Jpn. J. Appl. Phys. Vol. 38 (1999) pp. L 1538–L 1540
Part 2, No. 12B, 15 December 1999

A Simple and Material Independent Method for the Determination of Anchoring Properties of Rubbed Polyimide Surfaces

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(Received September 6, 1999; accepted for publication November 10, 1999)

A method to determine liquid crystal (LC) anchoring properties, that exploits the changes induced in a rubbed polyimide (PI) film upon exposure to linearly polarized ultra-violet light, has been devised. The width of the Gaussian PI chain distribution is determined from the measured rotation of the PI film's index ellipsoid, the long axis of which is also the LC easy axis, as a function of exposure time. A quasi-microscopic surface free energy is used to model the anchoring properties. This approach provides a simple LC material independent method for determining the LC anchoring properties.

KEYWORDS: liquid crystal, polyimide, anchoring properties, index ellipsoid, free energy

In recent years, surface anchoring of liquid crystals (LC) has acquired considerable attention from researchers, both, in fundamental and applied areas. Different methods,[1–6] based on Rapini-Papoular phenomenological model[7] for the surface free energy, have been used to determine the polar and azimuthal anchoring energies. Most of these methods, however, are restricted in their applicability either in strong or in weak anchoring regimes. Moreover, the anchoring energies obtained from these methods inherently depend on the LC material used. This is of limited use to researchers who wish to use a different LC material.

In this letter, we present an entirely different approach for determining the LC anchoring properties on rubbed polyimide (PI) surfaces which can be used in strong/weak anchoring conditions. This method is based on a simple model of the distribution of PI chains and of the LC-substrate interface free energy. It allows one to extract the average strength of LC-PI interaction. Once the strength of interaction is known for a given LC-PI combination, the changes in the anchoring properties induced by a specific extent of rubbing can be determined *without* assembling LC cells, thus avoiding a laborious process.

In our study, PI films were rubbed after preparation and subsequently exposed to linearly polarized ultraviolet (LPUV) light for different durations. To prepare the alignment layers used in this study, a polyamic acid solution of SE610 (Nissan Chemical Co.) was spin coated, at 3000 rpm for 30 s, onto indium tin oxide coated glass, soft baked (100°C for 10 min), and then hard baked at 220°C for 1 h. The films were then rubbed using a metal cylinder wrapped in velvet cloth. In order to get substrates with different anchoring properties, the number of rubbings was varied while keeping the pressure, the velocity of substrates (0.9 m/min), and the angular velocity of the cylinder (550 rpm) constant. A glass plate prepared in this manner was cut into four pieces. Two pieces were exposed to LPUV at 4.5 mW/cm^2 at 350 nm for different durations followed by optical retardation measurements. A He–Ne laser in conjunction with a photo-elastic modulator (PEM90, Hinds Instruments) with a fused silica head was used for optical retardation measurements. The remaining two pieces alongwith two other strongly rubbed pieces were used for azimuthal anchoring energy measurements for two different nematic LCs, viz. E7 (BDH Ltd.) and ZLI-4792 (Merck Chemicals).

In order to write the free energy, consider the situation in a LC cell as shown in Fig. 1. The cell is assumed to be of thickness d, filled with a chiral doped nematic LC having an induced pitch p. The bottom substrate is assumed to have strong enough anchoring to perfectly align the director along the rubbing direction. The azimuthal distribution of PI chains at the upper substrate is approximated by a Gaussian function centered about the rubbing direction ϕ_r.[11] The interaction between the LC director and PI chains oriented along respective directions ϕ_t and ϕ is approximated by a Rapini-Papoular type function, $C\sin^2(\phi-\phi_t)$, weighted by the distribution function. The free energy per unit area, F, is then given by the sum of the bulk and surface contributions,[12]

$$F = \frac{K_2}{2d}\left\{(\phi_0-\phi_t)^2 + \frac{Cd}{K_2}\int_0^{\pi} f(\theta,\ \phi)\sin^2(\phi-\phi_t)\mathrm{d}\phi\right\}$$

where, K_2 is the twist elastic constant of the LC, $\phi_0 = 2\pi p/d$ is the natural twist, and C represents the average strength of interactions between PI and LC molecules and is independent of the surface treatment for a given LC-PI combination. The probability distribution function is given by

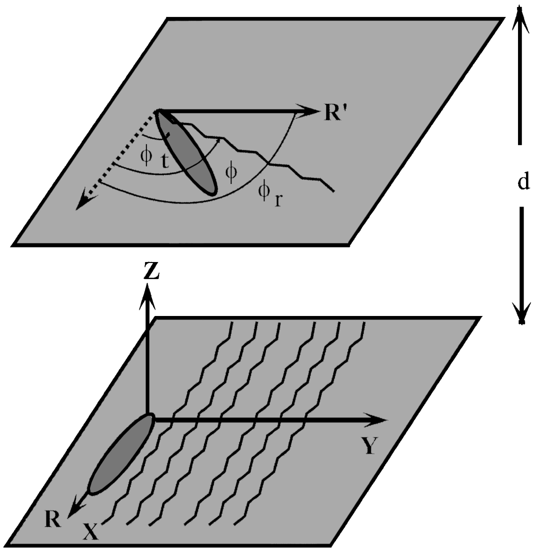

Fig. 1. Geometry of LC cell used in the model. $\boldsymbol{R}$ and $\boldsymbol{R}'$ are respective rubbing directions on substrates at $z = 0$ and $z = d$. The substrate at $z = 0$ is assumed to have strong anchoring. Angles ϕ_t, ϕ, and ϕ_r are the azimuthal coordinates of the LC director, PI chain, and $\boldsymbol{R}'$, respectively. The cell is filled with nematic LC doped with a chiral material which induces a pitch p.

