Control of the Anchoring Energy of Rubbed Polyimide Layers by Irradiation with Depolarized UV-Light

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Exposure of rubbing polyimide (PI) film to depolarized ultraviolet (UV) light suppressed the effective anchoring energy of liquid crystal (LC) with aligning surface. Polarized light changed the orientational distribution of PI molecules obtained by rubbing by changing both the anchoring energy and easy axis direction. These results show that ultraviolet exposure can be effectively used to control anchoring parameters.

KEYWORDS: liquid crystals, photoalignment, anchoring energy, polyimide, UV light

1. Introduction

Thin polyimide (PI) films are the most commonly employed liquid crystal (LC) alignment layers. They have good thermal stability and provide stable planar and tilted LC alignment. Two techniques are utilized to produce LC alignment on PI films. Standard method of rubbing PI films[1–3] changes the topography of the layer and induces an anisotropic orientation of polymer chains along the rubbing direction.[3] Conventional wisdom postulates that orientation of the polymer chains results in epitaxial alignment of the liquid crystal.[4,5]

More recently Hasegawa et al.[6] showed that irradiation of polyimides with polarized UV light produces planar alignment of LC with the orientation of the easy axis, *e*, perpendicular to the polarization vector, *E*. They assumed that irreversible chemical reaction caused by linearly polarized light results in an anisotropy of PI surface and in alignment of LC parallel to the easy axis. A theoretical model of LC photoalignment on PI films was proposed by Johnson et al.[7] In this model the alignment arises from the angular dependence of the probability of photoreaction. The resulting anisotropy of the photosensitive bond distribution results in an anisotropic interaction with LC, which induces an easy axis.

Kim et al.[8,9] believed that the alignment in polyimides is produced by photo-reaction of the C(O)=N bonds of the imide rings. UV irradiation selectively dissociates these photosensitive moeities. In the case of the initially isotropic PI films, polarized exposure produces an anisotropic angular distribution of disassociated and unreacted imide fragments. This theory is supported by the production of both UV-visible and infrared dichroism in the polarized UV exposed films. We postulate that interaction between the LC molecules and the unreacted moieties is stronger explaining why the director of the LC aligns perpendicular to the polarization of UV light.

Kim et al.[9] demonstrated that irradiation of rubbed PI surfaces with polarized UV light can be used to fine-tune the LC alignment by adjusting the angular distribution of the PI aligning fragments. Moreover they found that irradiation of the PI surface with unpolarized UV light destroys the rubbed-induced alignment.

In this paper we show that irradiation of rubbed PI layers with depolarized UV light can be used to control the anchoring energy of LC on the surface. Using both polarized and unpolarized UV exposure we can precisely control the alignment direction and anchoring energy and determine the distribution of the reacted polymer.

2. Light-induced Change in Anchoring Energy of Rubbed PI Surface

We have modeled the alignment of liquid crystal on a photo-exposed, rubbed PI surface. We assume the surface consists of long polymer chains, which contain axially aligned blocks with photosensitive groups. These blocks align the LC molecules parallel to their anisotropy axis. UV light irradiation leads to decomposition of the photosensitive fragments in the blocks. As a result, the LC aligns with the unreacted blocks and therefore perpendicular to the irradiation polarization direction.

The initial angular distribution of the photosensitive blocks is determined by the PI treatment. In the case of a layer made by spin-coating the precursor polyamic acid followed by thermal imidization, the angular distribution of the blocks is assumed to be isotropic in the azimuthal plane. Rubbing of the PI films results in anisotropic distribution of photosensitive blocks, which can be described as a Gaussian distribution:[9]

$$N_0(\phi) = N_0 \exp\left[-\frac{1}{2}\left(\frac{\phi - \phi_r}{w}\right)^2\right] \quad (1)$$

where N_0 is the concentration of PI blocks, ϕ_r is the direction of rubbing coinciding with the direction of the easy axis on the PI surface, and w is the width of the blocks distribution.

