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AN OBLIQUE ORIENTATION OF NEMATIC LIQUID CRYSTALS ON A PHOTOSENSITIVE ALIGNING POLYMER

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Abstract The problem of an oblique orientation of a liquid crystal in cells with light induced easy orientation axis is considered. Theoretical and experimental studies of the director distribution in a cell with a photosensitive orientant, fluorinated polyvinylcinnamate polymer film, are performed. The two exposure technique for liquid crystal oblique orientation and the condition for a new anchoring transition in a cell with a photosensitive orientant are also presented.

'RODUCTION

ently some groups have reported about the possibility of good quality ning of nematic liquid crystals (NLC) on photosensitive polymer films[1-] 'he aligning ability of these materials is determined by their anisotropy perties induced by light illumination. Photosensitive aligning materials e some advantages over usual rubbed polymer films. In contrast to the oing technology, there are no electrostatic charges and dust on the ning surface produced by rubbing. Besides, the photosensitive polymers w to control the direction of an easy orientation axis over the aligning ace and the azimuthal anchoring energy value.

The aligning properties of the photosensitive materials on the base of vinylcinnamate (PVCN) polymers were the most extensively studied and exhibit the most promise for applications[2,3]. The appearance of an easy axis induced by these materials is due to the photo-cross-linking intermolecular reaction under the action of polarized UV light. It was shown in[1] that for conventionally used NLC the PVCN film induces an easy axis, $\boldsymbol{e}$, perpendicular to UV light polarization vector, $\boldsymbol{E}_{UV}$.

In our paper[1] as well as in the work of M.Schadt et al[2] it was pointed out that a pretilt angle on PVCN is equal to zero or is very small. At the same time it is well known that a pretilt angle of a LC director is needed for the normal operation of twist and super-twist cells. Moreover, the different types of NLC devices demand different values of the pretilt angle. Actualy variations of the pretilt angle nedeed for practical applications lie in the range of $(0\text{-}15)^{\circ}$.

It should be noted that the anisotropy axis caused by linearly polarized light is nonpolar. Therefore, if even the photosensitive polymer provides an oblique orientation, this orientation should be twice degenerated and the problem of removing of this degeneration appears.

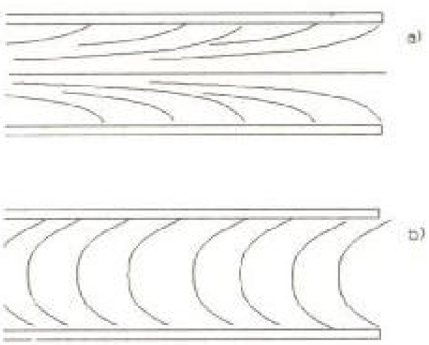

Fig.1

In the present paper we report the results of the investigation of the director distribution in the LC cells with the aligning surfaces made up of the flourinated PVCN (PVCN-F) films. It was interesting to know whether

the pretilt angle of the LC director on the orienting film of this material is equal to zero or the reverse tilt orientation (Fig.1a,b) results in the characteristics being inherent to the observed planar alignment. The influence of the trial of a LC cell fabrication on the director distribution have also been clarified. We believe this information allows to clear up the possibility to form the oblique LC director orientation by the orientant with the light induced aligning ability and to propose the reasonable model of NLC alignment on PVCN-F films.

BASIC EXPERIMENTS

Photosensitive PVCN-F polymer film exhibits a property to generate homogeneous alignment of NLC molecules after being irradiated with polarized UV light, λ_{uv}<0.36μm. To obtain an aligning coating, the PVCN-F films with thickness (0.2÷0.5)μm, spin-coated onto glass substrates were illuminated by the polarized UV light of a mercury lamp with the average power 250-500W. The linearly polarized exposure light field was formed in the plane of PVCN-F film by the quartz lens system and polarizing Glan-Thomson prism. The polarization vector $\boldsymbol{E}_{uv}$ was parallel to the one of the two sides of a glass substrate. The typical value of the light power density, I_o, in the plane of PVCN-F film was about 10 mW/cm^2. The exposure time t_{exp} was varied from zero up to 1 hour.

