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SURFACE DRIVEN TRANSITION IN A NEMATIC LIQUID CRYSTAL CELL

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Surface driven reorientation effects in a nematic liquid crystal cell caused by light-induced changes of the anchoring parameters were studied. Theoretical consideration of one-dimensional flat distributions of the director has shown that the director can undergo threshold reorientation between hybrid, homeotropic, and planar alignments as the anchoring energy varies continuously. The threshold reorientation takes place when the reference and light-induced easy axes are perpendicular. In the one-elastic-constant approximation the light-induced transition was found to be of second order as shown by a critical increase of the director thermal fluctuations in the vicinity of the transition point. These effects were experimentally studied in the cells containing 5CB liquid crystal aligned by the photosensitive azo-containing polymer layer.

1. INTRODUCTION

Reorientation effects caused by light acting on the aligning surfaces of liquid crystals have been intensively studied in the past decade [1–7] because of their fascinating expected applications and surprising nonlinear optic effects. The basic idea of this work is to control the orientation of the liquid crystal by the phototransformation of the aligning surface.

Ichimura et al. [1, 2] in their publications have carefully treated the change of the liquid crystal alignment under the action of light on the azo-containing aligning layers. It was found that trans-cis isomerisation of azo-inits results in the out-of-plane anchoring transition between the planar (the easy orientation axis **e** lies in the plane of the surfaces) and homeotropic (the vector **e** is normal to the cell surfaces) easy axis directions. In turn, the linearly polarized actinic light wave caused in-plane reorientation of the director on the polyvinyl-cinnamate polymer surface due to the cross-linking reaction between cinnamic acid groups [4]. A similar effect was observed under the action of linearly polarized light on azo-containing polymers [5–8] and under the action of light on the bulk of azo-containing nematic liquid crystal [9, 10].

The effects above can be explained by the light-induced changes of the anchoring parameters. In the macroscopic approach and Rapini approximation two basic parameters characterize the anchoring: the easy axis **e** and the anchoring energy W. Both parameters can be induced or changed by the action of light on the photosensitive aligning layer.

As was shown in our previous publications, the in-plane smooth and threshold reorientation effects can be described by changes in the azimuth anchoring energy [4, 8, 10]. These changes are due to the modification of the orientation distribution function of polymer fragments onto

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the aligning surface under the action of actinic light, i.e., a change in the order parameter of the fragments.

In accordance with the works of Ichimura et al. [1, 2], the out-of-plane reorientation is the result of trans-cis isomerisation of the side chain fragments of the aligning layer. There are two main microscopic scenarios of this effect. The first one is the percolation-like process due to the competition between the planar ability of cis-isomers and homeotropic properties of trans-isomers. This scenario should lead to a discontinuous change in the polar anchoring energy as the cis-isomer concentration increases. The second one is the smooth change of the total aligning ability of the mixture of trans- and cis-isomers, leading to a smooth change in the polar anchoring energy.

The aim of this work is to consider the out-of-plane surface driven reorientation effects in nematic liquid crystal cells caused by smooth changes in the polar anchoring energy and to discuss the microscopic scenario of the process realized under the trans-cis isomerisation of polymer fragments on the aligning layer.

2. THEORY

The system under consideration is a nematic liquid crystal bounded by two plates covered with alignment materials. The free energy of such a sample in the approximation of the surface Rapini potential has the form [11]

$$F = \frac{1}{2}\int \left(K_1(\mathrm{div}\,\mathbf{n}) + K_2(\mathbf{n}\mathrm{rot}\,\mathbf{n})^2 + K_3[\mathbf{n}, \mathrm{rot}\,\mathbf{n}]^2\right) dV - \\ - \frac{1}{2}W_0\int (\mathbf{n}\mathbf{e}_0)^2 dS - \frac{1}{2}W_L\int (\mathbf{n}\mathbf{e}_L)^2 dS, \qquad (1)$$

where K_i are the Frank elastic constants, $\mathbf{e}_{0,L}$ are the unit vectors along the easy axes on the surfaces, and $W_{0,L}$ are the anchoring energies which can depend on the light field intensity $I = E^2$.

