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Mechanically and Light Induced Anchoring of Liquid Crystal on Polyimide Film

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The interplay between the effects of mechanical rubbing and UV light induced deimidization on polyimide films has been studied. Exposure to depolarized UV light of rubbing PI film was found to suppress effective anchoring energy. Polarized light led to the alteration of the orientational distribution of PI molecules obtained by rubbing i.e to the change of both anchoring energy and easy axis direction. A simple model based on the selective UV light absorption with consequent deimidization of PI molecules describes the UV-initiated processes on the rubbed polyimide layers but contradicts the experimental data obtained for non-rubbed layers. The results obtained show that UV exposure can be effectively used to control anchoring parameters.

Keywords: liquid crystal; photoalignment; polyimide; anchoring

INTRODUCTION

Thin polyimide (PI) films are the most commonly employed liquid crystal (LC) alignment layers, since they have good thermal stability and provide stable LC alignment.

By now two techniques are utilized to produce high-quality LC alignment on PI films. Traditional one involves rubbing of the PI film coated on the substrate^[1,2]. Rubbing changes the topography of an alignment layer and induces an anisotropic orientation of polymer molecules along rubbing direction^[2]. The disadvantages of the rubbing method are generation of dust

particles, electrostatic charges, physical damage, and nonuniformities of the orienting surface. Although the mechanism responsible for the resultant alignment due to rubbing is not yet fully understood, it is believed that induction of the anisotropy of the polymer chains prevails over other mechanisms like production of "grooves" and change in the surface morphology.

The second and going ahead process is photoalignment method. PI films exposed to a linearly polarized ultraviolet light (UV) can be very effective as an alignment layers^[3-6]. The photoalignment method allows for an easy control of the alignment direction and anchoring strength - basic parameters which characterize the LC - PI film interface. Presumably, the photodecomposition of PI by UV exposure produces anisotropic Van der Waals forces, which align LC. The exposure of the UV light on PI layer also changes the morphological anisotropy of the film^[5].

In this work we concentrated on the influence of UV light on the properties of rubbed PI film. We have measured anchoring parameters of interface LC 5CB + rubbed PI film exposed both to depolarized and polarized light, and have measured optical birefringence of the PI film. We also present a phenomenological model to understand the relationship between the measured phase retardation, anchoring parameters and photochemical reaction in PI film.

EXPERIMENT

The chemical structure of PI material is presented in Fig. 1. The material was prepared by heat curing of the precursor polyamic acid which had been synthesized from the reaction between tetracarboxylic dianhydride and diamine.

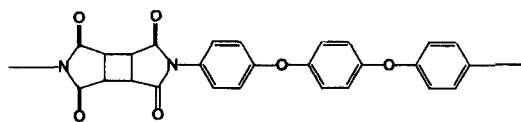


FIGURE 1. Chemical structure of polyimide material

PI films were deposited by first spin-coating dilute solutions of the respective polyamic acids on glass substrates covered with ITO electrodes and then

curing at 250 °C for an hour. The thickness of the PI film was about 5 nm. PI films were double rubbed in one direction. The rubbed substrates were exposed with UV light normal to the surface with 450 W Xenon lamp (Oriol, model 6266). The polarization of UV light was set with a surface film polarizer (Oriol, 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 set by positive quartz lens and controlled in the range 1-100 mW/cm².

LC alignment was studied in a combined sandwich cell filled with a 4'-n-pentyl-4-cyanobiphenyl (5CB or K15 from Merck). Thickness of the cell, $L=20\mu\text{m}$ was given by cylindrical spacers. Reference substrate was covered with a not-irradiated PI layer and the tested substrate was covered with irradiated PI. The not-irradiated polyimide surface provided the strong anchoring of LC parallel to the rubbing direction. The cell was filled with LC in the isotropic state ($T=100^\circ\text{C}$) and cooled down slowly to room temperature to avoid possible alignment in flow.

The alignment textures were analyzed in polarizing microscope. The director deviation onto UV-treated surfaces was measured as a function of the UV exposure time either with not-polarized light or with polarized light at different direction of light polarization, \mathbf{E} .

The effect of UV irradiation on anisotropic properties of the PI films was also investigated by measuring of a birefringence of PI films and observing surface morphology in AFM microscope. The corresponding techniques are described in Ref. [7].