We assume that the PI polymer chains do not change orientation after light-induced decomposition.[10] Therefore, according to the model proposed by Johnson et al.,[7] the angular distribution $N(\phi, t)$ of undamaged blocks can be found from the equation

$$\frac{\partial N(\phi, t)}{\partial t} = -\alpha \sigma_{ij} E_i E_j^* N(\phi, t) \quad (2)$$

where $\sigma_{ij} = \sigma_\perp \delta_{ij} + \sigma_a l_i l_j$ is a tensor of light absorption, l is a unit vector along the particular imide bond, E_i are components of the light vector *E*, α is the rate of photochemical dissociation. Solving eqn. (2) for the case of arbitrary polarized light, we obtain the angular distribution of the undamaged blocks in the form

$$N(\phi, t) = N_0(\phi) \exp\left\{-\alpha I t \left[\frac{\sigma_\parallel + \sigma_\perp}{2} + \frac{\sigma_a}{2}(\xi_1 \sin 2\phi + \xi_3 \cos 2\phi)\right]\right\}$$

$$= N_0(\phi) \exp\left\{-\alpha I t \left[\frac{\sigma_\parallel + \sigma_\perp}{2} + \frac{\sigma_a}{2}(1 - e^2)^{1/2} \cos 2(\phi - \psi)\right]\right\} \tag{3}$$

Here ξ_i are the Stokes parameters, I is the intensity of UV light, t_{exp} is the exposure time, ψ is the angle that the major axis of the polarization ellipse makes with the x axis in the plane of the PI surfaces, e is the ellipticity of the incident light.

Analyzing expression (3) we see, that elliptically or linearly polarized light changes the distribution function $N(\phi, t)$ in a complex way. This may result in changes of both the easy axis direction and anchoring energy on the aligning surface.[7–9,11] In contrast, circularly polarized light ($\xi_1 = \xi_3 = 0, \xi_2 = 1$) or completely depolarized light ($\xi_1 = \xi_2 = \xi_3 = 0$) does not change the angular distribution function of polymer fragments. Rather, this type of exposure only changes the number of undamaged blocks aligned in a given direction. Hence, the orientation of the distribution function is fixed while the concentration of the undamaged blocks changes. One can see from eq. (3) that it decreases exponentially with the exposure dose:

$$N(\phi, t) = N_0(\phi) \exp\left(-\alpha \frac{\sigma_\parallel + \sigma_\perp}{2} I t\right) \tag{4}$$

To find out how the change in the microscopic distribution of the polymer chains influences the macroscopic properties of the interface (the value of anchoring energy and direction of easy orientation axis) we assume that the interaction potential between the LC and polymer blocks is

$$U(\varphi_0, \phi) = C \sin^2(\varphi_0 - \phi), \tag{5}$$

where φ_0 is the director angle on the polymer surface with respect to the x axis and angle ϕ defines the axis of anisotropy of a polymer block to the same axis. In this case the surface free energy density of LC can be written as follows

$$f_{surf}(\varphi_0, t) = \int_{-\pi}^{\pi} U(\varphi_0, \phi) N(\phi, t) d\phi. \tag{6}$$

Integrating (6) we immediately obtain the corresponding surface torque

$$\tau_{surf} = \partial f_{surf}/\partial \varphi_0 = \frac{1}{2} W(t, w) \sin 2[\beta(t, w) - \varphi_0] \tag{7}$$

Where $W(t, w)$ is the surface anchoring energy, $\beta(t, w)$ defines the direction of the easy orientation axis.

For depolarized or circularly polarized light the easy axis direction remains fixed and coincides with the rubbing direction. The anchoring energy decreases exponentially with the exposure doze

$$W(t, w) = W_0(w) \exp\left(-\frac{t}{\tau}\right) \tag{8}$$

Here W_0 is the anchoring energy of unirradiated PI, $\tau = 2/\alpha I (\sigma_\parallel + \sigma_\perp)$ is the characteristic time of the dissociation of imide bonds.

Thus, treatment of the PI surface with depolarized light changes the strength of the easy orientation axis but does not affect its direction. Therefore, one can control anchoring parameters independently: the easy axis direction can be adjusted during the rubbing process. Then the fine-tuning of the anchoring energy can be achieved by exposure with depolarized light.

