

Pretilt angle generation on photoreactive polymer films

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The mechanism of liquid crystal pretilt angle generation on photoreactive polymer films doubly exposed to linearly polarized ultraviolet (uv) light has been investigated. The first exposure for time τ_1 is normal to the surface, and the film is subsequently irradiated for time τ_2 with obliquely incident uv light with a plane of polarization rotated by 90° with respect to that of the first uv light. The state of the polymer film after two exposures was characterized with a tensor order parameter, which then served as a boundary condition for the surface state of the nematic liquid crystal. The bulk liquid crystal behavior was investigated using Landau-de Gennes theory extended to include the possibility for weak surface interactions linear in the tensor order parameter. The pretilt angle was calculated as a function of both τ_1 and τ_2 , and as a function of the second uv light angle of incidence. The calculated behavior of the pretilt angle was found to be in qualitative agreement with experimental observations. Conclusions about the strength of the anchoring have also been made. [S1063-651X(98)16509-1]

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I. INTRODUCTION

Surface alignment of liquid crystals is of major importance for the proper operation of liquid crystal displays. At present, alignment is mainly achieved by mechanical rubbing of a polymer coated surface. This technique is simple and thermally stable but has been found to have the disadvantage of introducing dust particles and electrostatic charges into the liquid crystal cell, thus reducing the production yield of liquid crystal displays.

In recent years the method of photoalignment has been of great interest as a possible alternative to the rubbing technique. It was found that some photoreactive polymer materials can orient a liquid crystal after being exposed to linearly polarized uv light [1–4]. Originally, only single exposure normal to the polymer film was used, which resulted in a homogeneous liquid crystal alignment perpendicular to the polarization direction of the uv light. The pretilt angle, however, which is necessary to avoid reverse tilt disclinations in the twisted and supertwisted nematic devices, was found to be either zero or doubly degenerate if a one-time exposure method was used [5,6]. It was later realized that a double uv exposure scheme can be used for generating both a preferred axis in the plane of the film and a pretilt angle [7,8].

In this paper we investigate the mechanism of pretilt angle generation by concentrating on the double uv exposure scheme used by Wang *et al.* [8]. To describe the polymer film, we derive a tensor order parameter that depends on both exposure times, and we calculate the liquid crystal bulk behavior using the Landau-de Gennes theory. The details of the model, together with comparison of our calculations with the experimental results obtained by Wang, will be discussed in this paper.

II. THEORY

We describe the polymer film as a collection of rodlike ordering sites each represented by a unit vector $\hat{\xi}$ along the site orientation. The term ordering site can be associated

with a different ordering agent in the various aligning materials. In a previous work reported elsewhere [9] we investigated the easy axis generation on poly(vinyl cinnamate) (PVCN) or poly(vinyl 4-methoxy-cinnamate) (PVMC) type photoreactive polymers exposed to linearly polarized uv light, and there we considered the ordering sites to be the head-to-tail reactive sites and their photoreaction products. In the case when the photoreactive polymer is of polyimide type, uv irradiation causes breaking of the polymer backbone, and in this case the backbone can be considered as an ordering site. In general, however, the term ordering site can be thought of as any agent that can orient the liquid crystal and that can be characterized by its orientation along a particular direction. In this work we assume that the liquid crystal alignment induced on exposed polymer films is due to anisotropic destruction of ordering sites.

The double uv exposure scheme that we concentrate on is as follows: The polymer film is first exposed for time τ_1 to normally incident linearly polarized uv light. The propagation direction is described by the unit vector \hat{k} , and the lab reference frame is chosen in such a way that the \hat{x} axis coincides with the polarization direction \hat{E} of the uv light. In the second uv exposure the polarization is first rotated by 90° to be along the \hat{y} axis of the lab reference frame, and the film sample is tilted by an angle θ_{inc} [8]. This is equivalent to

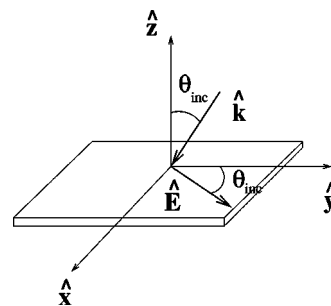


FIG. 1. Double uv exposure scheme: oblique exposure (the unit vectors \hat{k} and \hat{E} are both in the y - z plane).

having the second uv light propagating obliquely to the film as shown in Fig. 1, where both $\hat{\mathbf{k}}$ and $\hat{\mathbf{E}}$ are in the y - z plane. As a result, when a liquid crystal is in contact with a doubly exposed film, the bulk nematic director $\hat{\mathbf{n}}$ is found to be also in the y - z plane, and make a pretilt angle θ_e with the polymer surface.

