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Light-Induced Alignment of Liquid Crystals on Dye-Deposited Film

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Light-Induced Alignment of Liquid Crystals on Dye-Deposited Film

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Light-induced anchoring in dye-doped LCs is caused by light-induced adsorption of dye molecules from bulk to aligning surface and light-induced processes in a layer of dark-adsorbed dye molecules on this surface. We report on light-induced anchoring study due to processes in the adsorbed layer only. We modelled the adsorbed layer by coating of aligning surface by dye molecules and investigated orientation of undoped LC in a cell with dye film previously irradiated by polarized light. We found that desorption of dye from adsorbed layer is a predominant mechanism of light-induced anchoring resulting in the easy axis perpendicular to polarization of incident light.

Keywords: dye-doped liquid crystal; light-induced adsorption and desorption; light-induced alignment; light-induced anchoring

1. INTRODUCTION

Light-induced anchoring of dye-doped liquid crystals (LCs) on the non-photosensitive surface has been intensively studied for last decade [1–11]. A range of mechanisms is suggested to be a cause of producing of easy orientation axis at irradiation of LC cells by polarized

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light. Anisotropic light-induced adsorption of dye molecules from LC bulk onto the surface was considered as primary mechanism, which led to the producing of the easy axis predominantly parallel to the polarization of incident light, $\vec{E}$ [1]. Other mechanisms are connected with light-induced transformation of a dye layer or layer of LC molecules spontaneously adsorbed onto aligning surface. Photo-induced isomerisation [6], rotation [4] and desorption of adsorbed molecules [4,5] presumably result in the easy axis being perpendicular to the polarization of incident light. Recently Lee *et al*. found that the morphology of adsorbed dye layer may also affect the direction of the light-induced anchoring [10]. Besides, light-induced bulk director reorientation strongly influence at the dynamic of light-induced anchoring [11]. Diversity of the mechanisms makes the effect of light-induced anchoring rather complex phenomenon, which studying requires experiments where a number of the mechanisms are reduced to a minimum. In the Reference [4] we excluded the mechanisms connected with LC ordering and bulk director reorientation by exploring the light-induced anchoring in the isotropic phase; Ouskova *et al*. observed the director orientation in a cell with the dye-doped nematic LC irradiated in the isotropic phase by polarized light after cooling down the sample to the nematic phase. It was found that the easy axis was induced both toward and outward the polarization of the incident light depending on light intensity. We suggested that this behaviour was connected to the existence of two different mechanisms of photoalignment: light-induced desorption of dye molecules from a dark-adsorbed dye layer that produced the easy axis, $\vec{e}$, perpendicular to $\vec{E}$, and light-induced anisotropic adsorption of dye molecules from the bulk on aligning surface that produced $\vec{e}$ parallel to the incident light polarization, $\vec{E}$. The resulted orientation of easy orientation axis was supposed to be determined by competition of these two processes.

The aim of the present paper is to study a light-induced anchoring due to processes, which taken place in the adsorbed layer only. To achieve this, we modelled an adsorbed layer with dye coating of the aligning polymer film, and investigated the orientation of pure LC in a cell with dye film previously irradiated by polarized light.

2. EXPERIMENTS

In Reference [4,5] the light-induced anchoring was studied in the combined cells. The combined cells were made from the reference substrate and tested substrate and comprised LC pentyl-cianobephynyl (5CB) doped with azo-dye Methyl Red (MR). Reference substrate was covered with rubbed polyimide, provided strong planar anchoring, and the tested substrate was coated with isotropic layer of fluorinated

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polyvinyl-cinnamate (PVCN-F). According to [4,5], both MR molecules in LC bulk and MR molecules spontaneously adsorbed on the tested surface played significant and different role in producing of light-induced easy axis on the tested surface. To exclude the effect of "bulk" dye molecules, here we made the combined cell (thickness $L = 30\,\mu m$) with the tested surface coated with a layer of MR molecules and filled with pure LC *after* irradiation. In this system the thin ($\sim$100 nm) dye film modelled a dark adsorbed layer and concentration of "bulk" dye molecules was negligibly small.