THEORETICAL APPROACH, RESULTS, AND DISCUSSION

Phenomenological approach to the surface free energy

We assume that photoreaction involves photosensitive imide bonds causing photochemical dissociation of them. The time dependent angular distribution of photosensitive bonds is $N(\theta, \phi, t)$. Within the framework of the model proposed by Chen et.al.^[8] the photoreaction rate is proportional to the light adsorption

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

where $\sigma_{ij} = \sigma_{\perp} \delta_{ij} + \sigma_a l_i l_j$ is a tensor of light absorption, E_i are components of the light vector \vec{E} , δ is the rate constant of photochemical dissociation. Considering a two-dimensional system in which all molecules lie in plane parallel to substrate we have

$$N(\phi, t) = N_0(\phi) \exp \left\{ -\alpha t \left[\frac{\sigma_{\parallel} + \sigma_{\perp}}{2} + \frac{\sigma_a}{2} (\xi_1 \sin 2(\phi_0 - \phi) + \xi_3 \cos 2(\phi_0 - \phi)) \right] \right\}$$

Here $N_0(\phi)$ is the initial angular distribution of photosensitive bonds, $\alpha = \delta \vec{E} \vec{E}^*$, ξ_i are the Stokes parameters, ϕ_0 is the azimuthal angle for the UV direction.

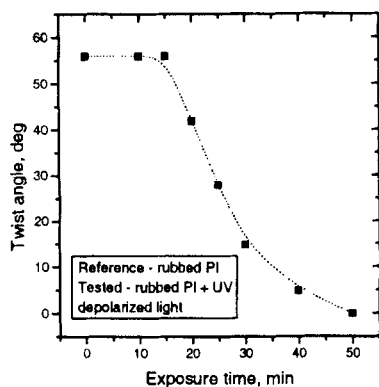


FIGURE 2 Director deviation as a function of the UV exposure time for rubbed PI film. Depolarized light.

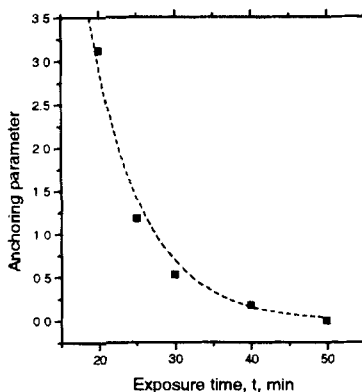


FIGURE 3 Anchoring parameter vs. exposure time. The dashed line represents the fit of the data to Eq. 4

The orientational distribution that polymer chains acquire during rubbing is assumed to be Gaussian peaked in the direction of rubbing [6]

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

w is the width of distribution, ϕ_r is the azimuthal angle for the rubbing direction.

We assume that interaction potential between the LC with alignment direction ϕ_0 and polymer bond with an orientation at ϕ is proportional to $U(\phi_0, \phi) = \sum_{n=1, \infty} C_n \sin^{2n}(\phi_0 - \phi)$. Then the surface free energy density can be expressed as follows

$$f_{surf}(\phi_0, t) = W \int_{-\pi}^{\pi} U(\phi_0, \phi) N(\phi, t) d\phi \quad (2)$$

The free energy of the LC cell can be presented as

$$F = \frac{1}{2} K_2 \int (\partial \phi / \partial z)^2 dV + \int f_{surf}(\phi, t) dS$$

Application of variational procedure gives distribution of the director in the cell and boundary conditions

$$\begin{aligned} \phi &= \phi_0 (1 - z/L) \\ K_2 \phi_0 / L - \partial_{\phi_0} f_{surf}(\phi_0, t) &= 0 \end{aligned} \quad (3)$$

Thus, measurements of the director deviation as a function of the exposure time provide the complete information about surface anchoring potential.

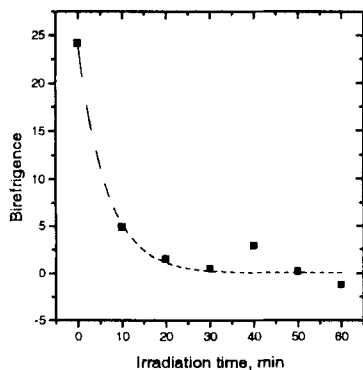


FIGURE 4 Phase retardation of rubbed PI film exposed to depolarized UV light

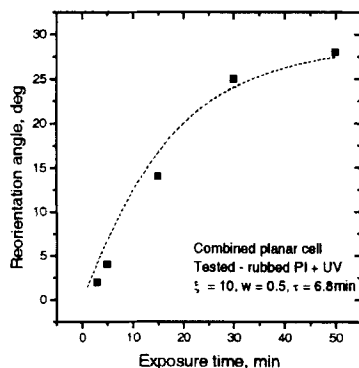


FIGURE 5 Director deviation on the rubbed PI surface exposed to polarized UV light

Alignment of LC on rubbed PI film exposed to depolarized UV light

To study changes in anchoring parameters during the UV exposure twisted LC cell was assembled. The angle between rubbing directions on the reference and tested substrates was $\beta = 57^\circ$. Director deviation on the tested surface was measured as the function of the exposure time; the results are shown in Fig. 2.