Let us consider the geometry realized in the experiment described below (Fig. 1). The top plate is the reference one and is characterized by an easy axis direction $\mathbf{e}_{ref} = (0, \cos\alpha_{ref}, -\sin\alpha_{ref})$ and constant (large) anchoring energy W_{ref}. The bottom photosensitive surface is the control one with the homeotropic easy axis $\mathbf{e}_{con} = (0, 0, 1)$ and the anchoring energy W_{con}. Let us assume that the incident light gives rise to the additional planar easy axis $\mathbf{e}_{ind} = (0, 1, 0)$ on the control surface with the anchoring energy W_{ind}. Both W_{con} and W_{ind} depend on the light intensity I. We also suppose that the director characteristic

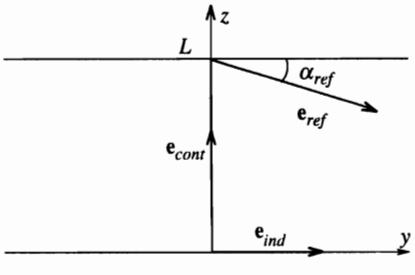

Fig. 1. Geometry of the out-of-plane director reorientation. Bottom surface is the control, upper is the reference one; $\mathbf{e}_{con}$, $\mathbf{e}_{ind}$ and $\mathbf{e}_{ref}$ are the initial, induced and reference easy axes, correspondingly

reorientation times are much shorter than the time over which the anchoring energy varies. In this case the director distribution is determined by the minimum of the total free energy at each instant of time. Further we also assume that the director reorientation occurs in the yz-plane («flat» reorientation). Thus, in the one-elastic-constant approximation, the free energy (1) can be brought into the form

$$\frac{F}{S} = \frac{1}{2}K\int_0^L \theta_z'^2 dz - \frac{1}{2}W_{ref}\cos^2(\alpha_{ref} - \theta_{ref})\big|_{z=L} - \frac{1}{2}(W_{con} - W_{ind})\sin^2\theta_{con}\big|_{z=0}, \quad (2)$$

where $\theta(z)$ is an angle between the y-axis and the director, and L is the cell thickness. Minimization of the free energy (2) leads to the equation for the director distribution

$$\theta_z'' = 0 \quad (3)$$

and the boundary conditions

$$\begin{aligned} L\theta_z' + \frac{1}{2}(\xi_{con} - \xi_{ind})\sin 2\theta\big|_{z=0} = 0, \\ L\theta_z' + \frac{1}{2}\xi_{ref}\sin 2(\theta - \alpha_{ref})\big|_{z=L} = 0, \end{aligned} \quad (4)$$

where $\xi_\mu = W_\mu L/K$ ($\mu = con, ind, ref$) are the anchoring parameters. In the case of infinite anchoring on the reference surface the solution to the equation (3) takes the form

$$\theta = \theta_{con} + (\alpha_{ref} - \theta_{con})z/L, \quad (5)$$

where θ_{con} is the tilt angle on the control surface and can be found from the implicit equation

$$\alpha_{ref} - \theta_{con} = \frac{1}{2}(\xi_{ind} - \xi_{con})\sin 2\theta_{con}. \quad (6)$$

From (6) one can obtain the conditions for the stability of the director distribution (5). As a result we find that for $\alpha_{ref} = 0$ and $\xi_{ind} - \xi_{con} = \Delta\xi > -1$, only the planar distribution is stable. For $\Delta\xi > 1$ the hybrid distribution with tilted orientation of director on the surfaces is realized. In this case decreasing ξ_{ind} causes the tilt angle θ_{con} to increase monotonically, i.e., smooth reorientation of director toward $\mathbf{e}_{con}$.

For $0 < \alpha_{ref} < \pi/2$, increasing ξ_{ind} results in a monotone decrease of the tilt angle θ_{con} with no critical points for $\Delta\xi$.

For $\alpha_{ref} = \pi/2$ the only $\theta_{con} = \pi/2$ solution is stable for $\Delta\xi < 1$. For $\Delta\xi > 1$, the director distribution becomes tilted and the angle θ_{con} decreases toward $\mathbf{e}_{ind}$ with the increase of ξ_{ind}.

Thus, for $\alpha_{ref} = 0$ and $\alpha_{ref} = \pi/2$ the reorientation shows the threshold behavior as the anchoring energy on the control surface varies (Fig. 2). In the one-elastic-constant approximation this reorientation is a second-order orientational transition, so that the director fluctuations are assumed to exhibit a critical behavior in the vicinity of the transition point.