Dye layer was made from a weak solution of MR (weight concentration $c = 0.05\%$) in isopropyl-alcohol spin-coated ($\sim$7000 rpm) on a surface of PVCN-F film. The MR-layer was firstly irradiated with polarized light from *He-Cd* laser (wavelength $\lambda = 0.44\,\mu m$, power $P < 4\,mW$). The laser beam was focused onto dye layer by the lens. The diameter, d, of the laser beam in the plane of the tested surface was 0.25 mm. The substrate was irradiated with a beam of different light intensities, $I = 4P/\pi d^2$, for different exposure, t. The angle between rubbing direction and light polarization, $\vec{E}$, during exposure was 45°. After irradiation of the MR layer we filled this cell with pure 5CB. By this procedure the final alignment on the tested surface was determined just by light-induced processes in the MR-layer.

The light-induced textures of the irradiated areas were examined with polarized microscope. We observed twist structures in the illuminated areas caused by appearance of the light-induced easy axis on the tested substrate, $\vec{e}_{test}$, not parallel to the direction of rubbing on the reference surface. We found that the twist angle in the irradiated area strongly depended on exposure, intensity and doze of irradiation, but the sign of the twist deformation kept constant: turn of the director in the twist structure was always outward the light polarization vector $\vec{E}$ that corresponded to the direction $\vec{e}_{test}$ being perpendicular $\vec{E}$ [5]. This result qualitatively differs from the observation in the cells with dye-doped 5CB [2,4,5] where the sign of the light-induced twist and light-induced easy axis direction depended on the intensity.

The spatial distribution of director turn $\varphi(r)$ in the irradiation area on exposure, t, is depicted in Figure 1. Basing on a set of $\varphi(r)$-distribution we measured the dependence of the twist angle on the exposure. The dependence of the twist angle on the irradiation time in the centre of the spot that is in the maximum of incident light energy is presented in Figure 2. One can see non-monotonic dependence $\varphi(t)$; the director turn achieving the maximum at $t \approx 60$ min followed by slow decrease of the director turn was observed.

It should be noted that despite a decrease of the light-induced director turn at the long exposures, we could not achieve its complete

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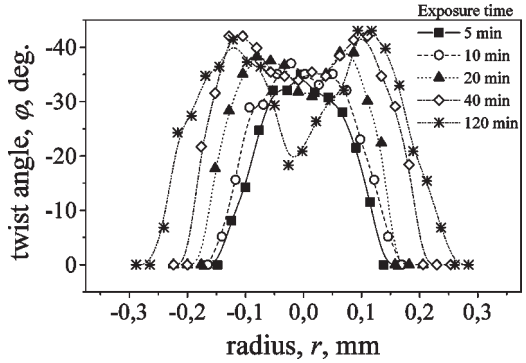

FIGURE 1 The dependence of spatial distribution of LC director in the twist structure after irradiation of dye film on exposure time t. $I = 4$ W/cm^2.

disappearance; the quasi-steady value was appeared to be $\varphi \approx 10^\circ$. At the same time, consequent irradiations of the tested substrate in the same place with light polarization in two mutually perpendicular directions compensate each other and can result in $\varphi \approx 0$. For instance, the consequent irradiation with $t_{exp1} = 2$ h (angle between $\vec{E}$ and rubbing direction, $\phi = 45^\circ$) and $t_{exp2} = 4$ h ($\phi = -45^\circ$) did not cause a twist structure in the irradiated area.