It is seen that twisting angle decreases upon exposure indicating that depolarized light causes decreasing of the anchoring coefficient, which can be due to the photochemical dissociation of imide bonds^[5,6]. After 50min of UV exposure the planar alignment was achieved, i.e. the broken bonds do not influence the orientation of LC. The observation in AFM showed the simultaneous disappearance on the UV treated PI surface of the microscopic grooves induced by a rubbing process.

Assuming that rubbing provides strong anchoring of LC and keeping only the first term in the expansion of interaction potential $U(\varphi_0, \phi)$ we obtain the following equation for the director deviation on the control surface

$$\varphi_0 + \xi \exp\left[-\frac{1}{2}\alpha(\sigma_{\parallel} + \sigma_{\perp})\right] \sin 2(\varphi_0 - \phi) = 0 \quad (4)$$

It is seen that in our model the anchoring parameter decreases exponentially with time when film is exposed to the depolarized light. The decay constant is determined by the efficiency of deimidization process. Calculated from the experimental data anchoring parameter with fitting curves are presented in Fig. 3, where $\alpha(\sigma_{\parallel} + \sigma_{\perp}) = 0.15 \text{ min}^{-1}$. Thus, our model well describes the experimental data for the rubbed surface in spite of lacking

of the contribution of micro-grooves due to rubbing. It means that this contribution is weak in our case.

Optical retardation measurements of the PI film

The broken bonds also reduce the polarizability of the PI molecules, so that the optical retardation of the PI film decreases during the film exposure (Fig. 4). The total optical retardation can be written as [6]

$$R(t) = R_0 \int_0^{\pi/2} (2 \cos^2 \phi - 1) (1 - N(\phi, t)) d\phi \quad (5)$$

In the case of depolarized light $\xi_{1,2} = 0$ and the total optical retardation is

$$R(t) = \tilde{R} \exp\left(-\alpha t \frac{\sigma_{\parallel} + \sigma_{\perp}}{2}\right) \quad (6)$$

where $\tilde{R} = -R_0 \int_0^{\pi/2} (2 \cos^2 \phi - 1) N_0(\phi) d\phi$.

Thus, the optical retardation measurements should give the same exponential decay as the measurements of twist angle. Indeed, these times agree within the limits of experimental error.

Alignment of LC on rubbed and not rubbed PI films exposed to polarized UV light

The next set of experiments was performed to study the change in the anisotropic distribution of PI chains induced by rubbing under the linearly polarized UV light exposure. The geometry of the cell was as follows: rubbing directions coincide, but polarization direction of UV light makes an angle $\frac{1}{4}\pi$ with respect to the rubbing. Thus, the twist angle increases with exposure. Corresponding measurements of the director angle are presented in Fig. 5. The dashed line in Fig. 5 represents the fit of the data to the Eq. (3) with $w = 0.5$, anchoring strength $\xi = 10$, and characteristic time $\tau^{-1} = \alpha(\sigma_{\parallel} + \sigma_{\perp}) = 0.147 \text{ min}^{-1}$. Good agreement between the experimental data and theoretical calculations points again on the validity of our approach to the description of photoalignment on the rubbed surface.

The analogous experiment with not-rubbed PI layer resulted in a different conclusion. In this experiment the angle between the easy axes on the reference and tested surfaces was $\frac{1}{4}\pi$. The results presented in Fig. 6 demonstrate fast nonlinear increase of the reorientation angle, ϕ , followed by its saturation with the increase of the exposure. This fast growth of the director cannot be described by the model proposed by Chen *et al.* Besides, our measurements showed that the dependence of the birefringence of the not-rubbed PI film on exposure time has evident maximum in the same exposure range.

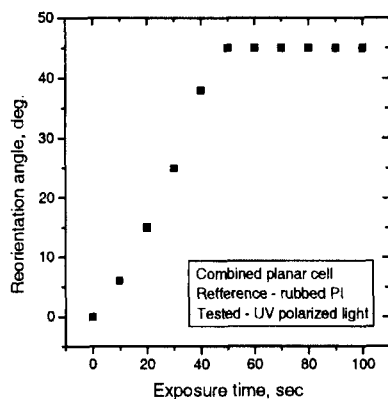


FIGURE 6 Director deviation on the non-rubbed PI surface exposed to polarized UV light

Thus, we can state that the developed approach is not valid in the case of not-rubbed PI layers. We believe that the main reason leading to this discrepancy is neglecting of mutual interaction between LC layer and PI bonds: photosensitive fragments can be re-oriented by liquid crystal strengthening the anchoring energy.

CONCLUSIONS

It is evident that details of the competition between the effects of rubbing and UV light exposure deserve further investigations. The phenomenological model of anchoring proposed by Chen *et. al.* works for rubbed PI films and fails to explain exposure time dependence of the photoinduced anchoring for non-rubbed films. Combination of rubbing and UV exposure provides a powerful method for controlling and tuning parameters of the PI - LC interface.

Acknowledgments

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