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Material-independent determination of anchoring properties on rubbed polyimide surfaces

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A material-independent method for determining liquid-crystal (LC) anchoring energy on rubbed polyimide (PI) surfaces has been devised. This method exploits the changes in the easy axis of rubbed PI film induced by exposure to linearly polarized UV (LPUV) light. 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 LC easy axis as a function of exposure time. A quasimicroscopic free energy of the LC-substrate interface is used to model LC anchoring properties. The experimental and calculated values of the azimuthal anchoring energy are in good agreement and found to depend inversely on the width of the distribution function. The measurements of the width of the chain distribution function provide a simple LC material-independent method for determining the LC anchoring properties. With this method, it is also possible to calculate the strength of the interaction between PI chains and LC molecules. [S1063-651X(99)04612-7]

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I. 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. Technologically, it is crucial to have a reliable procedure that permits good control of alignment and yields high-quality alignment of LCs used in electro-optic devices. Surface treatments, such as obliquely evaporated SiO_x layers, Langmuir-Blodgett films, and rubbed polymer films, have been used to obtain homogeneous alignment of LCs [1]. In recent years, photoalignment [2–4] has emerged as a promising noncontact 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 the Rapini-Papoular phenomenological model [5] for the surface free energy, such as surface disclinations [6], Fre̊edericksz transition [7,8], high field [9], Cano wedge cell [10], optical reflectometric method [11], retardation vs voltage (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.

In this paper, a fresh and very different approach for determining the LC anchoring properties on rubbed polyimide (PI) surfaces is presented. A simple model is used to describe the distribution of PI chains and the LC alignment. Although the microscopic origin of alignment of LCs on the PI surface is not yet fully understood, the anisotropic distribution of PI chains on the surface is believed to be responsible for the alignment [13–15]. In an untreated PI film, the PI chains are randomly distributed. Surface treatment (i.e., rubbing) breaks the symmetry by reorienting these chains and inducing LC alignment along the easy axis, i.e., the rubbing direction. The width of the azimuthal distribution of these chains can be determined from the measurements of the rotation of the easy axis of a rubbed PI film as a function of the LPUV exposure time. A simple quasimicroscopic model of the free energy of the system is proposed and used to calculate the azimuthal anchoring energy. The azimuthal anchoring energies for different LCs are measured for different rubbing strengths. The model's predictions of the dependence of azimuthal anchoring energy on the width of the distribution show good agreement with the experimental results.

II. THE MODEL

Let us assume that the orientation of PI chains can be described by a distribution function $N_o(\theta,\phi)$, where θ and ϕ describe polar and azimuthal angles of a unit vector along the direction of chains as shown in Fig. 1. We further consider the dependence of the distribution function on the orthogonal polar and azimuthal angles to be separable, i.e., $N_o(\theta,\phi)=N_o(\theta)N_o(\phi)$. Let us further assume that

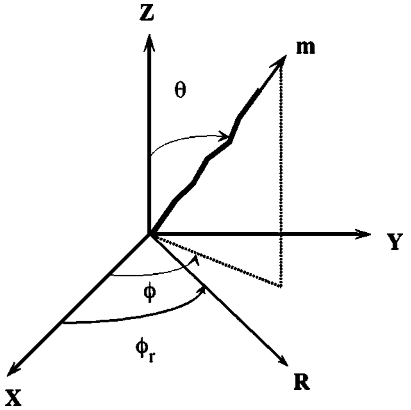

FIG. 1. Schematic representation of the orientation of the PI chain and the rubbing direction in the laboratory frame. **m** and **R** are unit vectors along the direction of the PI chain and the rubbing direction, respectively.