3. MODEL AND DISCUSSION

Alignment of LC on the irradiated MR layer means appearance of anisotropy axis in the layer due to irradiation with polarized light. There are three basic mechanisms of light-induced anisotropy in organic

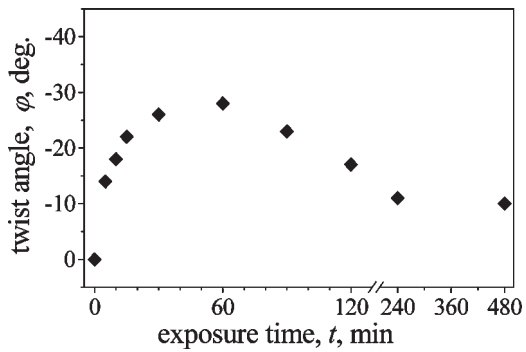

FIGURE 2 The dependence of the twist angle on the irradiation time in the center of the induced twist structure. $I = 4$ W/cm^2.

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films containing dichroic molecules; polarization selective phototransformation of molecules (trans-cis isomerisation, photodegradation, etc) [12], desorption of the molecules [4,5] and reorientation of the molecules [13]. All these processes lead to anisotropic orientational distribution of molecules with the maximum perpendicular to polarization of the incident light that was observed in our experiments.

Reorientational mechanism can be excluded from the consideration since it results in monotonic increase of the anisotropy with exposure and the following saturation of the anisotropy corresponding stationary reorientation of molecules perpendicular to $\vec{E}$. At the same time, we observed non-monotonic exposure dependence of the light-induced twist, which has one-to-one correspondence with the exposure dependence of light-induced anisotropy. Besides, the reorientational mechanism allows multiple over-reorientation of the anisotropy axis that was not observed in our case.

Phototransformation mechanism is also unlikely in our experiment. The basic photo-chemical process in MR is trans-cis (cis-trans) isomerisation, which leads to blue (red) shift of initial absorption band. Meanwhile, we did not see any change of the shape of the absorption band of the MR-film after irradiation but just decrease of its amplitude (see Fig. 7 from the Ref. 4). It should be noted that the results depicted in Figure 7 can be also explained by destruction of MR molecules but the energy $h\nu$ of the incident light is not enough for this effect.

Thus, a light-induced desorption of MR molecules from the dye layer is most likely mechanism of the light-induced anchoring in our experiment. Before irradiation dye layer has macroscopically isotropic distribution function of MR molecules on the surface. We assume that MR molecules absorb light only when they long axes parallel to $\vec{E}$. The molecules that absorb light are desorbing from the surface. Therefore after light treatment the dye layer most of MR molecules are oriented perpendicular to $\vec{E}$ that provides easy orientation in the same direction. To describe the alignment of LC in the cell, we need to solve a problem of director profile over the cell's thickness taking into account angular distribution of MR molecules on the substrate.

Director profile in planar cell with strong anchoring at one substrate (reference substrate) and finite anchoring at another substrate (tested one) is determined by the minimum of the total free energy per unit surface area:

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

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where K_{11}, K_{22}, K_{33} are the splay, twist and bend elastic constants respectively, W_S is the anchoring energy due to asymmetric distribution of MR molecules at tested substrate.

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

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

Solution to this equation reads $\varphi(z) = az$, where parameter $a = \frac{1}{K_{22}}\frac{dW_S}{d\varphi}\Big|_{z=L}$. Now we can write nonlinear equation for director orientation at the tested substrate:

$$\varphi_{z=L} = \frac{L}{K_{22}}\frac{dW_S}{d\varphi}\Big|_{z=L}.$$

To proceed further one needs to know the anchoring energy W_S dependence on the director orientation and light polarization. We assume that anchoring energy of LC molecules at the tested surface has the Rapini-type form:

$$W_S(\varphi, t) = \frac{1}{2} w_{MR} \int_0^{2\pi} (\vec{n} \cdot \vec{e}_{MR})^2 f(\theta, t) d\theta, \tag{1}$$

where w_{MR} is a parameter characterizing interaction between LC and MR molecule; unit vector $\vec{e}_{MR}$ gives orientation of MR molecules long axis, $\vec{e}_{MR} = (\sin\theta, \cos\theta, 0)$; $f(\theta, t)$ is the distribution function of MR molecules at the tested surface; θ is the azimuthal angle of dye molecules' orientation with respect to rubbing direction.