3. Experiment

We tested the above theory using a polyimide with the chemical formula shown in Figure 1. The chemical structure is consistent with the theory developed above. The polymer consists of axially aligned blocks of relatively photostable benzene and the photosensitive cyclobutane tetracarboxylic dianhydride groups. As was shown in our previous paper,[12,13] these groups are easily decomposed under UV-light exposure by cyclobutane ring cleavage. We found that polarized irradiation produced planar alignment of the LC perpendicular to the polarization of UV light.[9] As postulated above, the LC aligns along the axis of remaining PI chains.

The precursor polyamic acid films were synthesized from the reaction between tetracarboxylic dianhydride and diamine. The polyamic films were deposited by first spin-coating dilute solutions of the polyamic acid on glass substrates covered with ITO electrodes. The resulting polyamic films were imidized by curing at 250°C for 1 h. The thickness of the resulting PI film was about 5 nm. PI films were rubbed in one direction. The rubbed substrates were exposed with UV light produced by a 450 W Xenon lamp (Oriel, model 6266). The light was incident normal to the surface. The UV light was polarized with a surface film polarizer (Oriel, model 27320) whose effective range was between 230 nm and 770 nm. The power of UV light after passing through the polarizer was about 1 mW at 254 nm. The intensity of UV light in the plane of the film was in the range 1–100 mW/cm^2.

The anchoring energy on the irradiated PI surface was studied in a twist cell filled with a 4′-n-pentyl-4-cyanobiphenyl (K15, Merk). Thickness of the cell, $L = 20 \mu m$, was controlled by cylindrical spacers. The reference substrate used an unirradiated rubbed PI layer producing strong planar anchoring of the LC. The tested substrate was covered with PI, that have different strip-like regions irradiated for different times. The angle between the easy axis on the reference substrate, e_{ref} (given by the rubbing direction) and the light-induced easy axis on the tested substrate, e_{test} (given by polarization of the light) was $\varphi_r = 57°$. The cell was filled with LC in the isotropic state ($T = 100°C$) and slowly cooled to room temperature to avoid possible flow alignment.
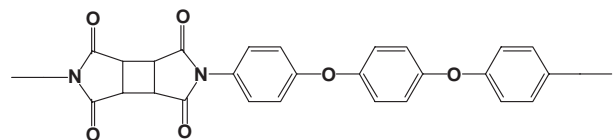

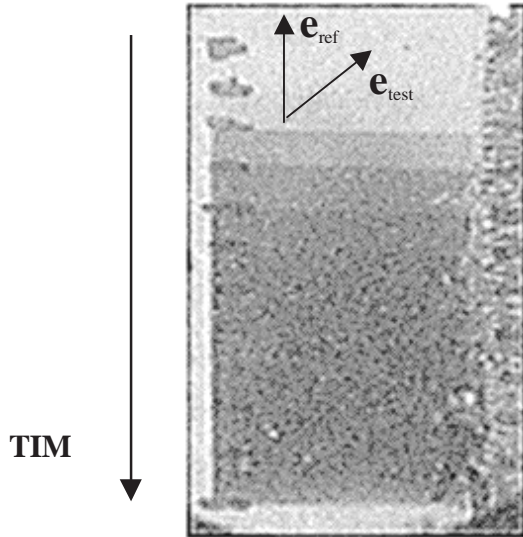Fig. 1. Chemical structure of polyimide material.