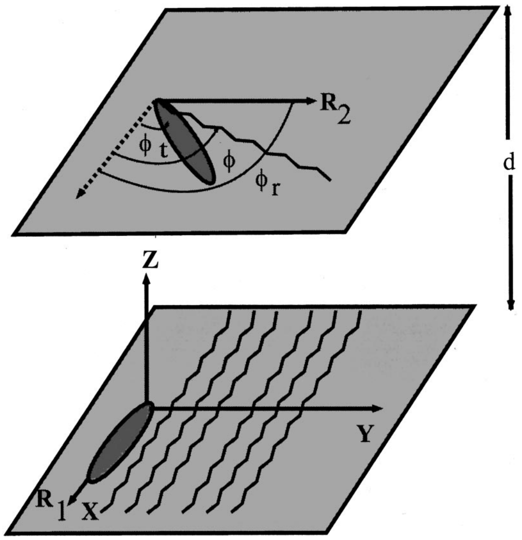

FIG. 2. Geometry of the LC cell used in the model. $\mathbf{R}_1$ and $\mathbf{R}_2$ are respective rubbing directions on substrates at $z=0$ and $z=d$. The substrate at $z=0$ is assumed to have strong anchoring. Angles ϕ_t, ϕ, and ϕ_r are the usual azimuthal coordinates of the LC director, PI chain, and $\mathbf{R}_2$, respectively. The cell is filled with nematic LC doped with a chiral material inducing a pitch p.

$N_o(\theta,\phi)$ for an untreated surface is azimuthally isotropic and that the anisotropy induced by rubbing can be approximated by a Gaussian distribution centered around the rubbing direction. The distribution of PI chains on rubbed polyimide film can then be described as [16]

$$N_o(\theta,\phi)=N_o(\theta)e^{-(\phi-\phi_r)^2/2\omega^2}, \tag{2.1}$$

where ϕ_r specifies the rubbing direction, ω is the width of the distribution, and $N_o(\theta)$ is the normalization factor such that

$$\int_0^\pi \int_o^\pi N_o(\theta,\phi)\sin\theta\, d\theta\, d\phi=1.$$

Let us now consider a cell made with two rubbed substrates located at $z=0$ and $z=d$, as shown in Fig. 2, 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. (2.1). The interaction between the LC director and PI chains oriented along the respective directions ϕ_t and ϕ can be written using a Rapini-Papoular-type function, $C\sin^2(\phi-\phi_t)$, weighted by the distribution function. The azimuthal surface free energy per unit area of the interface is given by the ensemble average,

$$F_s=\frac{1}{2}\int_0^\pi Cf(\theta,\phi)\sin^2(\phi-\phi_t)\,d\phi,$$

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

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

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 ω.

If p is the pitch of the LC, the natural twist of the director (i.e., with no treatment of the top surface)near the top surface, i.e., at $z=d$, is $\phi_0=2\pi d/p$. In the framework of the continuum elastic theory, the bulk free energy per unit surface area of the twisted nematic (TN) cell is given by [17]

$$F_e=\frac{K_2}{2d}(\phi_0-\phi_t)^2,$$

where K_2 is the twist elastic constant of the nematic LC. The equilibrium twist angle ϕ_t^0 at the top surface is determined by minimization of the total free energy $F=F_s+F_e$ given as

$$F=\frac{K_2}{2d}\left\{(\phi_0-\phi_t)^2+\frac{Cd}{K_2}\int_0^\pi f(\theta,\phi)\sin^2(\phi-\phi_t)\,d\phi\right\} \tag{2.2}$$

with respect to ϕ_t.

In the weak anchoring limit, the width of the PI chain distribution $\omega\to\infty$ and the distribution function $N(\theta,\phi)$ becomes independent of ϕ and the surface energy, F_s, becomes independent of ϕ_t. Consequently, the director orientation on the surface is determined solely by the natural twist ϕ_0. On the other hand, in the case of strong anchoring, the equilibrium orientation of the director is dictated by a delicate interplay between the surface and bulk contributions.

