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We have found that producing a light-induced easy axis in a liquid crystal cell doped with methyl red can result in surface director reorientation both toward and outward the polarization of the incident light. This pointed out two different mechanisms of light-induced anchoring in the system. We proposed that these mechanisms are light-induced anisotropy in the adsorbed MR-layer and light-induced adsorption of MR molecules on the substrate. The study of light-induced anchoring in the isotropic phase showed that the mechanism of light-induced anisotropy in adsorbed MR-layer prevails at small light intensities, whereas the mechanisms of light-induced adsorption dominates at high intensities.

Keywords: liquid crystal alignment; photoalignment; azo-dye; adsorption

INTRODUCTION

Effects of aligning and re-aligning of liquid crystal (LC) by means of light have assumed a great deal of interest during the last decade

because of the technological applications and the astonishing science[1-3]. One of the most interesting photoalignment effects is producing of an easy orientation axis, ***e***, on not-photosensitive surface at irradiation of a filled LC cell. This effect was firstly observed in cells filled with dye doped LCs[4-5]. Recently the same effect was found in a cell filled with pure LC, 5CB[6]. The nature of this phenomenon has not been finally set and is a subject of discussion.

There are two basic models of the effect. In the paper[6] it was found that in a cell with pure 5CB the easy axis induced by UV light was perpendicular to the light vector ***E***. To explain this result, it was proposed that light-induced easy axis appeared in the adsorbed layer which had formed *before* light irradiation. The probable mechanisms of the light-induced anisotropy may be light-induced reorientation of the adsorbed molecules to an orientation which is perpendicular to the vector ***E***, photo-transformation and desorption of adsorbed molecules. All these mechanisms should result in the easy axis perpendicular to the vector ***E***.

In the paper[5] it was reported that in a cell with LC 5CB doped the direction ***e*** was close to the polarization of incident visible light ***E*** with Methyl Red (MR). To explain this result, it was proposed the other model. It was suggested that the producing of the easy axis was caused by adsorption of MR molecules by the surface *during* light irradiation. This process is the most effective for the molecules whose long axes are parallel to the vector ***E***. It results in anisotropic distribution of adsorbed molecules and, in turn, in producing of the easy axis. The direction of the easy axis depends on the order parameter of LC, S_{surf}, nearby the surface; if the order parameter is small, the easy axis is close to the direction of the light polarization.

A layer of adsorbed molecules should ever exist on the aligning surface. Therefore, it seems reasonable to think that this layer may play an essential role not only in the case of[6] but also in any effects light-induced anchoring, including the effects that we observed in 5CB doped with MR[5].

The aim of the present work is to move forward in understanding of the mechanism of producing of the easy axis in cells filled with 5CB doped with MR. In this concern, kinetic, exposure and temperature characteristics of light-induced anchoring have been studied. The results obtained show that both the mechanisms noted above contribute to the resulting anchoring.

EXPERIMENT AND DISCUSSION

The experimental procedure is similar to the one described in[5]. The light-induced anchoring of 5CB doped with MR (weight concentration is about 0.5%) was examined in the "combined" cell that limiting surfaces consisted of the *reference* and the *test* substrate. The reference glass substrate was covered with rubbed polyimide that provided strong planar alignment of LC. This surface aligned 5CB in the cell parallel to the rubbing direction. The test surface was covered with isotropic non-rubbed layer of fluorinated poly(vinyl)-cinnamate (PVCN-F). The cell was filled with LC in the isotropic phase ($T \approx 70°C$) and cooled down to the room temperature in magnetic field, $\boldsymbol{H}$ = 5kG, parallel to the rubbing direction of the reference surface. In this way, a high-quality planar structure was produced.

The experiments were carried out in 24 hours after the cell was prepared to achieve the equilibrium state of the cell. The cell was placed normally to the exciting beam of He-Cd laser (wavelength λ = 0,44μm, power P < 8mW). The exciting beam was focused onto the LC layer from the side of the control surface by the lens L. The diameter of the beam in the plane of the cell was 0,25mm. The polarization $\boldsymbol{E}$ of the exciting beam was set at an angle 45° to the initial orientation of the director in the cell. The cell was irradiated at different intensities of the exciting light, I, and different exposure times, t_{exp}. The light-induced textures of the irradiated areas were examined with a polarized microscope.

As in the work[5], the observations of the cell after irradiation have showed that twisted structures were induced in the illuminated areas. Analysis of the textures has revealed that the director on the reference surface did not change, and the twist structure is caused by the turn of the director on the tested surface, $\boldsymbol{d}_{test}$. Generally, the director turned to $\boldsymbol{E}$-direction over the irradiated area that corresponds to the model of light-induced anchoring.

The value of the twist angle, φ_t, depended on both the intensity and the exposure time (see Fig.1) and was proportional to the irradiated doze $D=It_{exp}$ up to D = 2400 J/cm^2. The twist angle practically did not depend on temperature up to the clear point (Fig.2.).