After the illumination of the films, the PVCN-F cell was assembled, which gap was adjusted using teflon strips with the thickness of 20μm. Cells were filled with NLC mixtures conventionally used for twist indicators (ЖК-1282; ЖК-1285, NIOPIK, Russia). Filling was performed in a nematic phase at room temperature due to capillary effect. The orientation of the NLC layer in the cells was changing in time in some complicated manner and came to the equilibrium state in several days.

Filled cells show a good quality planar alignment for PVCN-F aligning coatings with $t_{exp} > 5$ - 7 min. The average director $\boldsymbol{d}$ orientation measured by traditional polarization microscopy method or the light scattering technique[3] is perpendicular to $\boldsymbol{E}_{uv}$[1].

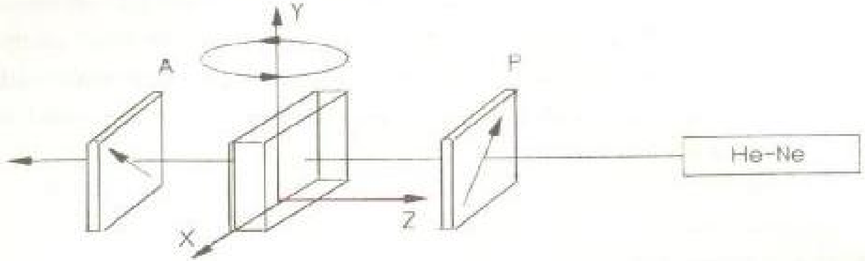

Fig.2

We have studied the dependence of the NLC orientation parameters, the value and the direction of a LC director pretilt angle on the PVCN-F film exposure time and LC flow direction at a cell filling.

The pretilt angle θ_s was measured by the well known method of the LC cell rotation between the crossed polarizers[7] (hereafter referred as a "cell rotation method")(Fig.2). A LC cell was adjusted between the crossed polarizers so that director $\boldsymbol{d}$ made an angle 45^0 to both their axes. The cell was rotated around the axis OY, perpendicular to the director. The dependence of the system transparency $T(\varphi)$ for a weak He-Ne laser beam ($\lambda = 0.63$ µm) on the angle φ between the beam and the cell normal was measured. In the case of a uniform director orientation through over a cell the value of a pretilt angle θ_s may be estimated by the expression[8]:

$$\theta_s \approx \frac{\Delta\varphi}{(n^o + n^e)}, \qquad (1)$$

Here $\Delta\varphi$ is the shift of the symmetry axis of the curve $T(\varphi)$ about the point $T(\varphi=0)$, n^o and n^e are the refractive indexes of ordinary and extraordinary waves respectively, the angle θ_s is determined as the angle between the aligning surface and the direction of $\boldsymbol{d}$ near it.