Minimization of Eq. (2.2) with respect to ϕ_t gives

$$C=\frac{2K_2(\phi_t^0-\phi_0)}{d\int_0^\pi f(\theta,\phi)\sin 2(\phi-\phi_t^0)\,d\phi}, \tag{2.3}$$

where ϕ_t^0 is the actual twist angle that minimizes the total free energy.

It should be noted that when the PI surface has strong anchoring, i.e., all PI chains are aligned along the rubbing direction, $\omega\to 0$ and the probability distribution function $f(\theta,\phi)$ vanishes everywhere except at $\phi=\phi_r$, where it is unity. In this limit, Eq. (2.3) reduces to

$$C=\frac{2K_2\{\phi_t^0(\omega=0)-\phi_0\}}{d\sin 2\{\phi_r-\phi_t^0(\omega=0)\}}.$$

This result is similar to the expression previously used to determine the azimuthal anchoring energy W_ϕ [10,18,19] with $\phi_t^0(\omega=0)$ replaced by ϕ_t^0. Unlike the azimuthal anchoring energy function W_ϕ, 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

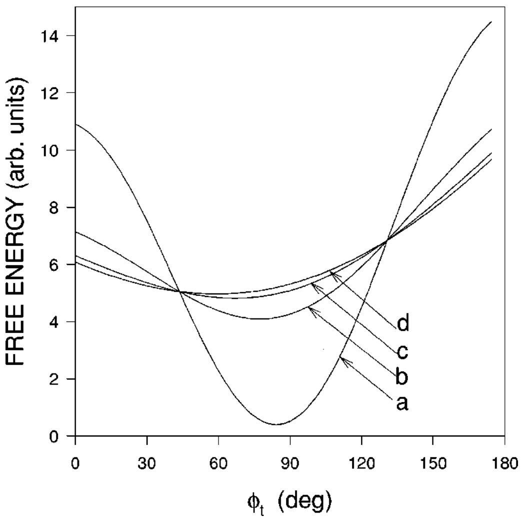

FIG. 3. Variation of total free energy based on Eq. (2.2) with director twist angle for $\phi_0 = 57.3°$, $\phi_r = 90°$, and $Cd/K_2 = 10$ for different surface properties; (a) $\omega = 0.1$ radian, (b) $\omega = 1.0$ radian, (c) $\omega = 2.0$ radian, and (d) $\omega = 10.0$ radian.

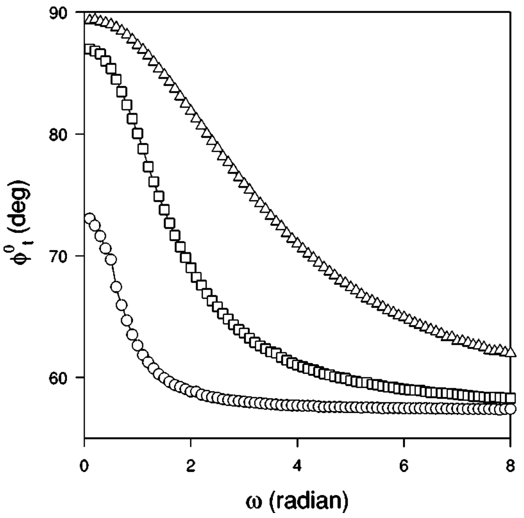

FIG. 4. Theoretical dependence of equilibrium director twist, ϕ^0_t [the orientation of the LC director on the surface at $z = d$ that minimizes free energy given by Eq. (2.2), see text], on the width of the distribution. The ○, □, and △ correspond to $Cd/K_2 = 1$, $Cd/K_2 = 10$, and $Cd/K_2 = 50$, respectively. The values of ϕ_0 and ϕ_r are the same as given in Fig. 3.

director orientation which can be determined using an optical technique [18]. A method to measure the width of the distribution will be described later.

