induced distribution of dark-adsorbed MR molecules decreases at long exposure times and this mechanism of light-induced anchoring depletes with time. At the same time, the reservoir of MR molecules in the LC bulk is almost infinite and anchoring due to light-induced adsorption of them is dominant at high dose. Calculation of the evolution of the total angular distribution function of the MR molecules on the aligning surface at light irradiation has allowed us to quantitatively describe the experiments presented here, and qualitatively describes other experiments on light-induced anchoring as well.

It should be noted that our model is valid for irradiation of dye-doped LC only in the isotropic phase. In the case of irradiation of a cell in the nematic phase, the bulk director reorientation [24], drift of the easy axis [6], and the surface director reorientation effect [25] must be taken into account. These effects complicates the evolution of the surface distribution function of dye molecules requiring consideration of the mutually dependent anisotropic light-induced

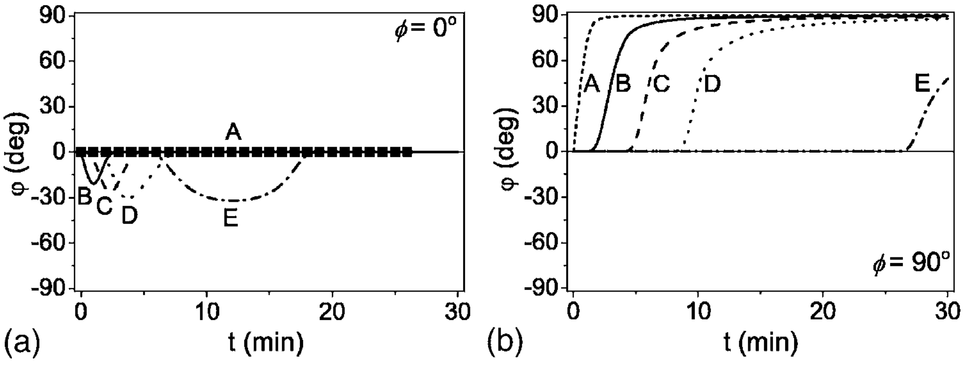


FIG. 8. Dependence of twist angle φ on exposure time t at various geometries: (a) $\phi=0°$; (b) $\phi=90°$; (*A*) $I=50$ W/cm^2; (*B*) $I=10$ W/cm^2; (*C*) $I=6$ W/cm^2; (*D*) $I=3$ W/cm^2; (*E*) $I=1$ W/cm^2.

"bulk" and "surface" distribution functions of the dye molecules.

ACKNOWLEDGMENTS

The authors are very thankful to Kenneth D. Singer or attentive manuscript reading and valuable remarks, and to A. Iljin and N. Aryasova for useful discussions. The research described was made possible in part by CRDF Grant No. UK-P1-2598-KV-04 "Insight in the Physical Phenomena behind the Light-Absorption-Induced Surface Anchoring," Scientific Research Project Agreement for young scientists No. 2MB/231-05-13 "Dynamic Photo-Induced Orientation of Liquid Crystals for Integrated Microelements" of National Academy of Sciences of Ukraine (NASU), and Budget Project "Investigation of Electro- and Magneto-optical, and Photorefractive properties; Structure and Phase States of Nano-composites Based on Liquid Crystals with Organic and Inorganic Dopants" of NASU.

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