

## O-13 DETERMINATION OF ANCHORING PROPERTIES ON RUBBED POLYIMIDE SURFACES

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A new method to determine liquid crystal (LC) anchoring properties on rubbed polyimide (PI) surfaces, that exploits the changes in the easy axis of rubbed film induced by exposure to linearly polarized UV light, has been devised. The distribution of PI chains in a rubbed film is approximated by a Gaussian function and its width determined from the measured rotation of the film's easy axis as a function of exposure time. A simple microscopic model of the PI chain distribution and surface free energy is suggested to describe the LC anchoring properties on rubbed PI films. A close agreement between the experimental values and predictions of the model for the dependence of the azimuthal anchoring energy on the width of the distribution validates the model. The measurements of the width of the chain distribution function provide a simple LC material-independent method for determining the LC anchoring properties. Additionally, the model permits to calculate the strength of LC-PI interaction.

### 1. Introduction

The alignment of liquid crystals (LCs) on solid substrates involves a wide variety of interfacial phenomena (such as surface ordering, surface transitions, surface wetting etc.) which are not well understood. Surface treatments, such as, obliquely evaporated SiO<sub>x</sub> layers, Langmuir-Blodgett films, rubbed polymer films have been used to obtain homogeneous alignment of LCs [1]. In recent years, photo-alignment [2-4] has emerged as a promising non-contact technique because of its simplicity and easy control of the alignment direction and anchoring energy.

Alignment layers prepared by different techniques or processed differently using a specific technique result in different anchoring properties. It is essential to acquire a good understanding of anchoring properties of the surfaces involved to be able to control the LC alignment. Different methods, based on Rapini-Papoular phenomenological model [5] for the surface free energy; such as, surface disclinations [6], Fr ederick transition [7,8], high field [9], Cano wedge cell [10], optical reflectometric method [11], RV technique [12] etc. have been used to measure the polar and azimuthal anchoring energies. However, the anchoring energies obtained from these methods inherently depend on the LC material used, which makes it difficult to isolate the contribution of the

morphological effects from that of chemical interactions.

Recently, it has known that the distribution of polymer chain can be measured with linearly polarized UV exposure followed by rubbing [13,14]. In this work, a new approach for determining the LC anchoring properties on rubbed polyimide (PI) surfaces by measuring the order of alignment of polymer chain described by the width of the distribution is presented. The main features of the experimental results are described by a simple model.

### 2. Experimental

A polyamic acid solution of SE610 ( Nissan Chemical Company) was spin coated on 52 mm x52 mm ITO coated glass at 3000 rpm for 30 secs. The films were soft baked at 100 °C for 10 min for solvent evaporation followed by 1 hour hard bake at 220 °C for imidization. Those films were then rubbed using a metal cylinder wrapped in velvet cloth. The cylinder was spun at a constant angular velocity 550 rev/min. In order to get substrates with different anchoring properties, the number of rubbings with same pressure was varied while keeping the velocity of substrates constant at 3.0 ft/min.

The azimuthal anchoring energies on the surfaces were measured using the method proposed by Akahane *et al.* [15]. A 450W Xenon lamp (Oriel, model 66021)

was used as the UV source. The intensity of collimated beam of LPUV light after the UV sheet polarizer ( Oriel, model 27320) on the films' surface was approximately 4.5 mW/cm<sup>2</sup> at 350 nm wavelength.

A photo-elastic modulator (PEM90, Hinds Instruments) with a fused silica was used for optical retardation measurements. The optic axis of the PEM, placed between crossed polarizers, was kept at an angle of 45° to the axes of polarizer and analyzer. The substrates were mounted on a motorized rotation stage in between the PEM and the analyzer. A collimated beam of light from a He-Ne laser incident normally to the substrate was parallel to the axis of rotation of the substrate. The signal from the photo-detector placed after the analyzer was fed to a lock-in amplifier (EG & G Princeton Applied Research, model 5210) tuned to 50 kHz signal from PEM. By monitoring transmitted light from the substrate it was possible to measure the optical retardation with a precision of ± 0.01°.

### 3. RESULTS and DISCUSSIONS

An untreated PI film possesses azimuthal symmetry and hence is optically isotropic. Upon rubbing, the symmetry is broken and the distribution of PI chains becomes anisotropic. Initially, the optical retardation induced by rubbing increases rapidly but then, as the chain alignment saturates, the rate of increase is diminished. From previous studies [13,14], we found that the distribution of PI chains on rubbed polyimide film can be described by Gaussian distribution as

$$N_0(\theta, \phi) = N_0 e^{-\frac{(\phi - \phi_r)^2}{2\omega^2}} \quad (1)$$

where  $\phi_r$  specifies the rubbing direction,  $\omega$  is the width of the distribution,  $N_0$  is the normalization factor. The easy axis of the rubbed PI film is profoundly affected by LPUV exposure because of the dissociation of the photosensitive bonds.