To describe the polymer film after two uv exposures we introduce a tensor order parameter

$$Q_{ij}^p = \frac{1}{2} \langle 3 \xi_i \xi_j - \delta_{ij} \rangle, \quad (1)$$

where the average is taken over the distribution function of the ordering sites. The unit vector $\hat{\xi}$ that describes the site orientation is fully specified by the azimuthal angle ϕ and the polar angle θ , which in this case is defined with respect

to the plane of the film so that $\hat{\xi} = \cos \phi \cos \theta \hat{\mathbf{x}} + \sin \phi \cos \theta \hat{\mathbf{y}} + \sin \theta \hat{\mathbf{z}}$. In order to derive the distribution function of the sites, we use the model proposed by Chen *et al.* [10] according to which the anisotropic part of the probability for a photoreaction is proportional to $(\hat{\xi} \cdot \hat{\mathbf{E}})^2$. Suppose that at zero exposure time there are N_0 ordering sites, and they are distributed according to some initial distribution function $f_0(\theta, \phi)$. After the first exposure the number of ordering sites is given by

$$N_1(\theta, \phi; \tau_1) = N_0 f_0(\theta, \phi) \exp[-\alpha \tau_1 \cos^2 \theta \cos^2 \phi], \quad (2)$$

where α is a parameter that characterizes the isotropic part of the probability for a photoreaction. After the second exposure the number of ordering sites left in the film is given by

$$N_2(\theta, \phi; \tau_1, \tau_2) = N_1(\theta, \phi, \tau_1) \exp[-\alpha \tau_2 (\cos \theta \sin \phi \cos \theta_{\text{inc}} - \sin \theta \sin \theta_{\text{inc}})^2]. \quad (3)$$

In all calculations we have considered the original distribution of ordering sites to be isotropic in ϕ and Gaussian around $\theta = 0$ in θ , that is, $f_0(\phi, \theta) \sim e^{-(\theta/\sigma)^2}$, where $\sigma/\sqrt{2}$ is the standard deviation. With this assumption the distribution function of the ordering sites after two exposures is given by

$$f(\theta, \phi; \tau_1, \tau_2) = \mathcal{N} \exp\left[-\left(\frac{\theta}{\sigma}\right)^2\right] \exp[-\alpha \tau_1 \cos^2 \theta \cos^2 \phi] \exp[-\alpha \tau_2 (\cos \theta \sin \phi \cos \theta_{\text{inc}} - \sin \theta \sin \theta_{\text{inc}})^2], \quad (4)$$

where the normalization factor \mathcal{N} is chosen in such a way that

$$\int_{-\pi}^{\pi} \int_{-\pi/2}^{\pi/2} f(\theta, \phi; \tau_1 = 0, \tau_2 = 0) \cos \theta d\theta d\phi = 1. \quad (5)$$

In order to calculate the values of the polymer tensor order parameter elements [Eq. (1)], the two-dimensional integrals involved in taking the average were solved using the method of Gaussian quadratures [11]. For all values of the parameters entering the ordering sites distribution function, the off-diagonal elements Q_{12}^p and Q_{13}^p were found to be zero. This indicates that the tensor Q^p can be diagonalized in a coordinate system that is obtained from the lab reference frame through a rotation around the $\hat{\mathbf{x}}$ axis by a particular angle that we call θ_p .

For the description of the liquid crystal we use the biaxial tensor order parameter

$$Q_{ij} = \frac{S}{2} (3 n_i n_j - \delta_{ij}) + \frac{P}{2} (m_i m_j - l_i l_j), \quad (6)$$

where S is the usual uniaxial order parameter and P is a measure of the biaxiality. The unit vectors $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{l}}$ are the local principal axes where the liquid crystal order parameter is diagonal. Since in the calculation of the bulk behavior the polymer tensor values are used as boundary conditions, and because only the Q_{23}^p ($=Q_{32}^p$) off-diagonal element is

different from zero, the directors $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{l}}$ can be chosen in such a way that $\hat{\mathbf{n}} = \cos \theta \hat{\mathbf{y}} + \sin \theta \hat{\mathbf{z}}$, $\hat{\mathbf{m}} = \sin \theta \hat{\mathbf{y}} - \cos \theta \hat{\mathbf{z}}$, and $\hat{\mathbf{l}} = \hat{\mathbf{x}}$.