The validity of the model is tested by studying the equilibrium twist as a function of the width of the distribution. The total free energy is calculated as a function of the director twist ϕ_t for different values of ω. Figure 3 shows the dependence of the free energy on ϕ_t for $\phi_0 = 57.3°$, $\phi_r = 90°$, and $Cd/K_2 = 10$. It is clear from the figure that for large values of ω, the free energy is minimum at $\phi_t = 57.3°$. Large values of ω correspond to an almost random distribution of PI chains, each influencing the orientation of the local director. The resultant torque exerted on the director by these chains is zero and the orientation of the director is dictated by the natural twist as determined from the minimum free energy at $\phi_t = 57.3°$. On the other hand, when more PI chains are oriented along the rubbing direction, ω is small and the free energy is minimum for a director nearly parallel to the rubbing direction, $\phi_r = 90°$. However, as seen in Fig. 4, the direction of alignment depends not only on the width of distribution but also on the strength of the LC-PI interaction and the twist elastic constant, K_2. When LC-PI interaction is weaker than K_2 (i.e., the ratio Cd/K_2 is small), a better alignment of PI chains, i.e., smaller ω, is needed to generate the same twist angle.

III. EXPERIMENT

A polyamic acid solution of SE610 (Nissan Chemical Company) was spin-coated on 52 mm×52 mm ITO coated glass at 3000 rpm for 30 sec. The films were soft-baked at 100 °C for 10 min for solvent evaporation followed by 1 h of hard bake at 220 °C for imidization. Typically this process resulted in 460 Å thick films. 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 the same pressure was varied while keeping the velocity of substrates constant at 0.9 m/min. Two 26 mm×26 mm pieces cut from one 52 mm ×52 mm substrate were used for the azimuthal anchoring energy measurement for two different nematic LCs, viz., E7 (BDH Ltd.) and ZLI-4792 (Merck Chemicals). The azimuthal anchoring energies on the surfaces were measured using the method proposed by Akahane *et al.* [18]. The other set of two 26 mm×26 mm pieces was used for LPUV exposure and for optical retardation measurements. A 450 W xenon lamp (Oriel, model 66021) was used as the UV source. The intensity of the collimated beam of LPUV light after the UV sheet polarizer (Oriel, model 27320) on the films' surface was approximately 4.5 mW/cm^2 at 350 nm wavelength.

A photoelastic modulator (PEM90, Hinds Instruments) with a fused silica head 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°.

IV. RESULTS AND DISCUSSION

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. Figure 5 shows the variation of the optical retardation Γ of films as a function of the number (or extent) of rubbings. Initially, the optical retardation induced by rubbing increases

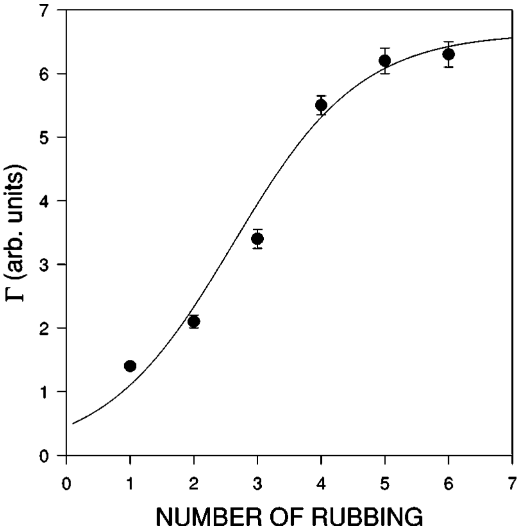

FIG. 5. Variation of optical retardation, Γ, with the number of rubbings (solid curve is a guide to the eye).

rapidly, but then, as the chain alignment saturates, the rate of increase is diminished.

When a film having an initial distribution of PI chains given by Eq. (2.1) is exposed for a time t to normally incident LPUV light, the resultant distribution function is given by [20]

$$N_o(\theta,\phi)=N_o(\theta)e^{-(\phi-\phi_r)^2/2\omega^2}e^{-\alpha t\cos^2(\phi_o-\phi)\sin^2\theta},$$

where α is a constant which depends on the PI, θ and ϕ are the spherical polar coordinates, respectively, of a unit vector along the direction of the photosensitive bonds, and ϕ_0 is the azimuthal orientation of the electric field vector which is parallel to the substrate.