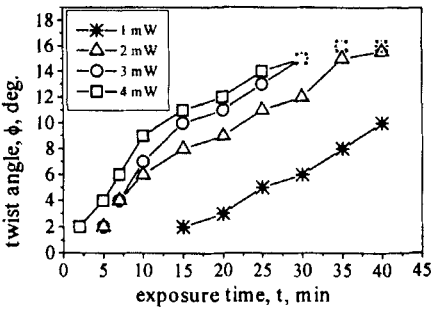

FIGURE 1. Twist angle dependence on exposure time at different intensities. Cell thickness - 20μm.

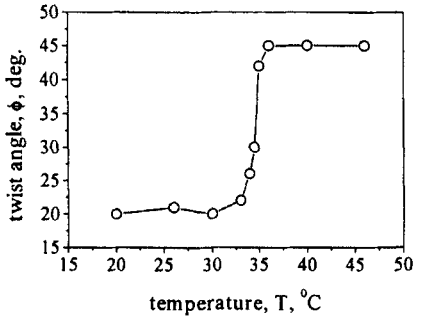

FIGURE 2. Temperature dependence of twist angle. Cell thickness - 20μm, irradiation time - 40min

Some of the results obtained, however differed from the behavior described above. Unlike the results of[5], the maximum twist angle we observed did not achieve 45° but reached a maximum value of 26°. This value was the same for the cells with thickness 15, 24 and 65μm. It means that LC elasticity did not affect substantially the orientation of LC on the tested surface, and the angle φ_t = 26° determined the direction of the easy axis on the tested surface. In the

model of light-induced adsorption the angle φ_1 is connected with the surface order parameter, S_{surf}, by the equation:

$$\varphi \approx \frac{\pi}{2} - \Theta + \delta ,$$

where

$$\delta = \frac{2}{15} \frac{US_{surf}}{kT} \sin 2\Theta ,$$

Θ is the angle between vectors $\boldsymbol{E}$ and initial direction of $\boldsymbol{d}$, U is the energy of intermolecular interaction in LC.

One can see that under $S_{surf} = 0$ the direction $\boldsymbol{e}$ coincides with the direction of $\boldsymbol{E}$. The deviation δ for $\boldsymbol{e}$ and $\boldsymbol{E}$ not being parallel depends on Θ and S_{surf}, and it increases with the increase of these parameters. In our experiments $\Theta = 45^0$ and $\delta = 26^0$. Considering that $U/kT \approx 4,5$[7] we have $S_{surf} \approx 0,5$. This value is much bigger than estimated in Ref.5 ($S_{surf} \approx 0,1$). Presumably, this is caused by the difference in the method of producing the LC cell; in the work[5] the cell was cooled down from the isotropic phase without aplication of magnetic field. Another reason can be difference in the isomer composition of PVCN-F. Recently it was found that isomer composition play a crucial role in the anchoring properties of PVCN based materials[8].

Sometimes we observed unusual textures in the irradiated areas. On the periphery of the irradiated area the twist angle changed the sign to negative, i.e. the director turned *outward* polarization, $\boldsymbol{E}$. Moreover, sometimes the whole irradiated areas demonstrated negative twist angle. We could not find conditions necessary to produce these textures. Namely, we did not find any correlation between appearance of these structures on one side and thickness of the cells and parameters of irradiation (exposure and intensity) on the other side.

The possibility to induce the negative twist angle in the cell may be naturally explained by proposing that both the mechanism of light-induced adsorption[5] and the mechanism of the easy axis producing in the adsorbed layer[6] take place. We believe that the factor resulting in poor reproducibility of the textures with negative twist is a complex dynamic character of easy axis producing in a mesophase.

Qualitatively the appearance of the easy axis in a nematic state can be described as follows. The switching-on of the light causes a fast director reorientation over the aligning surface *outward* the incident light polarization due to Janossy effect[9-10]. Furthermore, much slower processes of light-induced adsorption and light-induced anisotropy in the adsorbed layer begin. The direction of the easy axis depends on the surface order parameter of LC, initial direction of the anisotropy in the adsorbed layer and does not coincide with the directions $\boldsymbol{E}$ and $\boldsymbol{d}$. Appearance of the axis causes a slow reorientation of the director to its direction. Immediately it results in changes of conditions of light-induced adsorption, producing of the anisotropy in the adsorbed layer and parameters of Janossy effect, and, in turn, in a drift of the easy axis. Thus, direction of the easy axis and the direction of its drift are the result of a complex interaction of several light-induced processes in the bulk and at the surface of LC. Efficiencies of these processes are determined by numerous factors (light intensity, local surface composition and morphology, cell thickness *etc.*). Therefore, it is very difficult to predict the steady direction of the light-induced easy axis in a mesophase, which may be very sensitive to small deviations of the experimental conditions.