The thermal fluctuations $\delta\mathbf{n}$ of the director in a cell with arbitrary anchoring have been considered in detail in [12, 13]. In line with the approaches developed there the director fluctuations $\delta\mathbf{n}$ can be regarded as a superposition of the eigenfunctions of the operator $-(K/2)\Delta$ and have the form

$$\delta n_\alpha(\mathbf{r}) = \exp(i\mathbf{q}_\perp\boldsymbol{\rho})\sum_j \left\{\delta n_{\alpha j}^+ \exp(iq_z^j z) + \delta n_{\alpha j}^- \exp(-iq_z^j z)\right\}, \quad (7)$$

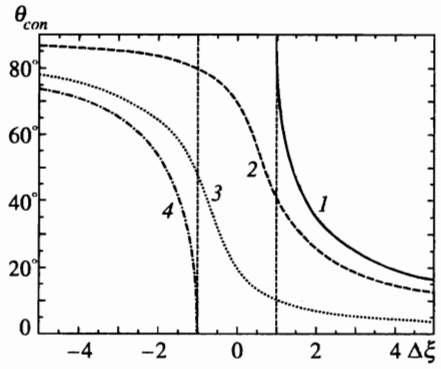

Fig. 2. Calculated dependence of the tilt angle θ_{con} on the control surface on the anchoring parameter $\Delta\xi$ at the different tilt angles α_{ref} on the reference surface: *1* — $\alpha_{ref} = 90°$; *2* — $\alpha_{ref} = 70°$; *3* — $\alpha_{ref} = 20°$; *4* — $\alpha_{ref} = 0°$

where $\alpha = x, y$, $\mathbf{q}_\perp = (q_x, q_y, 0)$ is the wave vector of fluctuations in the plane of the cell surfaces, $\boldsymbol{\rho} = (x, y, 0)$, and the sum is over the discrete modes of the fluctuation wave vectors q_z^j.

Let us consider the case of $q_x = 0$ and the out-of-plane part of the fluctuations (δn_y) which is responsible for the *ee*-scattering of light and corresponds to the situation realized in the experiment [11]. The boundary conditions (4) linearized with respect to the director fluctuations, which determine the values of q_z^j, have the form

$$\begin{aligned} &L\delta n_{y,z} - (\xi_{con} - \xi_{ind})\delta n_y\big|_{z=0} = 0, \\ &L\delta n_{y,z} + \xi_{ref}\delta n_y\big|_{z=L} = 0. \end{aligned} \tag{8}$$

Substituting (7) in the boundary conditions (8), we obtain an equation for the q_z-components of the fluctuation wave vectors:

$$\operatorname{tg} t = \frac{t(\xi_{ref} + \Delta\xi)}{t^2 - \xi_{ref}\Delta\xi}, \tag{9}$$

where $t = q_z L$.

Application of the equipartition theorem of classical statistical mechanics gives the fluctuation amplitudes

$$|\delta n_{yj}^{+}|^2 = A\left\{2 + \frac{2\Delta\xi}{\Delta\xi^2 + t^2}(1 - \cos 2t) - \frac{\Delta\xi^2 - t^2}{t(\Delta\xi^2 + t^2)}\sin 2t\right\}^{-1}, \tag{10}$$

where $A = k_B T/KV(q_\perp^2 + q_z^{j^2})$. It is seen that the denominator in (10) can be equal to zero for some definite values of $\Delta\xi$ and t. This means that the amplitude of the lowest fluctuation mode experiences an infinite growth, i.e., a second-order structural transition occurs. In the case of a strong anchoring on the reference surface this condition reduces to the existence of the solution to the system of equations

$$\begin{aligned} &\Delta\xi \operatorname{tg} t = t, \\ &t^2 - \Delta\xi(1 - \Delta\xi) = 0. \end{aligned} \tag{11}$$

The first equation corresponds to Eq. (9) for $\xi_{ref} = \infty$ and the second one to the vanishing of the denominator in (10). It is apparent, that $t = 0$, $\Delta\xi = 1$ is the solution of this system and thus defines the transition point.

The asymptotic behavior of the fluctuation wave vector and amplitude of fluctuation in the limit $\Delta\xi \to 1$ has the form

$$q_z L \sim \sqrt{1-\Delta\xi}, \quad |\delta n_{y1}|^2 \sim \frac{1}{4VKq_\perp^2(1-\Delta\xi)}. \tag{12}$$

It is seen the lowest mode of the splay-bend director fluctuation diverges when $\Delta\xi \to 1$. Moreover, the behavior of δn_{y1} in the vicinity of the point $\Delta\xi = 1$ is typical of the second-order transitions.