The easy axis of the rubbed PI film is profoundly affected by LPUV exposure because of the dissociation of the photosensitive bonds. The equilibrium orientation, ϕ_s, of the easy axis is determined from the extremum of the distribution function [19]. If $\phi_r=0$, the ϕ_s satisfies the equation

$$t\sin 2(\phi_0-\phi_s)+B\phi_s=0, \tag{4.1}$$

where $B=1/(\alpha\omega^2\sin^2\theta)$.

By measuring the optical retardation of a rubbed film subsequently 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 6 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 UV which is perpendicular to the direction of its polarization for SE610 [21]. The solid lines are the fits of Eq. (4.1) to the experimental data. It is clear from the figure that as the UV exposure time increases, the easy axis rotates and $\Delta\phi$ decreases and, after a long enough exposure, becomes zero.

When a PI film is exposed to LPUV, PI chains are broken due to irreversible photodissociation of *C*-*N* bonds which are along the long axis of the chains. The chains which are parallel to the polarization direction are most affected, whereas those that are perpendicular to polarization are unperturbed.

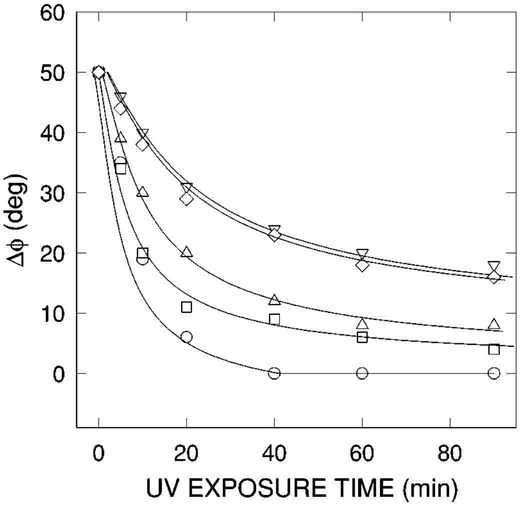

FIG. 6. The angle of rotation, $\Delta\phi$, of the easy axis with respect to the polarization direction of LPUV as a function of exposure time for one (○), two (□), four (△), five (◇), and six (∇) rubbings. The electric field of LPUV was at an angle of 40° with respect to the rubbing direction. The solid curves are the best fits to Eq. (4.1).

After a sufficiently long exposure, the easy axis rotates and becomes parallel to the UV's preferred direction. On the other hand, for stronger rubbing, PI chains are better aligned and consequently longer exposure time and/or higher UV intensity is needed to fully rotate the easy axis.

From the fits of Eq. (4.1) to the experimental data, the width of the Gaussian distribution is determined using a previous value of $\alpha=0.026$ min^{-1} [14]. The value of θ 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. Figure 7 shows the dependence of the width of the distribution on the number of rubbings. 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

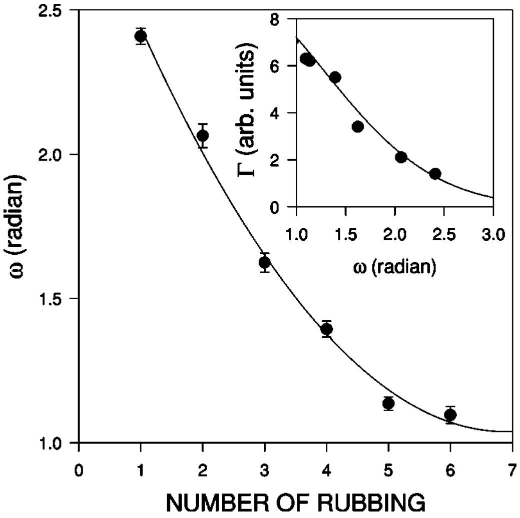

FIG. 7. Dependence of the width, ω, of the PI chain distribution function on the number of rubbings. The inset shows optical retardation, Γ, plotted as a function of the width of the distribution (the solid curves are a guide to the eye).