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

Any microscopic modifications induced on the surface by rubbing are reflected in the free energy through changes in the width, ω, of the distribution function.

The equilibrium orientation of the director is dictated by a delicate interplay between the surface and bulk contributions. Minimization of F with respect to ϕ_t gives,

$$C = \frac{2K_2(\phi_t^0 - \phi_0)}{d\displaystyle\int_0^{\pi} f(\theta,\ \phi)\sin 2(\phi - \phi_t^0)\mathrm{d}\phi}$$

where, ϕ_t^0 is the equilibrium twist angle at the minimum of the total free energy.

The value of C can be determined from the measured width of the distribution, and the equilibrium director orientation which can be obtained using an optical technique.[13)] It should be noted that when all PI chains are aligned along the rubbing direction (i.e., the strong anchoring limit), $\omega \to 0$ and the expression for C reduces to the azimuthal anchoring energy W_ϕ.[4,13)]

Validity of the model is tested by studying the equilibrium twist, ϕ_t^0, as a function of the width of the distribution. Figure 2 shows the dependence of ϕ_t^0 as a function of the distribution width for $\phi_0 = 57.3°$, $\phi_r = 90°$ and different values of Cd/K_2. It is clear that for large value of ω, i.e., for almost random distribution of PI chains, the orientation of the director is dictated by the natural twist. On the other hand, when ω is small or majority of PI chains are aligned along the rubbing direction, the free energy is minimum when the director is nearly parallel to the rubbing direction. The direction of alignment also depends on the strength of the LC-PI interaction relative to the twist elastic energy (i.e., the ratio Cd/K_2).

The distribution of chains in a rubbed PI film is profoundly altered by LPUV exposure because of the dissociation of the photosensitive bonds. When a rubbed film is exposed for a time t to normally incident LPUV light, the equilibrium orientation, ϕ_s, of the easy axis is determined from the extremum of the resultant distribution function.[14)] If $\phi_r = 0$, then ϕ_s satisfies the equation[12)]

$$t\sin 2(\phi_0 - \phi_s) + 1/(\alpha\omega^2\sin^2\theta)\phi_s = 0$$

where, θ is the usual polar coordinate of the PI chain, α is a constant which depends on the PI, and ϕ_0 is the azimuthal orientation of the electric field vector which is parallel to the substrate.

By measuring the optical retardation of a rubbed film, exposed to LPUV with its polarization at an angle $\phi_0 = 40°$ with respect to the rubbing direction, the angle through which the easy axis of the film rotates can be determined as a function of the exposure time. Figure 3 shows the time dependence of the rotation angle $\Delta\phi = \phi_s + 50°$. The angle $\Delta\phi$ is measured with respect to the direction of alignment preferred by the LPUV which is perpendicular to its polarization.[15)]

From fits of the above equation to the experimental data, the width of the Gaussian distribution is determined using $\theta = 90°$ (no pretilt) and a previous value of $\alpha = 0.026\,\mathrm{min}^{-1}$.[11)] Figure 4 shows the dependence of the width of the distribution on the number of rubbings under same conditions. For weakly (or less) rubbed surface, 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 the alignment of PI chains saturates.

The azimuthal anchoring energy on these surfaces has been measured for nematic LCs E7 and ZLI-4972 using the method proposed by Akahane *et al.*[13)] Figure 5 shows the dependence of the anchoring energy on the distribution width. The solid lines represent calculated values from the equilibrium director orientations based on the model for $\phi_r = 90°$, $\phi_0 = 57.3°$, and $p = 40\,\mu$m for corresponding LCs. The close agreement between the experimental and model predicted dependence of azimuthal anchoring energy on the distribution width justifies the validity of the model. 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

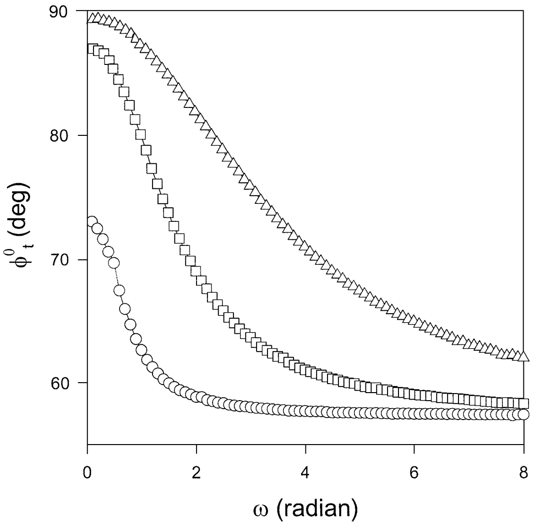

Fig. 2. Theoretical dependence of the equilibrium director twist, ϕ_t^0 (see text) on the width of the distribution for $\phi_0 = 57.3°$ and $\phi_r = 90°$. The symbols ○, □, and △ corrrespond to surfaces with $Cd/K_2 = 1$, $Cd/K_2 = 10$, and $Cd/K_2 = 50$, respectively.