This orientational transition is a light-induced anchoring transition and is the surface analog of the well known light-induced Frederiks effect [11]. In turn, the smooth surface director reorientation for an oblique easy axis direction is the analog of the giant optical nonlinearity widely studied in the past decade [14]. It should be noted that the director can undergo reorientation not only when W changes but also due to the changes of the Frank elastic constants or the cell thickness (the dimensionless parameter determining the director distribution in the cell is $\xi = WL/K$). The orientational transition at a critical cell thickness in a wedge-shaped cell was studied by Barbero et al. [15].

In summary, we emphasize the new facts. Firstly, smooth variation of the anchoring can lead to threshold reorientation of the director. Secondly, the threshold reorientation takes place only for a definite cell geometry, namely, when the easy axes are orthogonal on the aligning surfaces. Lastly, if the threshold reorientation occurs, the director thermal fluctuations increase near the transition point. Since the differential cross-section is proportional to the squared amplitude of the fluctuations, the intensity of the *ee*-scattered light should increase near the transition point.

3. MATERIALS AND EXPERIMENTAL PROCEDURE

The experiments were performed with a sandwich cell arrangement filled with the mixture of the liquid crystal $4' - n$-pentyl-4-cyanobiphenyl (5CB). The thickness of the cells was 70 μm. One of the aligning plates was the reference. We used three types of reference surfaces: a polydimethyl-siloxane (PS) layer (provides homeotropic alignment, $\alpha_{ref} = 90°$), an obliquely evaporated layer of In_2O_3 ($\alpha_{ref} \approx 30°$), and a rubbed polyimide (PI) layer ($\alpha_{ref} = 4.5°$). The angles α_{ref} were determined by zero magnetic and optical rotation methods [16] in the symmetric cells with a homogeneous director distribution.

The control surface was coated with a layer of photosensitive azo-polymer (AP) (Fig. 3) providing the homeotropic orientation of 5CB. This polymer belongs to a class of photosensitive polymers side fragments of which undergo the trans-cis isomerisation as well as the reorientation of trans-isomers perpendicular to the polarization vector of UV light [17, 18]. The initial absorption spectrum of AP and its transformation under UV-irradiation are shown in Fig. 3.

Thus, we used two initial liquid crystal alignments in the cells: the hybrid (PI or In_2O_3 reference surfaces) and homeotropic (PS reference surface). To observe reorientation of the director, the cell C was inserted in the optical circuit normally to the exciting UV beam from a Hg-lamp (Fig. 4). The control surface faced the Hg-lamp. The wavelength spectrum of the exciting light was given by the filter F_1 and is shown in Fig. 3. The polarization $\mathbf{E}_{exc}$ of the UV light was set by the Glan–Thompson quartz prism Pr. In the case of a hybrid cell with tilted liquid crystal alignment direction, $\mathbf{E}_{exc}$ was parallel to the director. It had an arbitrary direction when the cell with homeotropic orientation were used. The irradiated circle with

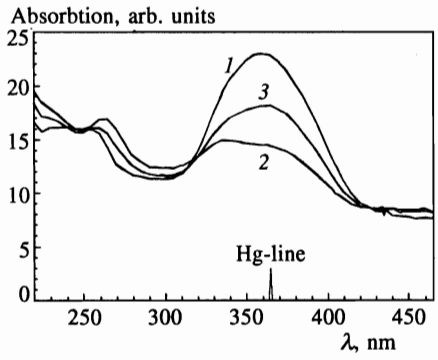

Fig. 3. The initial absorption spectrum of AP and its transformation under UV light irradiation: *1* — initial spectrum; *2* — spectrum obtained after the irradiation with exciting light of Hg-lamp; *3* — spectrum obtained in an hour after the irradiation

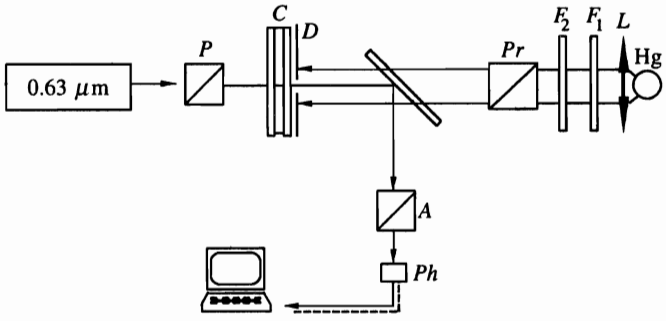

Fig. 4. Experimental setup

radius $R = 1.5$ mm and homogeneous light intensity distribution was formed by the condenser L and the diaphragm D attached directly to the cell. The UV light intensity I_{exc} was controlled in the range 0.5–50 mW/cm^2 with the filters F_2.