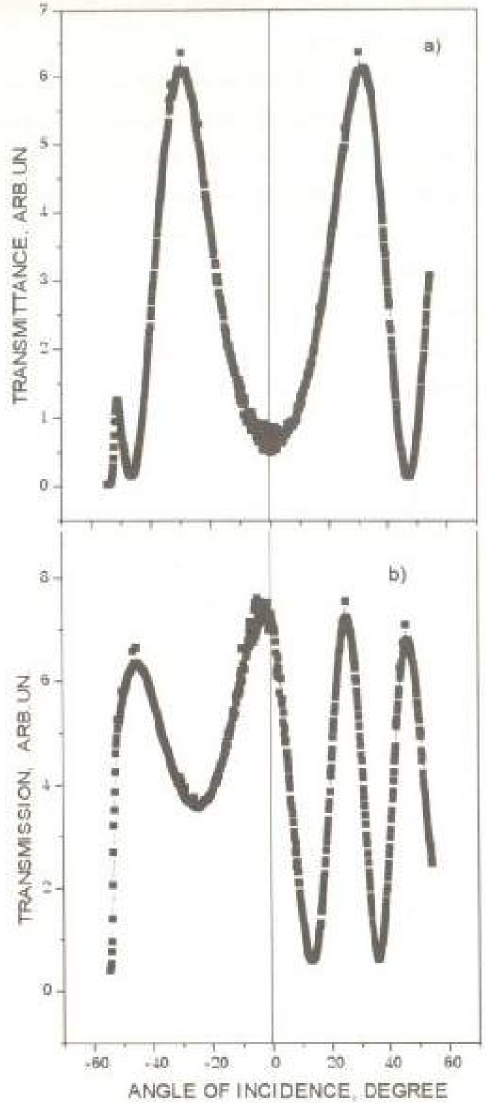

Fig.3

At the equal values of the exposure time of PVCN-F films coated every of the two cell substrates, $t_{exp,1} = t_{exp,2}$ no shift of the curve $T(\varphi)$ about the axis $\varphi = 0$ (Fig.3a) was observed. Such result is conventionally interpreted as zero pretilt angle in a tested cell[7]. Similar conclusion has been presented in the Reference 3 where this observation was firstly reported for PVCN oriented LC cell.

If $t_{exp,1} \neq t_{exp,2}$, some shift of $T(\varphi)$-curve symmetry axis about point $\varphi = 0$ appeared (Fig.3b) what is typical for an oblique orientation of a director in a tested cell[7]. The observed shift $\Delta\varphi$ depended on the time difference $\Delta t_{exp} = t_{exp,1} - t_{exp,2}$. The dependence $\Delta\varphi(\Delta t_{exp})$ which was obtained for cells filled with LC ЖК-1282 and $t_{exp,1} = 10$ min is shown in Fig.4. The sign of the shift was uniquely determined by the adjustment of the cell in the experimental set-up and the direction of the NLC flow in the process of cell filling. Namely, at the counterclockwise rotation of the cell the value of $\Delta\varphi$ was positive, if the surface irradiated with the more exposure time was presented to the laser beam and filling of the cell was made along OX axis in the side of X-s rise (Fig.2). The change of the LC flow direction or 180° turn of the cell, when the surface with shorter t_{exp} was facing to He-Ne laser beam, led to the change of $\Delta\varphi$ sign.

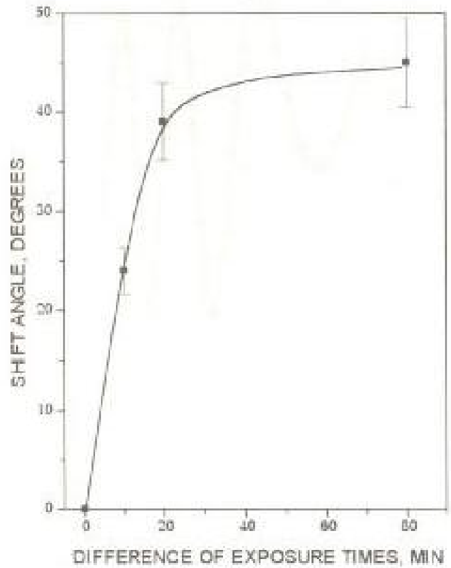

Fig.4

DISCUSSION AND RELATED EXPERIMENTS

1. The observed results can be reasonably explained if a **reverse** tilt orientation[9] $\theta_1 = -\theta_2$ is supposed to be formed in the cells at $\Delta t_{exp} = 0$ (Fig.1a,b). Under this condition the director distribution $\mathbf{d}(z)$ is symmetric with respect to the middle of the cell ($z = L/2$), and as in the case of zero pretilt angle the symmetric form of $T(\varphi)$ curve relatively to the axis $\varphi = 0$ have to be realized. If the pretilt angle on the PVCN-F surface is assumed to be dependent on the exposure time, the distribution $\mathbf{d}(z)$ should become asymmetric with respect to the middle of the cell when $t_{exp,1} \neq t_{exp,2}$. It has to be manifested in the observed shift of the symmetry axis of $T(\varphi)$-curve.