Distribution function $f(\theta, t)$ of MR molecules orientation under the illumination with polarized light is given by kinetic equation

$$\frac{\partial f(\theta, t)}{\partial t} = -\alpha I f(\theta, t) \cos^2(\theta - \phi), \tag{2}$$

where α is the efficiency of desorption; I is the light intensity; ϕ is the angle between light polarization and rubbing direction at upper substrate.

In the initial state $(t = 0)$ we suppose that MR molecules are oriented homogeneously $f(\theta, t = 0) = \left(\frac{N_0}{2\pi}\right)$, N_0 is the initial surface density of MR molecules on the surface.

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Solving the differential Eq. (2) we obtain the dye molecules' distribution function:

$$f(\theta, t) = \left(\frac{N_0}{2\pi}\right) \cdot e^{-\alpha I t \cos^2(\theta - \phi)} \tag{3}$$

The plots of the distribution function (3) at the polarization $\phi = \frac{\pi}{4}$ and exposure time t in a range $(0 \div 8)$h is depicted in Figure 3a. One can see that light-induced desorption leads to anisotropic angular distribution of MR molecules, which maximum is perpendicular to the polarization of the incident light.

To get the orientation of the LC on the tested surface, we need to get an expression for the anchoring energy, W_S, associated with anisotropic MR distribution. Substituting (3) to (1) one gets

$$W_S(\varphi, t) = \frac{N_0 w_{MR}}{4\pi} \int_0^{2\pi} \left[\cos^2\theta \cdot \cos^2\varphi + \sin^2\theta \cdot \sin^2\varphi + \frac{1}{2}\sin 2\varphi \cdot \sin 2\theta \right] \cdot e^{-\alpha I t \cos^2(\theta - \phi)} d\theta. \tag{4}$$

Thus at the tested surface the angle of LC director orientation is given by solution of nonlinear equation

$$\varphi(L, t, \phi) = \frac{N_0 w_{MR}}{2\pi} \frac{L}{K_{22}} \int_0^{2\pi} \sin[2(\varphi(L, t, \phi) - \theta)] \cdot e^{-\alpha I t \cos^2(\theta - \phi)} d\theta. \tag{5}$$

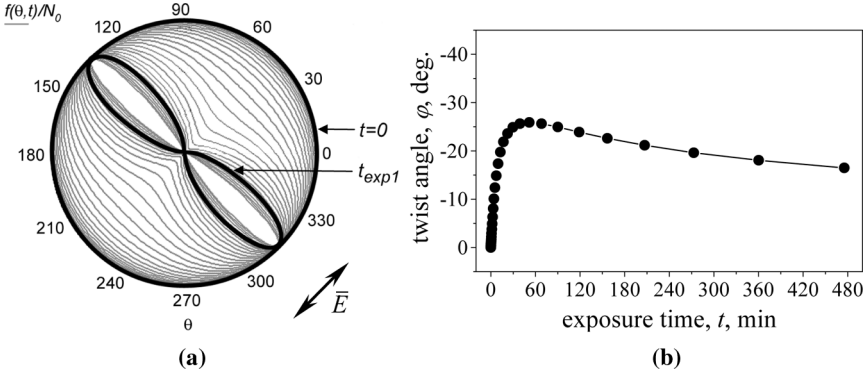

FIGURE 3 Calculated dependence of distribution function of dye molecules on the tested surface at irradiation (a); and dependence of director angle turn on exposure time (b). $\alpha = 2.5 \cdot 10^{-4}$; $I = 4$ W/cm^2; $\phi = \frac{\pi}{4}$; $N_0 = 10^{18}$ m^{-2}, $w_{MR} = 0.8 \cdot 10^{-24}$ J/molecule.