A probe beam from a He–Ne laser ($\lambda_{test} = 0.63$ mm, power $P_{test} = 0.5$ mW) passed through the polarizer P, cell C, diaphragm D, and analyzer A. The polarizer P and analyzer A were crossed and their axes made a 45 °angle with the projection of the director $\mathbf{n}$ on the aligning surfaces. The intensity I_{test}^{out} of the light behind the analyzer was measured by a photodiode Ph connected to the computer.

The action of the UV light did not affect either the reference aligning layer or the liquid crystal. Therefore, the change of I_{test}^{out} under UV irradiation indicated director reorientation in the cell caused by the phototransformation of the control surface.

The intensity I_{test}^{out} behind the analyzer is given by [19]

$$I_{test}^{out} = I_{test}^{in} \sin^2(\pi\Delta\psi/\lambda), \tag{13}$$

where

$$\Delta\psi = \int_0^L \left(\frac{n_o n_e}{\sqrt{n_o^2 + (n_e^2 - n_o^2)n_z^2}} - 1 \right) dz$$

is the phase difference of the extraordinary and ordinary waves, n_e and n_0 are the refractive indexes of liquid crystal for the extraordinary and ordinary waves, respectively, and $n_z = \sin\left[\theta_{con} + (\alpha_{ref} - \theta_{con})z/L\right]$.

To observe the critical behavior of the director fluctuations in the vicinity of the reorientation threshold we used the experimental set up for studying the Rayleigh scattering of light described in detail in Ref. [12]. The total *ee*-scattering in the range 2–10 mrad was detected through simultaneous irradiation with the exciting UV light.

4. EXPERIMENTAL RESULTS

The irradiation of cells with the exciting beam caused the test light to appear behind the analyzer, i.e., director reorientation occurred. After the UV light had been cut off the initial state was restored in several minutes.

Observations in a polarizing microscope of the irradiated area in the cells with initially homeotropic liquid crystal alignment (PS reference surface) revealed a typical schlieren structure of the tilted or planarly oriented liquid crystal. Sometimes monodomain orientation of liquid crystal occurred in this area. If hybrid cells were used (PI and In_2O_3 reference surfaces), tilted director alignment of the irradiated spot was observed. The irradiated area in this case was much less bright than that in the remaining part of the cell, which was attributable to the decrease of the director tilt in the cells under the UV light irradiation.

The dependence of the light intensity behind the analyzer $I_{test}^{out}(t_{exc})$ on the irradiation time t_{exc} is shown in Fig. 5 for different types of reference surfaces. It is seen that there is a smooth director reorientation in the hybrid cell with tilted direction of the easy axis $\mathbf{e}_{ref}$ (PI and In_2O_3 reference surfaces). In contrast, we have obvious threshold reorientation in the initially homeotropic cell (PS reference surface). The dependence $\theta_{con}(t_{exc})$ calculated in accordance with Eq. (13) for the threshold reorientation of director is shown in Fig. 6*a*.

The increase of I_{exc} caused an increase in the number of oscillation periods for all types of cells and is due to the increase in the maximum director deviation angle on the control surface. Within the limits of experimental error the dependence of the stationary value $\overline{\theta}(I_{exc})$ was linear up to $I_{exc} \simeq 20$ mW/cm^2. In the case of the homeotropic cells the «silent time» (time needed to achieve the threshold) was inversely proportional to the intensity I_{exc} (Fig. 7).