Let us consider the director distribution in the cell with a reverse tilt orientation and its connection with the measured value of $\Delta\varphi$. The total free energy of a NLC in the cell with the thickness L is expessed as follows:

$$F = \frac{1}{2}\int_0^L \left[K_1(div\vec{d})^2 + K_2(\vec{d}rot\vec{d})^2 + K_3[\vec{d} \times rot\vec{d}]^2\right]dz + \frac{1}{2}W_1\sin^2(\theta(0) - \psi_1) + \frac{1}{2}W_2\sin^2(\theta(L) - \psi_2) \quad (2)$$

Here K_i, $i = 1,2,3$ are the elastic constants, W_1 and W_2 are the anchoring energies of the NLC on the first and second surfaces, Ψ_1 and Ψ_2 are the angles between the easy axes $\mathbf{e}_1$ and $\mathbf{e}_2$ and the corresponding surface. The aligning surfaces lie in XY plane.

In the one elastic constant approximation the director distribution in the cell, $\mathbf{d}(z) = (0, \cos\theta, \sin\theta)$, corresponding to the minimum of (2) is described by the equation

$$\frac{d^2\theta}{dz^2} = 0, \quad (3)$$

at the following boundary conditions:

$$K\frac{d\theta}{dz} - \frac{W_1}{2}\sin 2(\theta - \psi_1) = 0; \quad z = 0,$$
$$K\frac{d\theta}{dz} + \frac{W_2}{2}\sin 2(\theta - \psi_2) = 0; \quad z = L, \tag{4}$$

The solution of (3) has the linear form:

$$\theta = Az + B, \tag{5}$$

where A and B are the constants to be found from the boundary conditions (4).

The analysis shows that several forms of solutions (5) satisfy the condition of minimum of the total free energy (2) at the boundary conditions (4). The global energy minimum corresponds to the agreed oblique orientation of NLC. In the approximation of a strong NLC anchoring ($W_1 = W_2 = \infty$) this type of orientation is discribed by the formula

$$\theta_{agr} = \psi_1 - \frac{\psi_2 - \psi_1}{L} z \tag{6}$$

The two lowest local minima of (2) correspond to the reverse oblique director distribution (Fig.1a,b). The first type of the reverse orientation corresponds to the value $\theta = 0$ in some definite plane of the cell volume (Fig.1a), and the second one corresponds to the value $\theta = \pi / 2$ (Fig.1b): In the case of a strong anchoring the solutions for these types of the director distribution take the forms:

$$\theta_{rI} = \psi_1 + \frac{\psi_2 - \psi_1}{L} z$$
$$\theta_{rII} = \psi_1 + \frac{\pi - \psi_2 - \psi_1}{L} z \tag{7}$$

The solutions (6)-(7) are shown in Fig.5. In the case of the reverse orientation and $\psi_2 = -\psi_1$ we have $\theta(L/2) = 0$ and the director distribution is symmetric. The difference between the tilts of the easy axes e_1 and e_2 leads to the linear shift of the point $\theta = 0$ toward the surface with the smaller angle Ψ_i. This resulted in the asymmetric director distribution in the cell, and as it was pointed earlier the asymmetry have to cause some shift of $T(\varphi)$-curve.

The values of the free energy F_{rI} and F_{rII} of the reverse distribution take the forms:

$$F_{rI} = \frac{1}{2} K \left(\frac{\psi_2 - \psi_1}{L} \right)^2 L,$$

$$F_{rII} = \frac{1}{2} K \left(\frac{\pi - \psi_2 - \psi_1}{L} \right)^2 L.$$

It is easyly seen that for $\psi_1 - \psi_2 < \pi / 2$ the first type of the reverse dictribution is more preferable.

