Model of liquid crystal alignment by exposure to linearly polarized ultraviolet light

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A simple theoretical model of liquid crystal (LC) alignment by exposure to linearly polarized ultraviolet (UV) light is proposed. The model predicts a universal relationship describing the change of the LC anchoring direction with exposure times, and the changes of polarization direction for the case of a double linearly polarized UV exposure process. This relationship is quantitatively confirmed by our experimental results on polyimide systems. The model also suggests that the LC anchoring strength can be controlled by UV exposure dosage. Pretransitional birefringent measurements show that the order parameter of a linearly polarized UV exposed polyimide surface is much lower than that of buffed polyimide films. [S1063-651X(96)10108-2]

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I. INTRODUCTION

The surface alignment of liquid crystals (LC's) is one of the few macroscopic phenomena in which the boundary plays an essential role in determining the behavior of the bulk phase. A practical application of this is that buffed, spin coated polyimide (PI) films align the LC optic axis in flat panel displays. Although the alignment phenomenon was discovered by Maugin in 1911 [1], the mechanism eluded researchers until recently. It is now quite generally believed that buffing induced near surface alignment of polymer chains induces LC alignment by orientational expitaxy [2–10]. Liquid crystal alignment by a photo-oriented surface has recently been given strong attention because of the importance of understanding fundamentals of LC alignment and application in LC displays as well [11–23]. The main reason for such an alignment is photoinduced optical anisotropy that could have both photochemical and photophysical origins. The photoinduced optical anisotropy effect induced by reversible photochemical reactions, for example, photochemical reasons of trans-cis transitions in azobenzene compounds, has been widely studied [11–15].

Recently, Dyadyusha and co-workers [16–18] and Schadt and co-workers [19,20] have reported alignment of LC's by poly(vinyl)4-methoxycinnamate (PVMi) and poly(vinyl) cinnamate (PVCi) films anisotropically crosslinked by exposure to linearly polarized UV light. The LC's align homogeneously on these films with the director oriented perpendicular to the direction of polarization. It is now known that the same result holds for a variety of PI's used in LC displays [22,23]. The mechanism of LC alignment on linearly polarized UV exposed films remains a challenge to scientists [17]. In this paper, a quantitative microscopic model to elucidate the photoalignment process is proposed, which shows that the photoinduced optical anisotropy effect induced by linearly polarized UV exposure is due to irreversible photochemical reactions. The model is confirmed by the results of the double linearly polarized UV exposure experiments designed to explicitly and rigorously test it.

II. MODEL

We consider that the important photoreactions involve axially symmetric photosensitive bonds having exposure time dependent angular distributions $N(\theta,\phi,t)$ relative to the optical electric field (polarization) direction $\mathbf{e}$ (see Fig. 1). We assume that the photoreactions for each class of photosensitive bonds follow uncoupled first order rate theory, and that the photoreaction coupling Hamiltonian $H \propto \mathbf{e} \cdot \mathbf{a}$, where $\mathbf{a}$ is the transition moment of the photosensitive bond. According to first order perturbation theory, the quantum yield rate is proportional to $(\mathbf{e} \cdot \mathbf{a})^2 = \cos^2\phi\cos^2\theta$. Further assuming that the initial distribution of photosensitive bonds in the spin coated PI film is azimuthally isotropic, $N(\theta,\phi,t)$ becomes

$$N(\theta,\phi,t) = N_0(\theta)e^{-\alpha t \cos^2\phi\cos^2\theta}, \qquad (1)$$

where $N_0(\theta)$ is the initial photosensitive bond angular distribution, and α is the constant that is related to detailed molecular structure and is averaged over wavelengths that can activate the photoreaction and weighted by the UV intensity spectrum. We see that azimuthal anisotropy is clearly induced by the anisotropy of the photoreaction rate constant during the linearly polarized UV exposure process that is
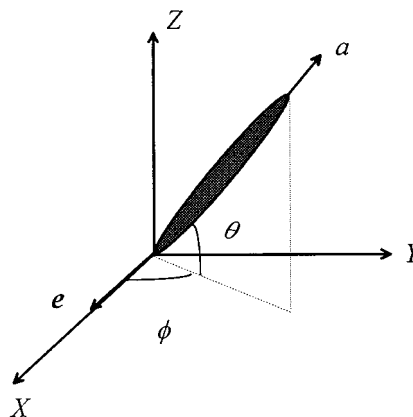