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Numerical solution of (5) with following parameters: $L = 30\,\mu m$; $K_{22} = 3.6{\cdot}10^{-12}$ N, $N_0 = 10^{18}$ m^{-2} is presented on Figure 3b. One can see that the calculated dependence of director orientation angle corresponds to experimental results (Fig. 2). It should be noted that there is a discrepancy in the calculated ($\sim 18^\circ$) and measured ($\sim 10^\circ$) values of the twist angles φ at the long exposures. We believe that this discrepancy is due to a finite absorption dichroism of MR molecules, which was suggested to be infinite in the calculation (we supposed that the MR molecules absorbs light with polarization along their long axes only).

Let's consider the described above experiment of the sequential expositions of the irradiated area with mutually perpendicular polarizations, which resulted in almost zero twist angle φ. During the first exposure ($\phi = \frac{\pi}{4}, t_{exp1} = 2\,h$) the calculated according (3) distribution function $f(\theta, t_{exp\,1})$ changes its shape from the circle one to anisotropic form depicted in Figure 3a (bold line). During the next exposure ($\phi = -\frac{\pi}{4}, t_{exp2} = 4\,h$) the polarization of the incident light is parallel to the direction of light-induced anisotropy (Fig. 4a). Therefore, this exposure decreases the MR molecules' amount that finally leads to disappearance of light-induced anchoring and to $\varphi = 0$. The following change of this anisotropic function during the sequent irradiation with $\phi = -\frac{\pi}{4}$ depicted in Figure 4a results in a final angular distribution of MR molecules.

The calculated according to (3), (5) dependence $\varphi(t, t_{exp1} = 2\,h, t_{exp2} = 4\,h)$ one can see in Figure 4b.

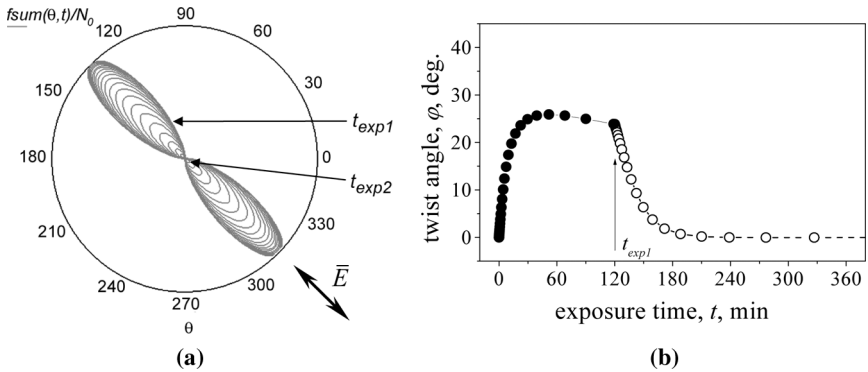

FIGURE 4 Calculated dependence of dye molecules distribution function on exposure time on the tested surface (a); and dependence of director angle turn on exposure time at sequentially irradiation with mutually perpendicular polarization (b).

4. CONCLUSIONS

We can conclude that our experiments and calculations point to selective desorption as a prominent mechanism of light-induced anchoring in dye doped liquid crystals. This mechanism is responsible for the producing of the easy axis, which direction is perpendicular to the polarization of the incident light. The results obtained support the ideas of our previous publication [4,5], which connect the final direction of the light-induced easy axis with a competition between light-induced adsorption and light-induced desorption of dye molecules. It should be noted that the weak point of our experiments is a possible difference between the modelling of layer by spin-coated MR molecules and dark-adsorbed layer of the same molecules in a real LC cell. Ideally, the modelling of layer should provide the same arrangement of the dye molecules that is issued at the spontaneous adsorption of MR from the LC bulk. The experiments in which we hope to realize this modelling of MR layer are on the way.

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