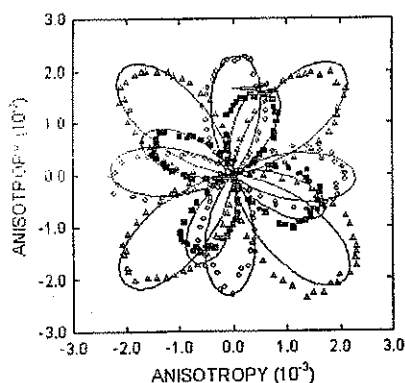


Figure 1. The angular dependences of optical anisotropy for a rubbed film. The open circles, filled squares, and open triangles represent exposures of 0, 5 and 20 min, respectively

Fig. 1 shows the time dependence of the measured optical anisotropy (birefringence), in polar coordinates, for rubbed PI film with LPUV exposures of 0 (circles), 5 (squares), and 20 (triangles) minutes. The polarization direction of LPUV light makes 50° with respect to the rubbing direction. After 20 minutes, the fast optical axis ( $\phi_s$ ) is rotated by 40°. The time dependence of the rotation angle  $\Delta\phi = \phi_s + 50^\circ$  is shown in Fig. 2. The angle  $\Delta\phi$  is measured with respect to the direction of alignment preferred by the UV which is perpendicular to the direction of its polarization for SE610 [16]. It is clear from the figure that as the UV exposure time increases the easy axis rotates and  $\Delta\phi$  decreases and after long enough an exposure becomes zero.

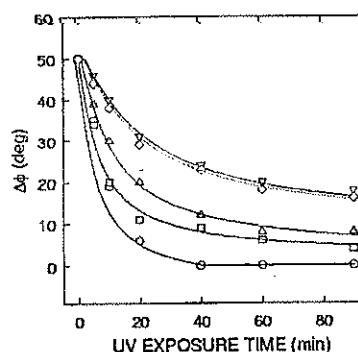


Figure 2. The angle of rotation,  $\Delta\phi$ , of the easy axis with respect to the polarization direction of LPUV as function of exposure time for one ( ), two ( ), four ( ), five ( ), and six (∇) rubbings. The solid curve are the best fits to Eq.(2).

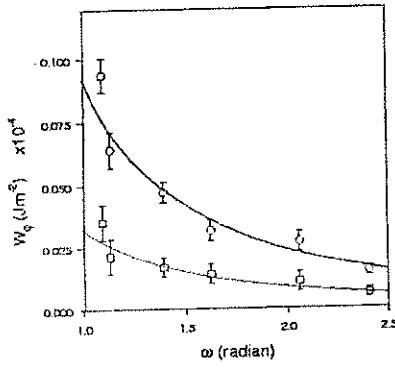
The equilibrium orientation,  $\phi_s$ , of the easy axis can be determined as [13,14]

$$t \sin 2(\phi_0 - \phi_s) + B\phi_s = 0 \quad (2)$$

where  $B = 1/(\alpha\omega^2 \sin^2\theta)$ . The solid lines are the fits of Eq. (2) to the experimental data. From the fitting process, the width of the Gaussian distribution is determined using a previous value of  $\alpha = 0.026$  [14]. The value of  $\theta$  is set to 90° because the chains on a PI film imidized at this temperature lie in a two dimensional plane parallel to the substrate. For weak or less rubbing the width is large due to the nearly random distribution of PI chains. However, with increased rubbing strength more PI chains are aligned and the width decreases until a saturation in the alignment of PI chains is reached.

The azimuthal anchoring energy on these surfaces has been measured for nematic LCs E7 and ZLI-4972. Fig. 3 shows the dependence of the anchoring energy on the distribution width.

## Determination of Anchoring Properties on Rubbed PI Surface



**Figure 3.** Dependence of the azimuthal anchoring energy,  $W_\phi$ , on the width of the distribution for nematic LCs ZLI-4792 ( $\circ$ ) and E7 ( $\square$ ). Solid curves are calculated using  $\phi_i^0$  from the model with  $\phi_0=57.3^\circ$ ,  $\phi_r=90^\circ$ ,  $p=40 \mu\text{m}$ , and  $Cd/K_2=18$  for E7 and  $Cd/K_2=40$  for ZLI-4792.