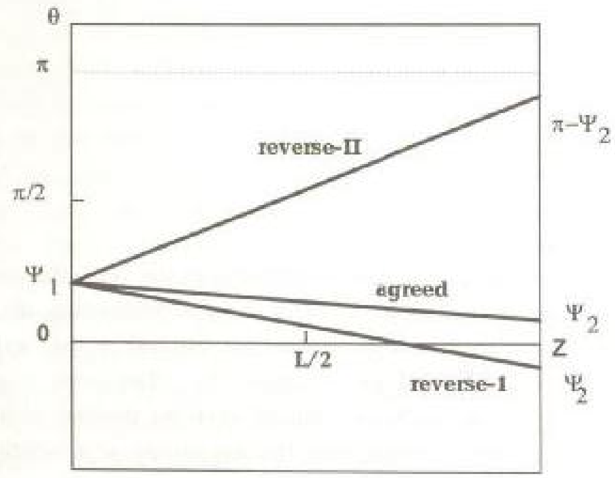

Fig.5

Let us suppose that the "reverse" tilt director distribution of the I-type is realised and try to find the condition when director reorients from the "reverse" distribution to the "agreed" one. We assume that anchoring at the first surface is strong and constant while the anchoring energy on the second surface is changed. In the case of $W_1=\infty$ and $W_2\neq\infty$ the value of director angle at the second surface $|\theta(L)|<|\psi_2|$. If $|\theta(L)|\to 0$ then transition from the "reverse" director distribution to the "agreed" one should occur. Taking into account new boundary conditions

$$\theta(0)=\psi_1,\qquad K\frac{d\theta}{dz}+\frac{W_2}{2}\sin 2(\theta-\psi_2)=0;\quad z=L, \tag{9}$$

and the equation $\theta(L)=0$ we obtain the following condition of the "reverse" to the "agreed" transition

$$\sin 2\psi_2=-2\frac{\psi_1}{\varepsilon_2},\quad \varepsilon_2=\frac{W_2L}{K} \tag{10}$$

or for small values of ψ_2

$$\psi_2\approx-\frac{\psi_1}{\varepsilon_2} \tag{10a}$$

Let us consider the relationship between the value $\Delta\varphi$ and the angles $\theta_{1,2}$ in the case of nonhomogeneous director distribution ***d****(z)*. The crystal rotation method have been developed for the case of the "agreed" oblique orientation and of equal pretilt angles $\theta_{1,2}$. Therefore, to establish the relation between $\Delta\varphi$ and $\theta_{1,2}$ we should solve the problem of polarized light propagation in the medium with the anisotropy axis which changes its direction with the linear low $\theta=Az+B$.

Here we restrict ourselves to the more simple approximation when the nonhomegeneous director distribution is replaced by the homogeneous one.

In this case the effective pretilt angle $\overline{\theta}$ is equal to the angle which is avereged over the cell thickness:

$$\overline{\theta}=\frac{1}{L}\int_0^L(Az+B)dz=\left(\frac{\theta_1+\theta_2}{2}\right), \tag{11}$$

$$\overline{\theta}\approx\frac{\Delta\varphi}{\left(n^o+n^e\right)}. \tag{12}$$

We have compared the results of $\overline{\theta}$ and $\Delta\varphi$ calculation performed by using formulas (11)-(12) and more exact computer simulation. It was found that the difference between the obtained values of $\Delta\varphi$ was not more that 10% for $\theta_{1,2}<10°$.

2. In order to check the suggestion whether the reverse tilt distribution of ***d****(z)* is realized in a cell oriented by the irradiated PVCN-F surface, some related experiments have been done. The basic idea of these experiments was to use the combined cells assembled of the reference aligning surface and the tested one. It is clear that the knowledge of the pretilt angle θ_{ref} on the reference surface allows us to estimate the value θ_{test} on the tested PVCN-surface with the use of (11)-(12).