FIG. 1. Geometry of a linearly polarized UV exposure. $\mathbf{e}$ is the UV electric field, and $\mathbf{a}$ is the transition moment of the photosensitive bond.
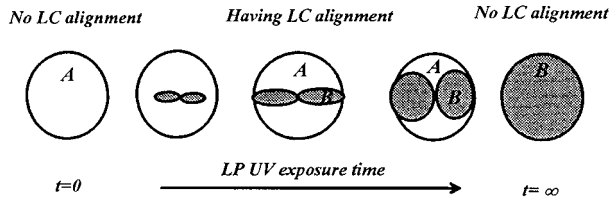
FIG. 2. Time evolution of surface anisotropy during linearly polarized UV exposure.

illustrated in Fig. 2. In order to explain why this anisotropic surface can induce the easy axis of a liquid crystal alignment, we simply assume the interaction potential between the LC medium with alignment direction ϕ_s and a polymer with an orientation at ϕ equal to $\Sigma_{n=1}^{n=\infty} C_n \sin^{2n}(\phi - \phi_s)$, where C_n is a constant related to detail intramolecular interactions. Then the surface free energy between LC media and the linearly polarized UV exposure surface $F_s(\phi_s, \theta, t)$ can be expressed as follows:

$$F_s(\phi_s, \theta, t) = \int_0^\pi \left[\sum_{n=1}^{n=\infty} c_n^A \sin^{2n}(\phi - \phi_s) N(\theta, \phi, t) \right.$$
$$\left. + \sum_{n=1}^{n=\infty} c_n^B \sin^{2n}(\phi - \phi_s)[1 - N(\theta, \phi, t)] \right] d\phi, \tag{2}$$

where c_n^A and c_n^B are the interaction coefficients of LC's with a left unreacted molecule (A) and photoreactive products (B) in the linearly polarized UV exposed films, respectively (see Fig. 2). Under the mean field framework, the azimuthal direction of the LC easy axis is determined by a minimum of F_s respective to ϕ_s, i.e., $[\partial F_s(\phi_s, \theta, t)/\partial \phi_s] = 0$. It is easy to confirm in mathematics that the easy axis direction satisfies the equation $\sin(2\phi_s) = 0$. Therefore, the LC easy axis can be either parallel or perpendicular to the UV polarization, depending on the relative values of c_n^A and c_n^B. It is independent of exposure time. If we assume that during UV irradiation some photosensitive chemical bonds of PI's are broken [23], the dispersive interaction between LC's and PI molecules contributed by van der Waals interactions would be reduced because the broken chemical bonds decrease the polarizability of PI molecules. Thus one can predict that the LC alignment on a linearly polarized UV exposed PI surface should be perpendicular to the polarization of a linearly polarized UV, which agrees with experiment [22,23]. We also predict that the anisotropy of the linearly polarized UV exposure surface is not a monotonic function of linearly polarized UV dosage. Note that long time exposure returns the system to isotropy because of the depletion of photosensitive bonds in all directions as $t \rightarrow \infty$. Thus LC alignment is finally lost, i.e., the possibility of unstable alignment due to UV exposure. It is, therefore, also a natural consequence of our model that optical birefringence reaches a maximum value [24] after a certain linearly polarized UV exposure time, as found experimentally by Schadt *et al.* [19] in a PVMCi system. This differs from the explanation of Schadt *et al.* [19] in that viscosity plays no role. Without the need of molecular motion, the birefringence or aligning strength decays to zero
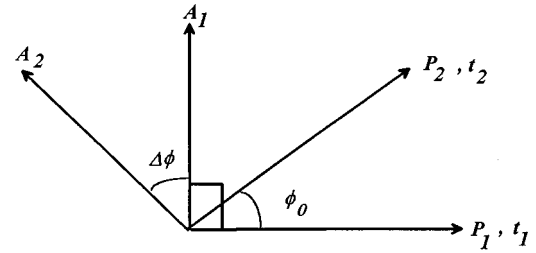

FIG. 3. Geometry for the double linearly polarized UV exposure. $\mathbf{P}_1$ and $\mathbf{P}_2$ are the polarization directions for the first and second linearly polarized UV exposure times. $\mathbf{A}$ is the LC easy axis (anchoring direction). $\Delta\phi$ is the LC easy axis change after the second linearly polarized UV exposure.

at long time exposure, as seen in Eq. (1). Since the PI's are far below their glass transition at room temperature, our assumption of immobility is reasonable. In summary, for the single linearly polarized UV exposure, before UV exposure, the spin coated PI film is isotropic. There is no preferable LC alignment direction on this film. As soon as you shine the PI film using linearly polarized UV light, the anisotropy starts to form [see Eq. (1)], and results in LC easy axis on the film. However, the LC easy axis is always perpendicular to the direction of the polarizer, and is independent of exposure time.

