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Light-Induced Anchoring and Transient Memory-Effect in Doped 5CB

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We report the effect of easy axis producing on isotropic polymer surface in cells with dye-doped liquid crystal (LC) irradiated with visible polarized light. We showed strong dependencies of the light-induced anchoring on the time passed from the cell's filling with LC. The cells made from the reference rubbed aligning surface and the tested isotropic surface and filled with doped LC were irradiated with light with polarization set at 45° to the rubbing direction. Twist structures resulted due to light-induced easy axis on the tested surface were studied. The twist angle decreased exponentially with cell's age. We believe that this behaviour is due to the anisotropic dark adsorption of dye on the substrate and formation of "dark" easy axis, which influences on the light-induced anchoring. This model is supported by experiments on time changes of cell's conductivity, surface plasmon resonance angle and the anchoring memory effect in a not-irradiated cell.

Keywords: liquid crystal; photoalignment; light-induced anchoring; adsorption; desorption.

INTRODUCTION

Photoalignment technique that provides unidirectional orientation of liquid crystal (LC) in a cell due to appearance of the anisotropy axis on a boundary surface upon polarized light irradiation[1-4] allows effective control of the anchoring parameters. One of the promising photoaligning methods involves light irradiation of a cell *after* its filling with LC. The effect of *in situ* photoorientation was firstly observed in cells filled with dye-doped LCs[5,6]. Voloshchenko *et al* showed in[6] that axis of easy orientation of LC on the surface, $\vec{e}$, was close to the direction of the exciting beam polarization $\vec{E}$. It was suggested that the producing of the easy axis be caused by light-induced dye molecules' adsorption on the surface. This process is the most effective for the molecules whose long axes are parallel to $\vec{E}$ that results in preferable orientation of adsorbed molecules parallel to $\vec{E}$.

Our recent studies of light-induced anchoring in isotropic phase[7] and nematic phase[8] of dye-doped LC and in the nematic phase of pure LC 5CB[9] showed that not only light-induced adsorbed layer but a layer of dark adsorbed molecules played an important role in final LC orientation.

Here we report the results showing that reliable characteristics of the light-induced anchoring effect can be achieved just after a certain period of time after cell's filling. We observed strong dependency of the light-induced anchoring on the cell's age. We believe that this fact points an important role of the process of dark adsorption of dye molecules in the mechanism of light-induced anchoring.

EXPERIMENTS AND DISCUSSION

The relaxation processes of light-induced anchoring parameters were studied in the combined cell consisted of the *reference* and the *test* substrate filled with nematic LC — 5CB (BDH Ltd., clear point $T_c = 36^\circ C$) doped with popular azo-dye methyl red (MR, Aldridge) having weight concentration $C_{MR} = 0.5\%$. The reference glass substrate was covered with rubbed polyimide that provided strong low tilted ($1-2^\circ$) planar alignment of LC. This surface aligned 5CB parallel to the rubbing direction. The other surface was covered with isotropic non-rubbed layer of fluoro-poly(vinyl)-cinnamate (PVCN-F) irradiated with non-polarized UV light from *Hg*-lamp having intensity 10 mW/cm^2

during 15 min. This irradiation cross-linked the polymer chains and made the polymer surface rigid. It prevented possible dissolving of the polymer by LC. Besides the UV treatment depressed effect of director sliding over PVCN-F surface observed in[10,11].

The cell was filled with mixture of 5CB and azo-dye MR in the isotropic phase ($T \approx 70^{\circ}$C) and cooled down to the room temperature in the magnetic field, $\vec{H}$ = 5 kG, being parallel to the rubbing direction of the reference surface. By this way the homogeneous planar structure with the director, $\vec{d}_{ref}$, parallel to the rubbing direction was produced. Calibrated spacers gave the cell's thickness equalled 45 μm. The pretilt angle of LC was in the range of 3–4°.

The experimental set-up is described in[8]. The cell was placed normally to the incident beam of *He-Cd* laser (wavelength $\lambda = 0.44$ μm, light power $P < 6$ mW). The incident beam was focused onto the LC layer from the side of the *test* surface by the lens. The diameter, D, of the laser beam in the plane of the cell was 0.25 mm. The polarization of the incident beam, $\vec{E}$, was set at the angle 45° to the initial director direction in the LC cell. The cell was irradiated at given light intensity, $\bar{I} = 4P/\pi D^2$, during different exposure, t_{exp}, at the different moments of time after cell's preparation.

The light-induced textures in the irradiated areas were examined with polarizing microscope.

The examination of the cells after irradiation showed the appearance of twist structures in the illuminated areas moreover the director on the reference surface did not change its orientation, $\vec{d}_{ref}$, and the twist structures were caused by the turn of the director on the test surface, $\vec{d}_{test}$. At used intensities and exposure times the director turned *toward* $\vec{E}$-direction over the irradiated area.

The experiment mentioned in[8] showed the dependence of cell's characteristics, namely light-induced reorientation of LC, on the time flowing after the cell's preparation, that is on the cell's age, t_{age}.