The reorientation of the director was accompanied by light scattering caused by fluctuations

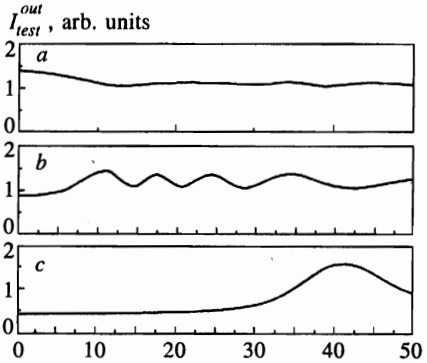

Fig. 5. Light intensity behind the analyzer $I_{test}^{out}(t_{exc})$ as a function of the irradiation time t_{exc}, for different types of reference surfaces: *a* — $\alpha_{ref} = 30°$; *b* — $\alpha_{ref} = 4.5°$; *c* — $\alpha_{ref} = 0°$

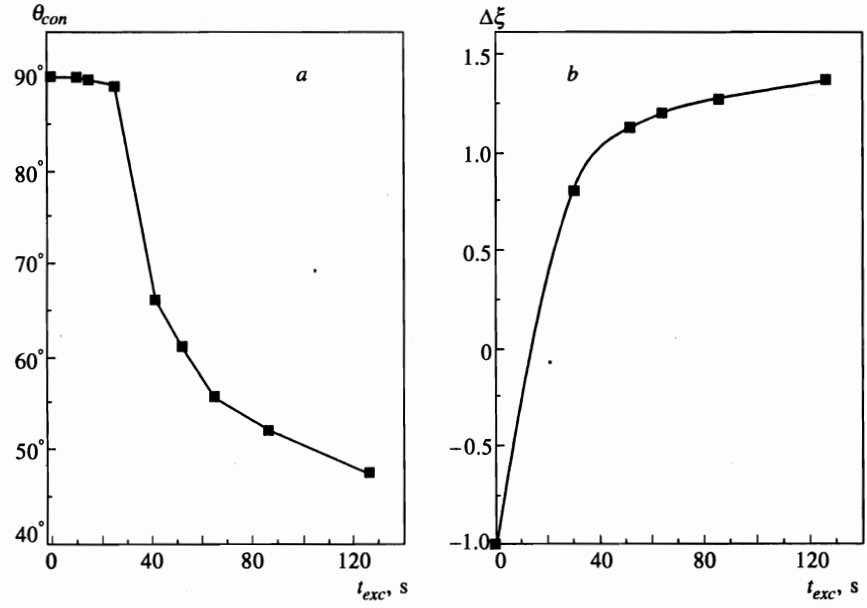

Fig. 6. *a*) Tilt on the control surface, $\theta_{con}(t_{exc})$, and *b*) the anchoring difference $\Delta\xi(t_{exc})$, calculated in accordance with Eq. (13)

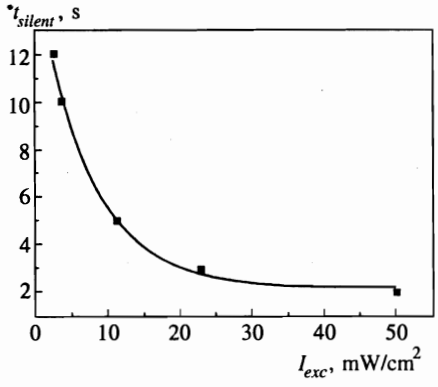

Fig. 7. Dependence of the silent time on the intensity of incident light

of the director. The light scattering intensity I_{sc}^{ee} increased with the irradiation time and then went through a maximum. Since the intensity of the scattered light I_{sc}^{ee} is proportional to $\sin 2\beta$, where β is the angle between the director **n** and the wave vector of the incident light [12, 13], this increase can be explained by the change in this angle during reorientation. In the homeotropic cell the scattering only increased with the reorientation. Evidently, it is due to the appearance of schlieren structure in the irradiated area.

It is significant that in the hybrid cells the increase in the light scattering began simultaneously with the director reorientation. At the same time, we found that the intensity of the scattered light increased before the director reorientation in the homeotropic cell. It is seen in Fig. 8 that a definite delay exists between the beginning of the light scattering increase

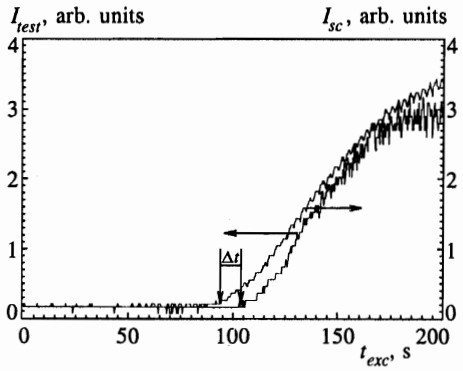

Fig. 8. Critical increase of the light scattering in the vicinity of the reorientation threshold. The increase in the light scattering starts earlier than the director reorientation and is due to the attainment of the critical value for the anchoring parameter

and the director reorientation. It should be noted that the value of this delay depended on the exciting light intensity I_{exc}: larger intensities gives smaller delays.