The free energy of the system can be written as

$$F = F_b + F_{\text{el}} + F_s, \quad (7)$$

where

$$F_b = \int_V \left[\frac{1}{2} A \text{tr} Q^2 - \frac{1}{3} B \text{tr} Q^3 + \frac{1}{4} C (\text{tr} Q^2)^2 \right] dV \quad (8)$$

is the bulk free energy and

$$F_{\text{el}} = \int_V \left[\frac{1}{2} L_1 \partial_i Q_{jk} \partial_i Q_{jk} + \frac{1}{2} L_2 \partial_i Q_{ij} \partial_k Q_{kj} \right] dV \quad (9)$$

is the elastic contribution. The coefficient A , B , C , L_1 , and L_2 are the usual phenomenological parameters entering the Landau-de Gennes free energy [12]. The term F_s represents the surface contribution to the free energy and can be described by the coupling of the liquid crystal order parameter with surface vectors characterizing the symmetry of the aligning film. For a surface favoring homeotropic or planar alignment only one such vector is sufficient, and this is the vector perpendicular to the plane of the film [13,14]. In the case of a doubly exposed polymer film, however, where the surface favors a preferred axis and a pretilt angle, an additional surface vector is necessary. We choose this vector to

be oriented along a direction perpendicular to the plane where the angle θ_p is defined, that is, the y - z plane.

To describe the surface free energy F_s we include only terms linear in the tensor order parameter. In general, five such terms can be formed [15] but only three of them are nonzero in our case; these are the terms that couple to the three independent nonzero elements of the tensor Q [Eq. (6)] at the surface. Thus, the surface free energy has the following form:

$$F_s = \int_S [G_1 A_i Q_{ij} A_j + G_2 B_i Q_{ij} B_j + G_3 (\hat{\mathbf{A}} \times \hat{\mathbf{B}})_i Q_{ij} B_j] dS, \quad (10)$$

where the unit vectors $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$ are such that $\hat{\mathbf{A}} = \hat{\mathbf{x}}$ and $\hat{\mathbf{B}} = \hat{\mathbf{z}}$, and G_1 , G_2 , and G_3 are surface coupling coefficients.

The liquid crystal tensor order parameter [Eq. (6)] has a different representation that is more convenient for performing numerical calculations [16]. With the substitution

$$\begin{aligned} x &= \frac{\sqrt{2}}{4} (3S - P) \cos 2\theta, \\ y &= \frac{\sqrt{2}}{4} (3S - P) \sin 2\theta, \\ z &= \frac{\sqrt{6}}{4} (S + P), \end{aligned} \quad (11)$$

the tensor Q can be written as

$$Q = \frac{1}{\sqrt{6}} \begin{pmatrix} -2z & 0 & 0 \\ 0 & z + \sqrt{3}x & \sqrt{3}y \\ 0 & \sqrt{3}y & z - \sqrt{3}x \end{pmatrix}. \quad (12)$$

Assuming that the liquid crystal order is uniform in all planes parallel to the surface, the rescaled total free energy of the system per unit area \mathcal{A} can be written as

$$\begin{aligned} \mathcal{F} = \int_0^\infty \left\{ \frac{t}{8} (x^2 + y^2 + z^2) - z \left(x^2 + y^2 - \frac{z^2}{3} \right) + \frac{1}{4} (x^2 + y^2 + z^2)^2 \right. \\ \left. + \frac{1}{2} [(x')^2 + (y')^2 + (z')^2] + \frac{\rho}{2} \left(\frac{1}{2} (y')^2 + \frac{(\sqrt{3}x' - z')^2}{6} \right) \right\} d\xi + \frac{-2\nu + \chi}{\sqrt{6}} z(0) - \frac{\chi}{\sqrt{2}} x(0) + \frac{\beta}{\sqrt{2}} y(0), \end{aligned} \quad (13)$$

where the tensor Q has been rescaled to $Q^{\text{sc}} = \alpha Q$, the scaling parameters are $\alpha = 27C/(\sqrt{6}B)$, $t/4 = 27CA/B^2$, $\rho = L_2/L_1$, $z = \xi\zeta$, $\xi^2 = \alpha^2 L_1/C$, $\gamma = L_1/(\xi\alpha^2)$, $\mathcal{F} = F/(\mathcal{A}\gamma)$, $\nu = G_1/(\alpha\gamma)$, $\chi = G_2/(\alpha\gamma)$, $\beta = G_3/(\alpha\gamma)$, and the derivatives are taken with respect to ξ .