The rubbed polyimid surface was chosen as a reference one. The characteristics of this surface were studied in the tentative experiments. Two types of the cells (L=20μm) composed of two rubbed polyimid aligning surfaces and filled with NLC ЖК-1285 were tested. In the cells of the first type the rubbing directions of the aligning surfaces coinsided. Such cells manifested the *T(φ)*-curves symmetric around *φ=0* axis, i.e. the reverse tilt orientation with $\theta_{ref,1}=-\theta_{ref,2}$ took place. In the cells of the second type the rubbing directions were oriented oppositely. In this case the displacement of the symmetry axis of T(*φ*)-curves with respect to the point *φ*=0 was obtained. The value of the displacement and its sign **did not depend** on the LC flow direction during cell filling. The value of the pretilt angle $\theta_{ref}=5°$ was calculated using(11),(12). We have also found that the sign of the pretilt angle does not depend on the direction of the LC flow relatively to the rubbing direction and is defined only by the direction of rubbing.

The combined cells had the same thickness and were filled with the same LC as cells assembled of the two rubbed substrates. The exposure time of the tested PVCN-F surface was 5 min. It was observed that the displacement $\Delta\varphi_{comb}$ depended on time passing since filling and was not equal to $\Delta\varphi_{ref}/2$ as have to be in the case of zero pretilt angle θ_{test} (see (11),(12)). Moreover, $\Delta\varphi_{comb}$ value and sign depended on the direction of filling. For the measurement which was done in one week after filling the displacement $\Delta\varphi_{comb,1}=-(20\pm5)°$if the filling direction coincided with the direction of rubbing on the reference surface, if LC flow was opposite to the rubbing direction of the reference surface, then $\Delta\varphi_{comb,2}=(30\pm5)°$ Substituting of the measured magnitudes $\theta_{ref}=5°$ and $\Delta\varphi_{comb,1}$, $\Delta\varphi_{comp,2}$ to (11)-(12) gives the value of $\theta_{test,1}\approx-(18\pm5)°$ and $\theta_{test,2}\approx(16\pm5)°$. The increase of the time between filling and measurements did not lead to the qualitative changes of the obtained results, but caused the decrease of θ_{test}. The quasi-steady state was reached in three weeks and corresponded to $\theta_{test}\approx4°$.

This data imply that PVCN-F surface provide the tilt orientation of NLC and the sign of the pretilt angle is determined by the filling direction. It also means that when the filling and rubbing directions coincide the reverse director distribution of the first type (Fig.1a) appears and the agreed distribution is realized in the opposite case.

These results makes it possible to interpret the observations presented in the previous section as follows. Filling of the cell consisted of two PVCN-F orienting surfaces results in a reverse tilt orientation of the director. Besides, the value $\theta_{1,2}$ depends on the exposure time t_{exp}. In the case of the equal exposure times it leads to the symmetric distribution ***d(z)*** and observed zero displacement $\Delta\varphi$. The different exposure times of the aligning surfaces cause the different values of the angles θ_1 and θ_2 and the displacement $\Delta\varphi$ of $T(\varphi)$-curve takes place.

We have tried to find the dependence $\theta_{test}(t_{exp})$ experimentally. For this purpose the series of the combined cells with the different exposure times of the PVCN-F surface has been made. The direction of the NLC flow during cells filling coincided with the direction of rubbing of the reference polyimid film. The dependencies $\theta_{test}(t_{exp})$ for one series are presented in Fig.6. The curves 1-3 correspond to the measurements performed in 2 days, 1 week and 2 weeks after the filling of the cell.

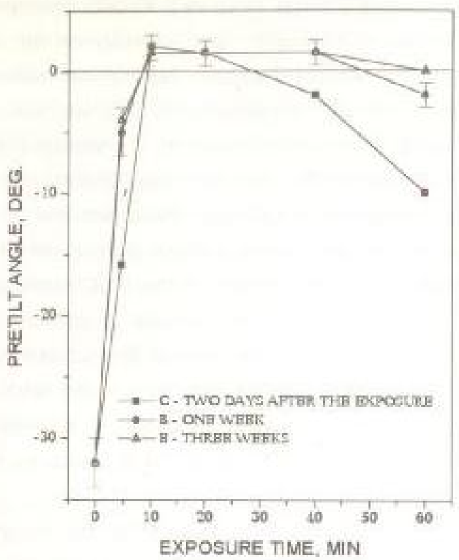

Fig.6

It is seen that in the combined cell the nonilluminated PVCN-coating provides the reverse oblique alignment of NLC. The action of polarized UV-light leads to decreasing of the pretilt angle. After $t_{exp}\geq5$min the weakly-tilted agreed alignment is realized. The further increase of the exposure time leads to lying of the director on the PVCN-F surface and θ_{test} becomes equal to zero.