5. DISCUSSION

The experimental results evidently show the threshold director reorientation in the homeotropic cell and critical behavior of the director fluctuation in the vicinity of the threshold point. There are two possible explanations of this effect. The first one is the discontinuous change of the anchoring energy on the control surface. Without doubt, if the difference $\Delta W = W_{ind} - W_{con}$ of the anchoring energies as a function of the excitation time has a break, the threshold reorientation of director should occur both in the hybrid and homeotropic cells. The second possibility is a smooth change in the difference ΔW with threshold director reorientation only in the homeotropic cell, which is due to the competition between bulk and surface torque and was discussed above (Sec. 2).

As the experiments have demonstrated, only the homeotropic cell exhibits threshold reorientation of the director. Hence, the model of smooth anchoring energy variation is valid in our case. Comparison of the experimental dependence $\theta_{con}(t_{exc})$, Fig. 6*a*, and the solution of Eq. (6) allows us to calculate the anchoring difference $\Delta\xi = \Delta W L/K$ at each instant of time. The results obtained for the homeotropic cell are shown in Fig. 6*b*. The initial value $W_{con}(t_{exc} = 0) \approx 4 \cdot 10^{-4}$ erg/cm^2 was measured independently in the symmetric cell by the H-field method proposed recently by Lavrentovich et al. [16].

It would appear reasonable that the light-induced changes in the anchoring energy $\Delta W = W_{ind} - W_{con}$ are due to the change in the concentrations C_{trans}, C_{cis} of trans- and cis-isomers under the action of UV light. In fact, this mechanism is responsible for the planar-homeotropic transitions in the cells with azo-polymer aligning material [1, 2]. Moreover, our studies of the absorption spectrum of a thick AP layer in the range of 300–800 nm revealed the typical transformation under trans-cis isomerisation of azo-dye [18] (Fig. 3).

Thus, the difference $\Delta W = W_{ind} - W_{con}$ is a function of C_{trans}, C_{cis}. At $C_{cis} = 0$ the homeotropic orientation of the easy axis is realized, whereas the planar alignment takes place for $C_{trans} = 0$. In this model C_{trans}, C_{cis} depend on the UV light intensity and give the experimentally obtained increase in the stationary value of the tilt angle θ_{con} with increasing I_{exc}. Moreover, at small irradiation times $C_{trans}(t)$, $C_{cis}(t)$ are linear, and the time needed to

achieve their critical values corresponding to the anchoring difference $\Delta\xi = f(C_{cis,trans}) = 1$ is irreversibly proportional I_{exc} as was found experimentally (Fig. 7). The saturation of the light-induced anchoring energy for long exposure times could be caused by the saturation of the concentration of cis-isomers and decimation of trans-isomers.

It should be noted that we observed a difference between the relaxation behavior of AP and liquid crystal in the cell after switching off the UV light. The characteristic time of AP absorption spectrum relaxation was one-two hours for the thick AP layer, while the recovering time of the initial homeotropic orientation in the cells was about several seconds. This result requires further study. However, we believe that it reflects the fact that if the relaxation time of the AP spectrum is determined by the lifetime of cis-isomers, t_{cis}, in the polymer matrix, the recovery time t_d of the initial director alignment is also determined by the orientational viscosity and elasticity of the liquid crystal and by the interaction between the liquid crystal and the cell walls (boundary conditions). It is well known that the value of t_{cis} strongly depends on the environment of cis-isomers, being hours in a polymer matrix and few seconds in a liquid crystal matrix [20, 21]. Since cis-isomers at the cell wall directly interact with liquid crystal molecules at the polymer surface, their lifetime should be comparable with the value of t_{cis} in a liquid crystal matrix, i.e., with the value observed in our experiments. Moreover, it is reasonable to suppose that steady homeotropic alignment occurs for a concentration of cis-isomers at the surface far from its equilibrium value that also makes $t_d \leq t_{cis}$. Besides, strong homeotropic anchoring of liquid crystal at the reference surface may also bring about the early recovery of the initial alignment.

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