Minimizing the total free energy \mathcal{F} [Eq. (13)] we obtain the following system of nonlinear differential equations

$$\begin{aligned} \left(1 + \frac{\rho}{2} \right) x'' - \frac{\rho}{\sqrt{12}} z'' - \frac{tx}{4} + 2xz - x(x^2 + y^2 + z^2) &= 0, \\ \left(1 + \frac{\rho}{2} \right) y'' - \frac{ty}{4} + 2yz - y(x^2 + y^2 + z^2) &= 0, \quad (14) \\ \left(1 + \frac{\rho}{6} \right) z'' - \frac{\rho}{\sqrt{12}} x'' - \frac{tz}{4} + x^2 + y^2 - z^2 - z(x^2 + y^2 + z^2) &= 0, \end{aligned}$$

with boundary conditions

$$\begin{aligned} \left(1 + \frac{\rho}{2} \right) x'(0) - \frac{\rho}{\sqrt{12}} z'(0) + \frac{\chi}{\sqrt{2}} &= 0, \\ \left(1 + \frac{\rho}{2} \right) y'(0) - \frac{\beta}{\sqrt{2}} &= 0, \\ \left(1 + \frac{\rho}{6} \right) z'(0) - \frac{\rho}{\sqrt{12}} x'(0) - \frac{-2\nu + \chi}{\sqrt{6}} &= 0, \end{aligned} \quad (15)$$

$$x'(\infty) = 0, \quad y'(\infty) = 0, \quad z'(\infty) = 0.$$

To calculate the bulk behavior of the liquid crystal, the values of ν , χ , and β such that $Q_{ij}(0) = Q_{ij}^p$ were found. In all calculations t was taken to be zero, which corresponds to the supercooling limit, and the value of ρ was chosen to be 1. The equations were solved numerically using the general purpose code COLNEW for systems of ordinary differential equations [17,18].

III. RESULTS AND DISCUSSION

The change of the distribution function [Eq. (4)] with exposure time is illustrated in Fig. 2. In Fig. 2(a) the initial distribution function $f(\theta, \phi; \tau_1 = 0, \tau_2 = 0)$ is plotted for a value of $\sigma = 10^\circ$, which is the value used in all calculations. After a single uv irradiation at normal incidence only ordering sites oriented along $\phi = \pm \pi/2$, and thus perpendicular to the uv light polarization direction, are left but the distribution function is still centered around $\theta = 0$. Therefore, no pretilt angle can be expected after irradiation with only normally propagating uv light. The distribution function after double uv exposure is shown in Fig. 2(b) for a particular value of θ_{inc} . As can be seen in the figure, the ordering sites are still located around $\phi = \pm \pi/2$ but now the polar part is shifted towards an angle $\theta \neq 0$. This asymmetry in the polar distribution can be expected to introduce a nonzero pretilt angle.

The behavior of the eigenvalues of the polymer tensor order parameter Q^p as a function of the normal exposure time $\alpha\tau_1$ in the case of normal exposure only is similar to

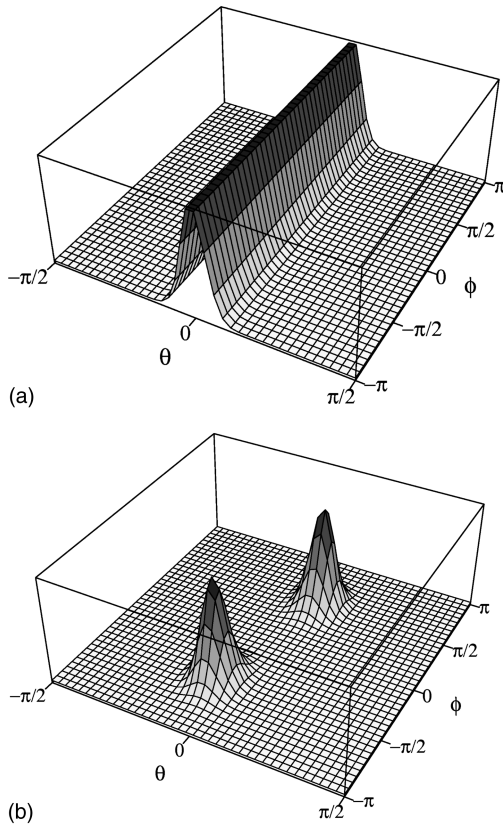


FIG. 2. Ordering sites distribution function for $\sigma=10^\circ$, $\theta_{\text{inc}}=40^\circ$ and (a) $\alpha\tau_1=0$ and $\alpha\tau_2=0$; (b) $\alpha\tau_1=12$ and $\alpha\tau_2=12$.