We measured the twist angle induced with light irradiation at different moments after filling the cell. The twist angle decreased exponentially with the cell's age to equilibrium state with two characteristic times $t_{light,1} \approx 30$ min and $t_{light,2} \approx 3$ hours (Fig.1[8]). The results were the same for different light intensity, exposure and for different cell's thickness.

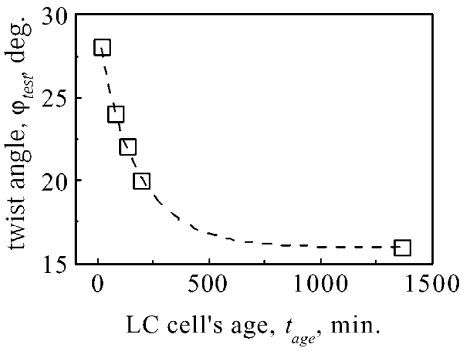

FIGURE 1. Twist angle dependence on cell's age. MR concentration $C_{MR} = 0.5\%$. Cell's thickness $L = 45$ μm. $\bar{I} \approx 5$ W/cm^2, $t_{exp} = 15$ min.

The value of twist angle just after preparation of the cell with PVCN-F-test surface, φ_{test}, was $\approx 30^{\circ}$ and depended on intensity of irradiation — the less intensity the less the twist angle of LC director[8,12].

To obtain more information about relaxation process in the cells with 5CB and MR without irradiation with polarized light we measured the cell's electric conductivity dependence on cell's age.

The symmetrical cell with substrates both coated with PVCN-F deposited on ITO electrodes was used. The cell was filled with 5CB and MR of different weight concentration ($C_{MR} = 0 \div 2\%$) from the isotropic state ($T \approx 70^{\circ}$C). The measurements were made with *L, C, R* digital device *Å7-8* with work frequency 1000 ± 10 Hz and possibility to measure conductivity, σ, in range 0.1 nSm – 1 Sm.

The experiment showed that with MR concentration (C_{MR}) growth the electric conductivity of LC cell almost linearly increased (Fig.2). Therefore, it is reasonable to suggest that LC cell's conductivity is preferably determined with MR-ions in our case. The dependence of the electric conductivity of the cell on time after preparation of the cell appeared to be exponential (Fig.3) with the characteristic time $t_{dark} \approx 40$ min. This value did not appear to depend on cell's thickness. The decrease of the initial conductivity was about 10% for $C_{MR} = 2\%$.

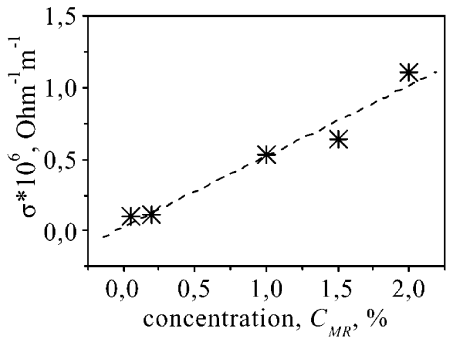

FIGURE 2. Cell's electric conductivity dependence on MR concentration in 5CB just after preparation of the cell. Cell's thickness $L = 5$ μì, $f = 1$ kHz.

The characteristic time of decreasing of LC cell's electric conductivity, t_{dark}, appeared to be nearly the same as characteristic time of relaxation of light-induced anchoring $t_{light,1} \approx 30$ min. This fact can give us a right to say about similarity of the processes.

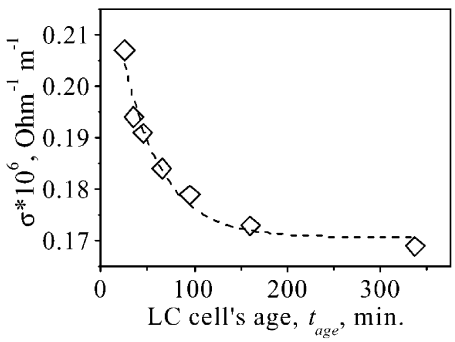

FIGURE 3. Cell's electric conductivity dependence on time after preparation of the cell. $C_{MR} = 0.5\%$. Cell's thickness $L = 5$ μì.

We suggest that the cause of the decrease of the conductivity of the cell with the cell's age is a dark adsorption of MR ions at the surface. Being adsorbed MR molecules do not take part in the

conductivity of the cell. Assuming that all MR molecules are charged it is possible to estimate the highest value of thickness of adsorbed MR layer, which appeared to be $d_{adsorb} = 5$ nm for $C_{MR} = 2\%$, and d_{adsorb} is less then 1 nm for $C_{MR} = 0.5\%$. It means, that in average, MR molecules cover the whole surface at $C_{MR} = 0.5\%$ and about five monolayers are on the surface at $C_{MR} = 2\%$ in the LC.