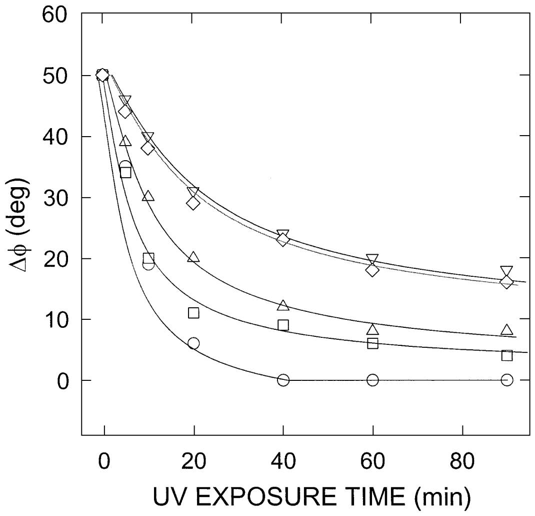

Fig. 3. The angle of rotation, $\Delta\phi$, of the easy axis with respect to the polarization direction of LPUV as a function of exposure time for one (○), two (□), four (△), five (◇), and six (▽) rubbings. The electric field of LPUV was at an angle of 40° with respect to the rubbing direction. The solid curves are the best fits as discussed in text.

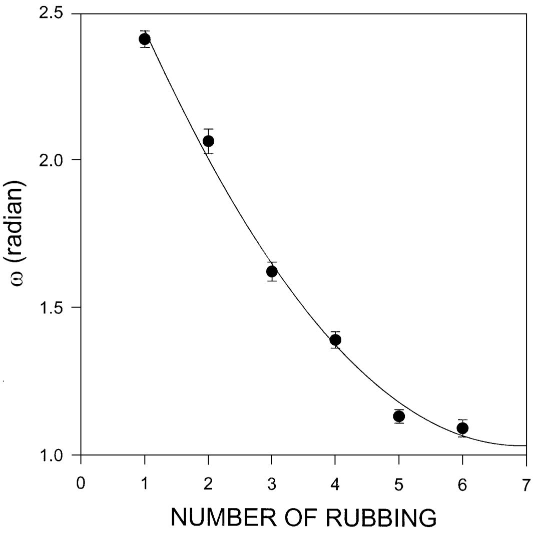

Fig. 4. Dependence of the width, ω, of the PI chain distribution function on the number of rubbings (the solid curve is guide to the eye).

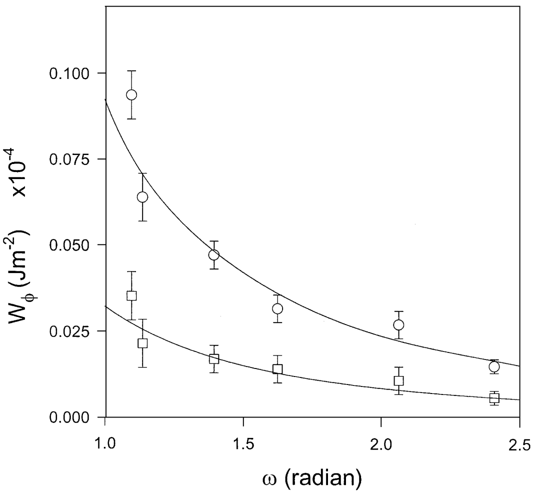

Fig. 5. Dependence of the azimuthal anchoring energy, W_ϕ, on the width of the distribution for nematic LCs ZLI-4792 (○) and E7 (□). Solid curves are calculated using ϕ_t^0 from the model for $\phi_0 = 57.3°$, $\phi_r = 90°$, $p = 40\,\mu$m, and $Cd/K_2 = 18$ for E7 and $Cd/K_2 = 40$ for ZLI-4792.

direction becomes higher with increasing rubbing strength. From the corresponding theoretical fit to the experimental data, the value of C is determined to be 1.41×10^{-5} Jm^{-2} and 3.92×10^{-5} Jm^{-2} for E7 and ZLI-4792, respectively. The difference between the values of C for two LCs indicates that the strength of the LC-PI interaction for these two LCs are very different owing to their different chemical nature.

It has been shown that simple models for PI chain distribution and surface free energy of the interface permit an experimental determination of the strength of LC-PI interaction. For a given LC-PI system, once the strength of interaction is known, one can determine the changes in anchoring properties induced by rubbing without fabricating LC cells. In conclusion, measurement of the width of the PI chain distribution provides a direct and simpler experimental way to determine anchoring properties over a wide range of anchoring strength.

This work was supported by the NSF Science and Technology Center ALCOM Grant DMR-89-20147.

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