To avoid these difficulties, we provided the study of light-induced anchoring in isotropic phase where the surface order parameter $S_{surf} = 0$ and there are no director reorientation effects. The experiments were carried out as following. The empty combined cell was put into the hot stage at T = 50°C; then the cell was filled with the mixture of 5CB and 0,5% of MR previously heated to the same temperature. After that the cell was irradiated with the beam of He-Cd laser. Finally, the hot stage was turn off and the cell cooled down smoothly to the room temperature.

The irradiation of the cell resulted in the appearance of twist structures that could be observed after the cooling of the cell to the nematic phase. In opposite to the mesophase, these structures were well reproduced.

The value and sign of the twist angle depended on the exposure time and intensity. At a given intensity the value φ_t increased with the exposure (Fig.3).

High intensity resulted in the director turn toward the vector $\boldsymbol{E}$ ($\varphi_t > 0$), and maximum value φ_t was appeared to be 45° (Fig.4). This result fits to the model of light-induced adsorption since in the case of

isotropic liquid $S_{surf} = 0$, and the light-induced easy axis is parallel to the vector $\boldsymbol{E}$.

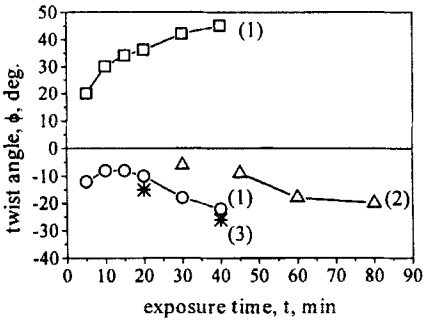

FIGURE 3. Twist angle dependence on exposure time and intensity. (1) $P = 4{,}5$mW, director in the center of the spot reorients to $\boldsymbol{E}$ (square), the periphery – outward $\boldsymbol{E}$ (circle); (2) $P = 0{,}06$mW, director in the whole spot reorients outwards $\boldsymbol{E}$; (3) $P = 0{,}27$mW.

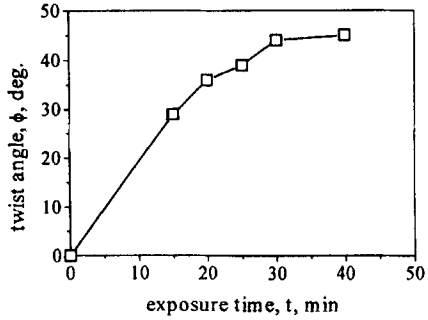

FIGURE 4. The dependence of twist angle on exposure time in isotropic phase. T = 50°C.

Small intensity caused the director turn outward the vector $\boldsymbol{E}$ ($\varphi_t < 0$) and easy axis perpendicular to $\boldsymbol{E}$. This result corresponds to the model of light-induced anisotropy in the adsorbed layer. The

independent experiments on the photoalignment of 5CB on irradiated spin-coated layer of MR[11] also showed the producing of the easy axis perpendicular to the vector ***E*** that support our model.

Because of the Gaussian distribution of the intensity of the incident beam, ring-structures with the change of the sign of the twist angle could be observed due to competition of two photoalignment mechanisms (Photo 1). Since the mechanism of light-induced anchoring

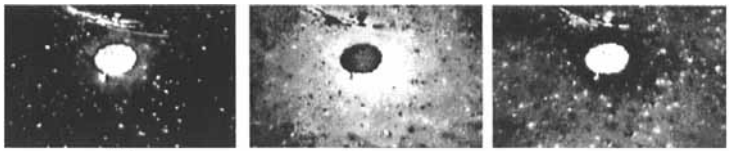

PHOTO 1. The ring-twist-structure of irradiated area. The cell between polarizers and analyzer. Polarizer axis is parallel to the rubbing direction. The angle between polarizers and analyzer is 90° (1), 135° (2), 68° (3)

prevails at high intensities, the diameter of the area with ***e*** parallel to ***E*** increased with the intensity.

Thus, the results of the studies of light-induced anchoring in the isotropic phase point out two mechanisms of easy axis producing. At small intensities the mechanism of light-induced anisotropy in the adsorbed MR – layer prevails whereas the mechanisms of light-induced adsorption dominates at high light intensities.

CONCLUSIONS

We found that the producing of a light-induced easy axis in the cell with MR doped liquid crystal can result in the surface director reorientation both to and out of the polarization of the incident light. This result points out two different mechanisms of light-induced anchoring in the system. We have proposed proposed that these mechanisms are light-induced anisotropy in the adsorbed MR–layer and light-induced adsorption of MR molecules on the substrate. The study of light-induced anchoring in the isotropic phase showed that the mechanism of light-induced anisotropy in adsorbed MR-layer prevails

at the small intensities whereas the mechanism of light-induced adsorption dominates at high light intensities.

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