Fig. 2. LC cell in crossed polarizers. The directions of rubbing on the reference and tested substrates are depicted with arrows. One can see the stripes, which brightness decrease with time that corresponds to the decrease of the twist angle.
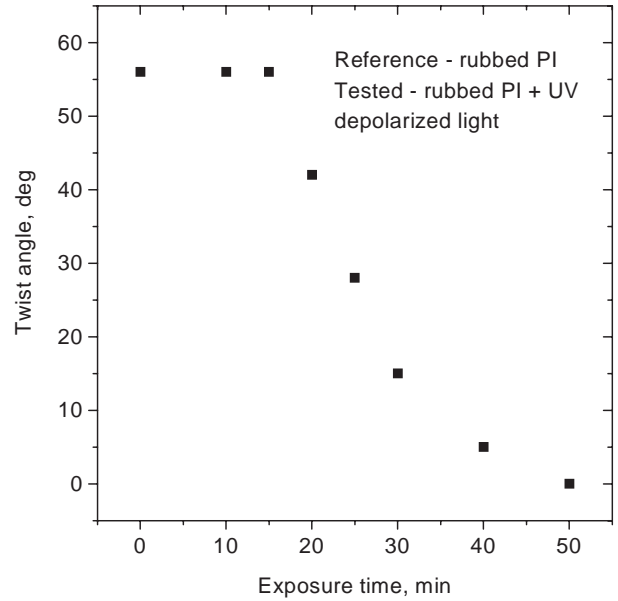

Fig. 3. Twist angle vs exposure time. Depolarized light.

The birefringence of K15 is rather high, $\Delta n = 0.18$. Correspondingly, for the chosen experimental conditions, the dimensionless ratio $2\pi\Delta nL/\lambda \gg 1$ and light beam propagates in the cell in the adiabatic (Mauguin) regime, i.e. the polarization follows the deviation of the director in the cell.[13] This allows the orientation of the director on the tested surface to be determined using polarizing microscope.

The rubbing direction was set parallel to the polarizer axis. The analyzer was rotated to obtain the minimum output in light intensity. In this position the angle between analyzer and polarizer axes corresponds to the twist angle, φ_0, between the director on the reference and tested surfaces.

We observed that the angle φ_0 was equal to $\phi_r = 57°$ in the unexposed regions of the tested surface and monotonically decreased with increase of the exposure time (Fig. 2 and 3). Uniform, homogeneous alignment was observed in the cell in the whole range of the exposure times. Finally, a good planar structure was achieved in the cell.[14]

The monotonic decrease of the director twist angle demonstrates a decrease in the anchoring energy with an increase in the exposure time. The value of the angle φ_0 can be found from the balance of surface and bulk elastic torques, which, according to eq. (7) has the form

$$\varphi_0 + \frac{1}{2}\xi \sin 2(\varphi_0 - \varphi_r) = 0, \qquad (9)$$

where ξ is the anchoring parameter, $\xi = WL/K_{22}$, K_{22} is the twist elastic constant.

The numerical solution to this equation for the experimental data φ_0 and parameters $K_{22} = 3.6 \times 10^{-7}$ erg/cm, $L = 20\,\mu$m is shown in Fig. 4. The exponential fitting curve is presented in the same figure with a dashed line. It is seen that the decrease in the anchoring energy is well described by the exponential function, demonstrating the validity of the
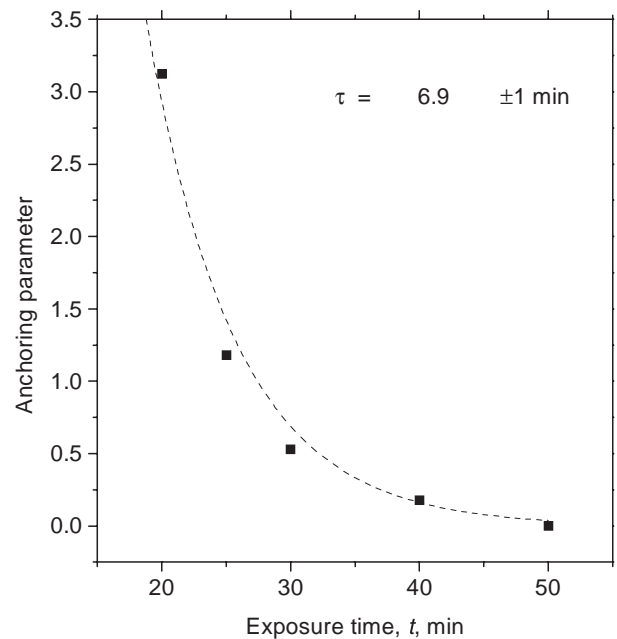

Fig. 4. Anchoring parameter vs the exposure time; depolarized light. Experimental data was calculated using eq. (9). Dotted line presents the exponential fit with $K_{22} = 3.6 \times 10^{-7}$ erg/cm, $L = 20\,\mu$m, $W_0 \sim 6 \times 10^{-3}$ erg/cm^2, and $\tau = 6 \pm 1$ min.