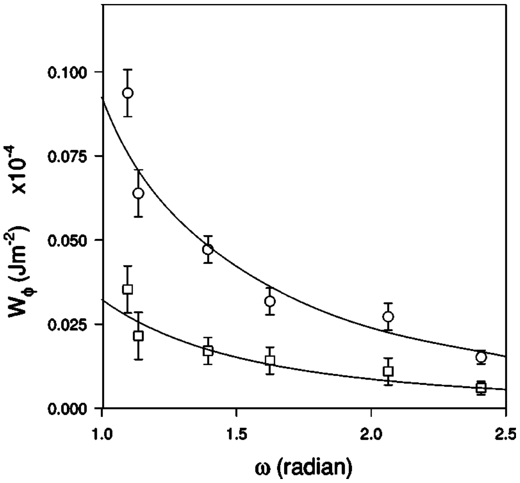

FIG. 8. Dependence of the azimuthal anchoring energy, W_ϕ, on the width of the distribution for nematic LCs ZLI-4792 (○) and E7 (□). Solid curves are calculated using ϕ_t^0 from the model with $\phi_0=57.3°$, $\phi_r=90°$, $p=40$ μm, and $Cd/K_2=18$ for E7 and $Cd/K_2=40$ for ZLI-4792.

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. Figure 8 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 $p=40$ μm 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 1.41×10^{-5} $\mathrm{J\,m^{-2}}$ and 3.92×10^{-5} $\mathrm{J\,m^{-2}}$ for E7 and ZLI-4792, respectively. The difference between the C values for two LCs indicates that the strengths of the LC-PI interaction for these two LCs are different owing to their different chemical structures.

Figure 9 shows the theoretical dependence of azimuthal anchoring energy on the strength of LC-PI interaction for E7 for interfaces with different ω. The linear dependence of the azimuthal anchoring energy on C suggests that LC anchoring is stronger for stronger LC-PI interaction, as anticipated. On the other hand, a better microscopic alignment of PI chains along the rubbing direction (i.e., smaller ω) leads to a rapid increase in azimuthal anchoring energy with an increase in the LC-PI interaction.

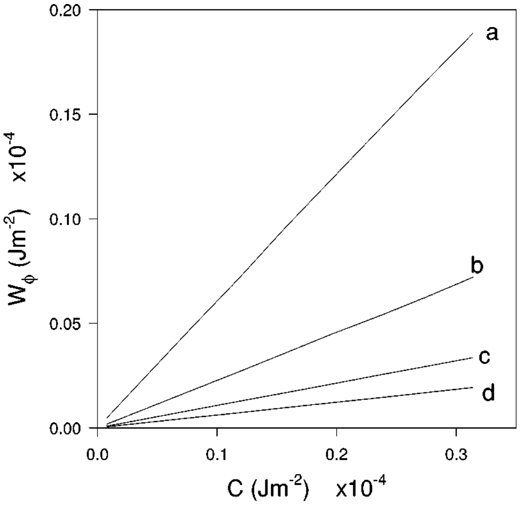

FIG. 9. Calculated azimuthal anchoring energy, W_ϕ, as a function of the strength of interaction, C, for the nematic LC E7 for (a) $\omega=2.0$ radian, (b) $\omega=1.5$ radian, (c) $\omega=1.0$ radian, and (d) $\omega=0.5$ radian.

V. CONCLUSION

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. In conclusion, with the help of the model presented here, one can isolate the contribution of the morphological changes induced by rubbing from the effect of chemical interactions. We believe that this simple model can be extended to determine the LC anchoring properties of the interfaces prepared by other techniques.

ACKNOWLEDGMENTS

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