that discussed for the case of PVCN films [9]. As expected from the symmetry of the distribution function, in this case the tensor Q^p is diagonal, and so the eigenvalues are equivalent to its diagonal values. The direction of the predominant orientation of the ordering sites is associated with the eigenvector corresponding to the eigenvalue of the largest magnitude. For small exposure times the eigenvalue of the largest magnitude is E_3 , and it is negative, which shows that the order favored by the polymer film is planar. At $\alpha\tau_1=0$ the eigenvalues E_1 and E_2 are equal, and therefore no preferred direction exists in the plane of the film. When $\alpha\tau_1$ is increased, the order favored by the polymer film is planar but biaxial, and a preferred in-plane orientation along the \hat{y} coordinate axis is gradually being established. For exposure times $\alpha\tau_1$ with values of approximately 2 and larger, the eigenvalue of the largest magnitude is always E_2 . Therefore, the orientation that the irradiated polymer film favors is perpendicular to the uv light polarization direction. In the model developed for PVCN-type photoreactive polymers, at large exposure times the eigenvalue of the largest magnitude was found to be a negative E_3 , and this was due to the assumption that new ordering sites were created at the same rate as the ones that were being depleted [9]. In the case considered here, however, ordering sites are only being destroyed, and even though the eigenvalue of the largest magnitude remains E_2 for very large exposure times, its value is decreasing, and thus the amount of orientational order at the surface is also decreasing.

For exposure times $\alpha\tau_1 > 0$ the largest eigenvalue in the bulk is always E_2 , and thus the bulk liquid crystal is oriented

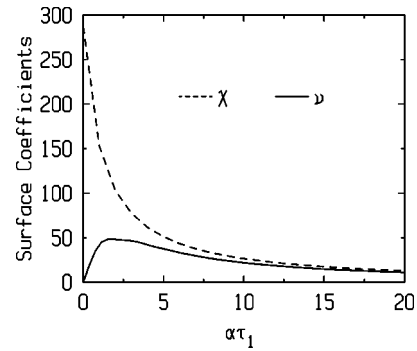


FIG. 3. Single uv irradiation: surface coefficients.

in a direction perpendicular to the uv light polarization direction. In the case of normal exposure only the surface coefficient β is always zero, reflecting the fact that no pretilt angle is generated. The surface coefficients ν and χ are plotted in Fig. 3 as a function of the normal exposure time. A positive ν favors a negative Q_{11} at the surface, and thus this coefficient gives an indication of how strongly the surface favors orientation in the \hat{y} - \hat{z} plane. Therefore, this coefficient can be related to the azimuthal anchoring strength. A positive χ corresponds to a surface favoring a negative Q_{33} , and thus an order in the \hat{x} - \hat{y} plane. The coefficient χ can be associated with the polar anchoring strength. As can be seen in the figure, the coefficient χ is always decreasing while ν has a peak at small exposure time, and this peak corresponds to time $\alpha\tau_1$ where E_2^p has a maximum. In addition, χ is orders of magnitude larger than ν for small exposure times. Using typical values for the coefficients B , C , and L_1 [19], we estimate the maximum value of G_2 (polar) to be in the order of 10^{-3} J/m², and G_1 (azimuthal) in the order of 10^{-4} J/m². These values are usually associated with strong anchoring. When the exposure time is increased, the value of χ becomes closer to that of ν , and they both decrease in magnitude when the exposure time is further increased. Therefore, the anchoring on a polymer film exposed for a very long time is expected to be weak.