The kinetics of dark adsorption of azo-dye MR dissolved in LC 5CB was studied on the surface of thin gold films by Surface Plasmon Resonance (SPR) technique. SPR was examined in the combined cell consisted of the reference and the test glass substrates. The reference surface was covered with rubbed polyimide. The test surface was on the base of prism coated with gold layer. Gold layer was covered with UV-irradiated PVCN-F layer. The cell having thickness 68 μm was filled with 5CB and 1.5 wt % of MR in the nematic phase. The measurements with SPR technique were carried out just after filling the cell (Fig.4).

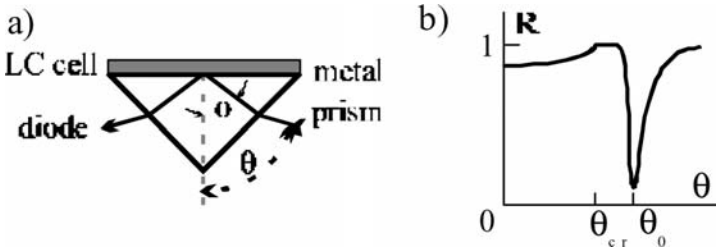

FIGURE 4. a) Scheme of investigation of formation of adsorbed layer of MR molecules in LC cell with Surface Plasmon Resonance Spectroscopy[13]. b) Reflection coefficient R versus light incident angle; θ_{cr} – critical angle of total internal reflection, θ_0 – surface plasmon resonance angle.

SPR gives the *in situ* information about refractive index of thin LC layer (~ 200 nm) nearby of the boundary surface. Therefore, the kinetics of the refractive index changing can be associated with the forming of the adsorbed layer on the boundary surface.

We have got the dependence of the SPR resonance angle on the time since the cell's preparation. Using this dependence, the kinetics of the growing of the adsorbed MR layer was obtained (Fig.5).

The characteristic time of MR layer appearance was found to be about 30 min.

Using Frenel's formulas and obtained experimental data the value of equilibrium thickness of MR layer was calculated. Within the limits of the experimental error the calculated value — 5 nm was the same as estimated with electric conductivity measurement.

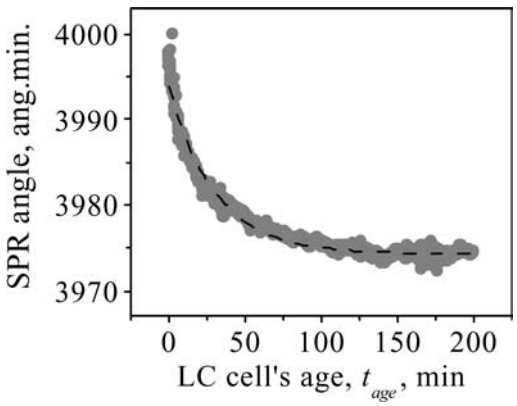

FIGURE 5. Dependence of SPR angle on cell's age. Cell's thickness $L = 68$ μm. MR concentration $C_{MR} = 1.5\%$.

All results we got point that the dark anisotropic adsorption of MR molecules on the aligning polymer surface after the cell's filling plays the important role in the spontaneous and light-induced anchoring in the studied system. Dark adsorption results in the producing of spontaneous "dark" easy axis, $\vec{e}_{dark}$ on the test surface parallel to the direction of rubbing on the reference surface, $\vec{d}_{ref}$. The following irradiation of the cell with light induces additional anisotropy on the test surface. It is reasonable to suggest that the processes of dark adsorption control the final direction of the director on the surface; spontaneous adsorption causes a formation of "dark" easy axis that leads to a competition of light-induced and "dark" anchoring. It in turn leads to the observed decrease of the light-induced twist angle with the age of the cell.

Our model is supported by the recently published results on the anchoring memory effect on PVCN-F surface[8]. The experiments with the combined cell with freely rotated test surface showed that the twist structures appeared after the cell's filling and consequent rotation of the test surface. The analysis of the twist textures showed that the value of

the induced twist angle depended on the cell's age with the characteristic time close to observed one in the experiments on electric conductivity and SPR measurements.

CONCLUSIONS

Thus, studying the dependence of light-induced anchoring of nematic LC 5CB doped with azo-dye MR on cell's age proved the presence of dark adsorption process in LC cell and showed its importance and influence in subsequent light-induced reorientation of LC director.

The effect of dark adsorption of LC and MR molecules on a substrate with aligning polymer layer is confirmed by electric conductivity measurements. The observed decrease of the initial conductivity with the age of the cell allowed estimating of the thickness of dark-adsorbed MR layer being few monolayers.

The investigation of the memory-effect also confirmed the presence of anisotropic layer of dark-adsorbed MR molecules, which forms "dark" easy axis parallel to the initial director orientation.

The decrease of the light-induced anchoring with the cell's age is a result of competition of the light-induced anchoring and formation of "dark" easy axis caused by MR molecules adsorption. The increase with time of the anchoring energy associated with the dark adsorption depresses the light-induced anchoring and results in the decrease of the reorientation angle. The existing of two characteristic times of relaxation process of light-induced anchoring can be explained with the presence of two processes: $t_{light,1}$ corresponds to "dark" MR layer formation, meantime $t_{light,2}$ can be associated with re-arrangement in this layer (e.g. dimerization of MR molecules).

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