Let us now consider a cell made with two rubbed substrates located at  $z=0$  and  $z=d$ , as shown in Fig. 4, and filled with a chiral doped nematic LC. The substrate at  $z=0$  is assumed to have strong enough anchoring to perfectly align the director along the rubbing direction  $x$ . The distribution of PI chains at the (upper) substrate at  $z=d$  is given by Eq. (1). The interaction between the LC director and PI chains oriented along respective directions  $\phi_i$  and  $\phi$  can be written using Rapini-Papoular type function,  $C\sin^2(\phi-\phi_i)$  [5], weighted by the distribution function. The azimuthal surface free energy per unit area of the interface is given by the ensemble average,

$$F_s = \frac{1}{2} \int_0^\pi C f(\theta, \phi) \sin^2(\phi - \phi_i) d\phi \quad (3)$$

where  $f(\theta, \phi)$  is the probability distribution function given as,

$$f(\theta, \phi) = \frac{e^{-(\phi-\phi_r)^2/2\omega^2}}{\int_0^\pi e^{-(\phi-\phi_r)^2/2\omega^2} d\phi} \quad (4)$$

and  $C$  represents the average strength of intramolecular interactions between PI and LC molecules. Any microscopic modifications of the films' surface is reflected in the free energy through changes in its width  $\omega$ .

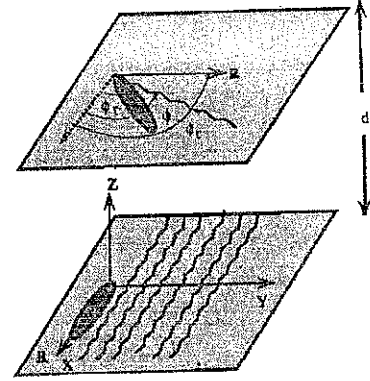
If  $p$  is the pitch of the LC, the natural twist of the director near the top surface is  $\phi_0=2\pi d/p$ . In the framework of the continuum elastic theory, the total free energy is given by [17],

$$F = \frac{K_2}{2d} \{(\phi_0 - \phi_i)^2 + \frac{Cd}{K_2} \int_0^\pi f(\theta, \phi) \sin^2(\phi - \phi_i) d\phi\} \quad (5)$$

where  $\phi_i$  is the equilibrium twist angle at the top surface. Minimization of Eq. (5) with respect to  $\phi_i$  gives,

$$C = \frac{2K_2(\phi_i^0 - \phi_0)}{d \int_0^\pi f(\theta, \phi) \sin 2(\phi - \phi_i^0) d\phi} \quad (6)$$

where  $\phi_i^0$  is the actual twist angle that minimizes the total free energy.



**Figure 4.** Geometry of LC cell used in the model.  $R_1$  and  $R_2$  are respective rubbing directions on substrates at  $z=0$  and  $z=d$ . The substrate at  $z=0$  is assumed to have strong anchoring. Angles  $\phi_i$ ,  $\phi$ , and  $\phi_r$  are the usual azimuthal coordinates of the LC director, PI chain, and  $R_2$ , respectively. The cell is filled with nematic LC dope with a chiral material inducing a pitch  $p$ .

It should be noted that when PI surface has strong anchoring i.e. all PI chains are aligned along the rubbing direction,  $\omega \rightarrow 0$  and the probability distribution function  $f(\theta, \phi)$  vanishes everywhere except at  $\phi = \phi_r$ , where it is unity. In this limit, Eq. (6) reduces to,

$$C = \frac{2K_2\{\phi_i^0(\omega=0) - \phi_0\}}{d \sin 2\{\phi_r - \phi_i^0(\omega=0)\}} \quad (7)$$

This result is similar to the expression previously used to determine the azimuthal anchoring energy  $W_\phi$  [10,15,18]. Unlike the azimuthal anchoring energy function  $W_\phi$ ,  $C$  in our model is constant for a given LC-PI system. The value of  $C$  can be calculated from the measured width of the distribution, and the equilibrium director orientation which can be determined using an optical technique [15].

The solid lines in Fig. 3 represent calculated values from the equilibrium director orientations based on the model for  $\phi_r=90^\circ$ ,  $\phi_0=57.3^\circ$ , and  $p=40 \mu\text{m}$  for corresponding LCs. The increase in azimuthal anchoring energy with a decrease in the width implies that the number of PI chains contributing to the LC anchoring along the rubbing direction becomes higher with increasing rubbing strength. From the corresponding theoretical fit to the experimental data, the value of  $C$  is determined to be  $1.41 \times 10^{-5} \text{ Jm}^{-2}$  and  $3.92 \times 10^{-5} \text{ Jm}^{-2}$  for E7 and ZLI-4792, respectively. The difference between the  $C$  values for two LCs indicates that the strength of the LC-PI interaction for these two

LCs are different owing to their different chemical structures.

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#### 4. CONCLUSIONS

It has been shown that a simple microscopic model of the PI chain distribution and surface free energy can be used to describe the LC anchoring properties on rubbed PI films. A close agreement between the experimental values and predictions of the model for the dependence of the azimuthal anchoring energy on the width of the distribution validates the model. The width of the Gaussian distribution can be measured and used to determine the degree of LC alignment induced by rubbing. Additionally, the model permits a direct experimental determination of the strength of LC-PI interaction. We believe that this simple model can be extended to determine the LC anchoring properties of the interfaces prepared by other techniques.

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