The behavior of the polymer eigenvalues of a doubly exposed film at a fixed normal exposure time was calculated as a function of the oblique exposure time. It was found that the largest eigenvalue always remains E_2^p . The same is true for the bulk behavior of the liquid crystal: E_2 is always the largest eigenvalue. In both cases the eigenvectors associated with E_2^p and E_2 lie in the \hat{y} - \hat{z} plane and make angles of θ_p and θ_L , respectively, with the \hat{y} axis. The behavior of θ_p and θ_L as a function of the oblique exposure time $\alpha\tau_2$ is demonstrated in Figs. 4(a) and 4(b), respectively. The angle θ_L is in fact the angle in the liquid crystal bulk in the absence of external deformation, and thus it is the pretilt angle that can be experimentally measured. As can be seen in the figure, the behavior of θ_L is considerably different from that of θ_p . While θ_p shows a relatively constant increase for the exposure times shown in the figure, θ_L has a peak at a certain oblique exposure time, and this result is very similar to the one observed experimentally [8]. This demonstrates that the generated pretilt angle is a result of relaxation of both order parameters S and P and the angle θ , and the bulk angle can be considerably different from the angle favored by the poly-

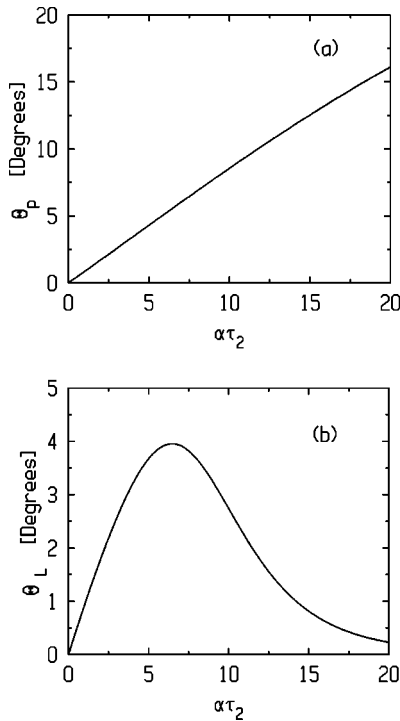


FIG. 4. θ_p (a) and θ_L (b) as a function of the oblique exposure time for $\alpha\tau_1=12$, $\theta_{inc}=40^\circ$, and $\sigma=10^\circ$.

mer film. It must be noted that although the results for θ_L presented in Fig. 4(b) are for a value of $\alpha\tau_1=12$, the behavior of θ_L is not unique to that value. In the case of $\alpha\tau_1=12$ the peak in θ_L was found to occur at the same ratio of τ_2/τ_1 as in the experiment reported by Wang *et al.* [8]. For other values of $\alpha\tau_1$ the peak in θ_L still exists but it occurs at a different τ_2/τ_1 ratio, and the magnitude of the angle is also different.

The behavior of the eigenvalues and the angle θ as a function of the distance from the surface for a particular oblique exposure time is shown in Figs. 5(a) and 5(b). Taking into account that the correlation length ξ for the case of 5CB was calculated to be $\sim 4 \times 10^{-8}$ m, it can be concluded that the bulk behavior is established at a distance of about 1000 Å away from the surface. In the bulk the liquid crystal is uniaxial ($E_1=E_3$), and the value of E_2 corresponds to the value of the uniaxial order parameter S for the particular temperature, which in this case coincides with the supercooling limit.

The behavior of the polymer eigenvalues of a doubly exposed film at a fixed oblique exposure time was calculated as a function of the normal exposure time. In this case the largest eigenvalue at the surface is always a positive E_1^p , and therefore the surface favors orientation along the \hat{x} axis of the lab reference frame. The solution where E_1 is the largest eigenvalue in the bulk liquid crystal always exists, and in this case the bulk angle θ_L is zero for any value of $\alpha\tau_1$. The solution with E_1 the largest, however, is not the stable solution for all values of $\alpha\tau_1$. For values of $\alpha\tau_1$ of approximately 2 and larger, a solution where E_2 is the largest eigenvalue in the bulk, and for which $\theta_L \neq 0$, starts to exist. The behavior of θ_p and θ_L as a function of normal exposure time is shown in Figs. 6(a) and 6(b), respectively. As can be seen in the figures, the behavior of the pretilt angle θ_L is again