There is not enough data to develope a microscopic theory of the NLC alignment on the PVCN-F films. Therefore the origin of such a behavior of the dependence $\theta_{test}(t_{exp})$ as well as the other details of the PVCN-F aligning ability are not clear yet and only some tentative speculations may be done.

There are three aligning agents which provide the aligning ability of PVCN-F film[2]. The first one is the main hydrogen-carbone polymer chain related to polyvinylalcohol. The second one is the photosensitive cinnamoyl fragments bonded to the main chain. The third one is the cyclo-butane fragments , which are formed as a result of the interchain photochemical reaction between cinnamoyl groups. It is well known that polyvinylalcohol provides an exact planar orientation and corresponding aligning agent does not change under the UV light action. Taking into account the fact of the oblique orientation on the nonirradiated film we can state that the pretilt angle for the NLC director is caused by cinnamoyl fragments. These fragments are spaced randomly on the nonilluminated surface. Our observation of the correspondence between the directions of filling and the sign of the pretilt angle on the tested surface points that this orientation degeneracy is removed by the alignment of the NLC molecules in the flow during filling. The appearance of cyclo-butane fragments results in the decrease of θ_{test}. It indicates that they reveal the tendency to orient LC molecules planarly. The anchoring energy associated with cyclo-butane fragments is the function of their concentration C and order parameter S. It is reasonable to suggest that the increase of C leads to the increase of W_{PVCN}.

The dependence $\theta_{test}(t_{exp})$ is supposed to be determined by the changes of the ratio between anisotropic cinnamoyl and cyclo-butane fragments and their spatial distribution. At the small exposure times $C \sim t_{exp}$ and $S=const$. It causes the decrease of the pretilt angle and the anchoring energy increase. At some exposure time the condition (10) is achieved and "reverse-agreed" orientation transition occurs. Considering the threshold angle $\theta_{thres}=5°$ one can takes that $\xi_{thres}=1$ and $W_{PVCN}=0.5\cdot10^{-3}erg\cdot cm^{-2}$. The further decrease of the pretilt angle in the agreed state can be associated with the further increase of the anchoring energy as well as with the lying down of the easy axis in the film plane. If to consider that the increase of W_{test} is a dominant factor in this region of the exposure times, then at t_{exp} ≥60min the strong anchoring on the PVCN-F film is realized. It corresponds to $\xi_{thres} \geq 10$, i.e $W_{PVCN} \geq 5\cdot10^{-3}$ $erg\cdot cm^{-2}$ ($L=20\mu m$, $K=10^{-6}$ dyn).

CONCLUSIONS

1. The photosensitive materials on the basis of PVCN can provide both a homogeneous and an oblique orientation of NLC on PVCN-F film illuminated with the polarized UV light. The degenaracy of an easy axis induced by irradiated PVCN-F surface is removed during a LC cell filling. An easy axis makes an obtuse angle with LC flow direction .

2. The photosensitive cinnamoyl fragments have the tendency to orient NLC obliquely while the photoproducts of their cross-linking -cyclo-butane fragments- reveal the planar aligning ability.

3. The angle between PVCN plane and the easy axis induced by the PVCN surface strongly depends on the exposure time of UV illumination, decreasing with the exposure time. The cause of such a behavior is the increase of the concentration of cyclo-butane fragments at the expence of the decrease of cinnamoyl groups.

4. A reverse as well as an agreed oblique director distributions can be realized in the cell with PVCN orienting surface. The condition of the transition from a reverse to an agreed distributions is considered.

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