Johnson model for our PI. The fitting of the dependence of $W(t_{exp})$ with exposure time allows evaluation of the anchoring energy $W_0 \sim 6 \times 10^{-3}$ erg/cm^2 and the characteristic rate $\tau = 2/\alpha I(\sigma_\parallel + \sigma_\perp) = (6 \pm 1)$ min of PI decomposition. The knowledge of the values W_0 and τ allows measurement of the width w of the distribution profile $N(w, t)$.

The angular distribution function, $N(\phi, t)$, for the case of linearly polarized light is given by the formula

$$N(\phi, t) = N_0(\phi) \exp\left\{-\alpha I t_{exp}\left[\frac{\sigma_\parallel + \sigma_\perp}{2} + \frac{\sigma_a}{2}\cos 2(\phi - \psi)\right]\right\} \qquad (10)$$

Both the concentration of undamaged bonds and the maximum of their angular distribution changes during irradiation. As a result, the anchoring energy decreases. The easy orientation axis rotates perpendicular to the UV light polarization direction.

The orientation of the director in a cell can be found from the balance of the surface and bulk torques

$$K_2\varphi_0/L - \tau_{\text{surf}}(\varphi_0, t, w) = 0 \qquad (11)$$

This equation can be solved numerically using the parameters W_0, and τ, determined above and the directions ϕ_r and ψ which are given by the experimental geometry. The experimental data for the angle φ_0, which we observed in the combined cell with initial planar alignment ($\phi_r = 0$) and the angle between the direction of rubbing and UV light polarization $\psi = 45°$ are presented in Fig. 5. The dashed line represents the fit of the data to the eq. (11) with $w = 0.5$, anchoring energy $W_0 = 1.8 \times 10^{-3}$ erg/cm^2 and characteristic time $\tau = 6$ min.

This is a sensitive method for the determination of the distribution width. The dotted lines in Fig. 5 are plotted for $w = 0.4$ and 0.6. The value of the anchoring energy strongly

depends on the value of the parameter w.

4. Conclusions

We have shown that irradiation of rubbed PI layer with depolarized UV light can be used to control the anchoring energy of LC on rubbed PI surface. Unpolarized exposure does not change the angular distribution function of the PI fragments. It does change the anchoring energy of the PI layer without reorientation of the easy axis on the PI surface. The combination of irradiation with depolarized and polarized light can be used for measuring the angular distribution of PI fragments.
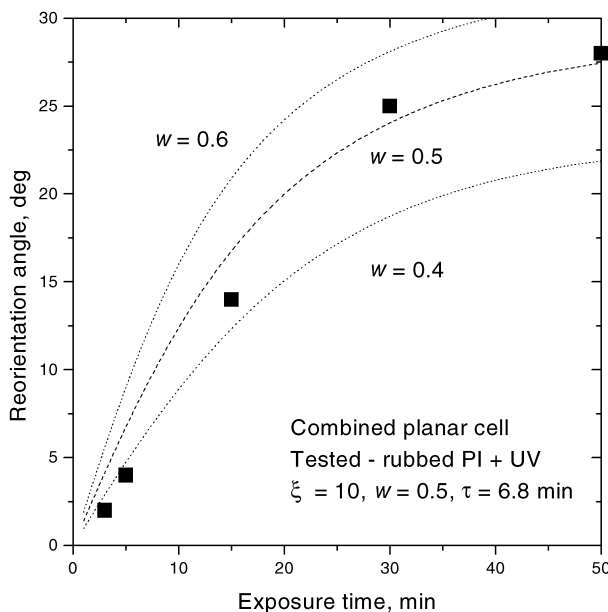
Fig. 5. Twist angle vs exposure time, geometry with polarized UV light. Different curves are plotted for different widths of the PI blocks distributions.

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