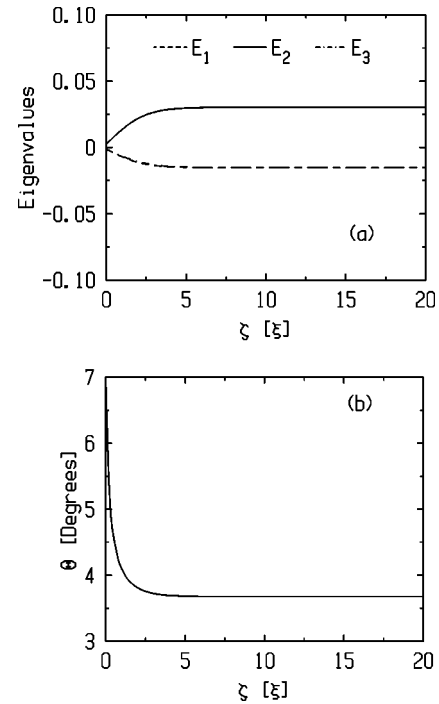


FIG. 5. Eigenvalues (a) and angle (b) as a function of the distance from the surface for $\alpha\tau_1=12$, $\alpha\tau_2=8$, $\theta_{inc}=40^\circ$, and $\sigma=10^\circ$. $E_1 \neq E_3$ in the interfacial region but appears to coincide in this scale.

considerably different from that of θ_p . Figure 6(b) illustrates the fact that the solution with $\theta_L \neq 0$ does not exist for small values of $\alpha\tau_1$. Calculations of the free energy have shown that the solution with largest E_1 and with $\theta_L=0$ is the stable one for values of $\alpha\tau_1$ up to ~ 2.5 . This result may explain

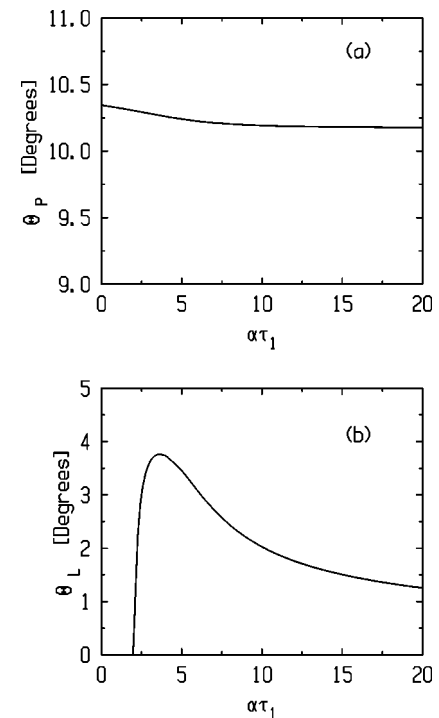


FIG. 6. θ_p (a) and θ_L (b) as a function of the normal exposure time for $\alpha\tau_2=12$, $\theta_{inc}=40^\circ$, and $\sigma=10^\circ$.

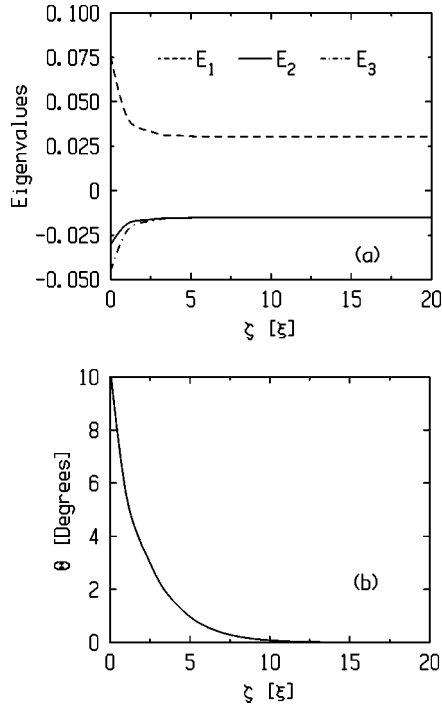


FIG. 7. Eigenvalues (a) and angle (b) as a function of the distance from the surface for $\alpha\tau_1=1$, $\alpha\tau_2=12$, $\theta_{\text{inc}}=40^\circ$, and $\sigma=10^\circ$.

the fact that in experiment only a decrease in θ_L is observed (no alignment has been achieved for small exposure times [8]). It must be emphasized that the behavior of θ_L presented in Fig. 6 is at a τ_2/τ_1 ratio different from the one reported in the experiment. Calculations performed using the experimental ratio showed a much weaker decrease in θ_L with the normal exposure time. This discrepancy could be due to the fact that the liquid crystal samples used in experiment for measuring the pretilt angle in the case of fixed normal and in the case of fixed oblique exposure times may not have been completely identical [20].

The behavior of the eigenvalues and the angle θ as a function of the distance from the surface for the solution with largest E_1 are presented in Figs. 7(a) and 7(b), respectively. It can be seen that the distance at which the bulk values of the liquid crystal tensor order parameter eigenvalues are established is again in the order of 1000 Å but the distance required for the angle θ to decay to its bulk value of zero is several times larger. This indicates that different values of the bulk angle may be measured at different points in the bulk, and therefore this result may explain the inability to experimentally determine a definite pretilt angle for small normal exposure times. In the case when the largest eigenvalue in the bulk is E_2 , the eigenvalues E_1 and E_2 exchange close to the surface, and the behavior of θ is similar to the one presented in the case of a fixed normal exposure time [see Fig. 5(b)].

The behavior of the angles θ_P and θ_L as a function of the oblique uv light angle of incidence θ_{inc} has also been calculated. A typical behavior is illustrated in Fig. 8 for fixed values of both exposure times. It was found that the positions of the maxima in θ_P and θ_L are practically unaffected by the actual values of $\alpha\tau_1$ and $\alpha\tau_2$ (as long as $\alpha\tau_1$ remains larger than $\alpha\tau_2$), although the values of the angles do change. The

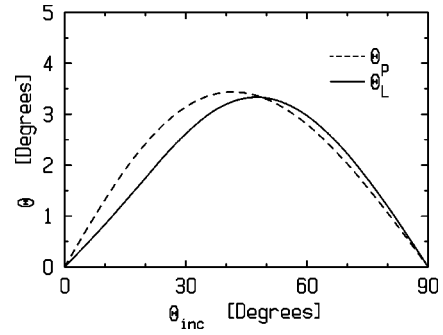


FIG. 8. θ_P and θ_L as a function of the oblique uv light angle of incidence for $\alpha\tau_1=12$, $\alpha\tau_2=4$, $\theta_{\text{inc}}=40^\circ$, and $\sigma=10^\circ$.

value of the standard deviation, however, does affect the angle θ_{inc} at which the maximum occurs: larger values of σ shift the position of the maximum to smaller θ_{inc} .

IV. CONCLUDING REMARKS

The pretilt angle generation on uv irradiated polymer films was investigated in this paper. The results indicate that the generated pretilt angle can be considerably different from the angle favored at the polymer surface, and is a result of the total relaxation of all degrees of freedom in the system. The calculated results are in a good qualitative agreement with the experimental observations [8]. The calculations also indicate that the behavior of the pretilt angle as a function of one exposure time holding the other one fixed does not depend only on the ratio of the two exposure times but also on their particular values.

Values of the surface coefficients ν , χ , and β at different double exposure conditions were also obtained in the course of performing the calculations. In order to estimate the polar and azimuthal anchoring strengths that are directly comparable with W_θ and W_ϕ defined in Frank theory with included weak anchoring in the Rapini-Papoular approximation [21], the effect of an external deformation on the polar and azimuthal angles at the surface should be calculated. This problem, however, involves solving a system of four nonlinear second order differential equations for the two order parameters S and P , and the angles θ and ϕ . Due to the existence of multiple solutions the problem is complicated, and the attempt we made to isolate the appropriate solutions did not give any definitive results.

An important aspect of the model developed in this paper is the fact that the values of the liquid crystal tensor order parameter at the surface were chosen to match those of the polymer film tensor. The calculations were performed only at a particular temperature but if this model is applied for different values of t , the temperature dependence will be transferred completely to the surface coefficients. It is well known that a temperature dependence is indeed exhibited by W_θ [22,23] and W_ϕ [24,25]. Therefore, according to the model, the amount of order favored at the surface remains the same at different temperatures but the strength of the anchoring changes. In the bulk the liquid crystal is always uniaxial, and the amount of orientational order depends only on the temperature.

Finally, it must be pointed out that an additional feature of the liquid crystal alignment on polyimide films exists: the

behavior of the liquid crystal depends on the curing temperature of the polyimide, which in turn affects the degree of imidization of the polymer [26]. This fact can be taken into account by considering a different initial distribution function of the ordering sites, or by assuming that only a certain percentage of the ordering sites participate in the liquid crystal alignment process for different degrees of imidization.

Calculations performed using these assumptions did indeed indicate a different liquid crystal behavior.

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