The theoretical model can be quantitatively tested by a double exposure experiment independently used by Palto and Durand [14] to test their model. The geometry is shown in Fig. 3. The distribution of photoreactive bonds after a double linearly polarized UV exposure can be calculated by applying Eq. (1) twice, which gives

$$N(\theta, \phi, t) = N_0(\theta) e^{-\alpha t_1 \cos^2\phi \cos^2\theta} e^{-\alpha t_2 \cos^2(\phi - \phi_0)\cos^2\theta}, \tag{3}$$

where ϕ_0 is the polarization direction change between the first and second exposures. The first and second exposure times are t_1 and t_2, respectively. We also assume that the initial distribution of photoreactive bonds is isotropic before the first UV exposure. Similarly, the azimuthal direction of the LC easy axis on a double exposed film can be determined by minimizing the surface free energy $F_s(\phi_s, \theta, t)$ respective to ϕ_s, using Eqs. (2) and (3). We found that the easy axis follows the extreme points of the azimuthal distribution of photosensitive bonds. On the basis of the experimental fact that the LC anchoring direction for a single linearly polarized UV exposure is perpendicular to the polarization direction, the LC anchoring direction should match the maximum point of the azimuthal distribution of photosensitive bonds. Specifically, the LC anchoring direction after the second linearly polarized UV exposure, ϕ_s, satisfies the following equation:

$$t_1 \sin(2\phi_s) + t_2 \sin 2(\phi_s - \phi_0) = 0. \tag{4}$$

As we mentioned above, the LC easy axis during the first linearly polarized UV exposure as shown in Fig. 3 is always perpendicular to the polarization P_1 and independent of the exposure time t_1. The LC easy axis changes only after the second UV exposure turns on. Therefore, the change of the

LC easy axis after the second UV exposure, $\Delta\phi$, is equal to $(\phi_s - \pi/2)$. Equation (4) is changed to

$$\frac{\sin(2\Delta\phi)}{\sin2(\phi_0 - \Delta\phi)} = \frac{t_2}{t_1}. \qquad (5)$$

Relationship (5) is also based on our assumption that the initial distribution of photoreactive bonds is isotropic before the first UV exposure. Equation (5) is also valid for multiphotoreaction processes, which can be like either crosslink processes as in PVMCi and PVCi systems [16–21], or perhaps deimidization processes in PI systems [23] or other possibilities, as long as they are independent. The merit of Eq. (5) is its universality. It is unrelated to any material parameters, and can be unambiguously tested by experiment.

III. EXPERIMENT

The photoreaction quantum yield rates α of PI's are much smaller than for PVCi or PVMCi. This fact and the strong anchoring of PI materials make it convenient to perform double linearly polarized UV exposure experiments on PI films. The materials we selected are Dupont PI2555 and Nissan PI610. Spin-coated Dupont PI films were soft baked at 100 °C for 5 min, then hard baked at 275 °C for about 2 h, whereas the Nissan PI films were hard baked at 220 °C for about 1 h. The photoinduced alignment process was accomplished with the collimated output of a Xe lamp polarized by an Oriel UV polarizing dichroic sheet. The intensity of UV in the UV B region after passing through the polarizer sheet was about 6 mW/cm^2. To verify Eq. (3), the LC anchoring direction was detected by measuring the twist angle of a cell under a polarizing microscope. One surface of such a LC cell is prepared by unidirectionally buffing a PI film. The other surface is prepared by the double linearly polarized UV exposure process. As is well known, a twisted LC cell acts like a pure optical rotator under the condition that the thickness of the cell is much larger than that of the first interference minimum [25]. The thickness of the test cells was 20 μm, and the nematic LC E7, from Merck, was used. On the other hand, due to the strong anchoring strength of both buffed PI [26] and linearly polarized UV exposed PI alignment layers [23], the easy axis direction of the linearly polarized UV exposed PI surface detected by measuring the twist angle of the above hybrid cell should not be affected by the buffed PI layer.

IV. RESULTS AND DISCUSSIONS

First we looked at a special case, i.e., $\phi_0 = 90°$. From Eq. (4), we find that the change of the LC anchoring direction satisfies the equation $\sin(2\Delta\phi) = 0$. $\Delta\phi$ can be either 0 or $\pi/2$. It is easy to confirm from the surface free energy Eq. (2) that the LC easy axis can be either one of the UV polarization directions, depending on the ratio of the two exposure times. If $t_2 > t_1$, the LC anchoring is parallel to the polarization of the first UV exposure, while the LC anchoring is parallel to the polarization of the second UV exposure if $t_2 < t_1$. The system loses alignment if $t_2 = t_1$. These expectations have been confirmed by West *et al.* [23]. If ϕ_0 is not equal to 90°, Eq. (5) tell us that the LC anchoring direction,
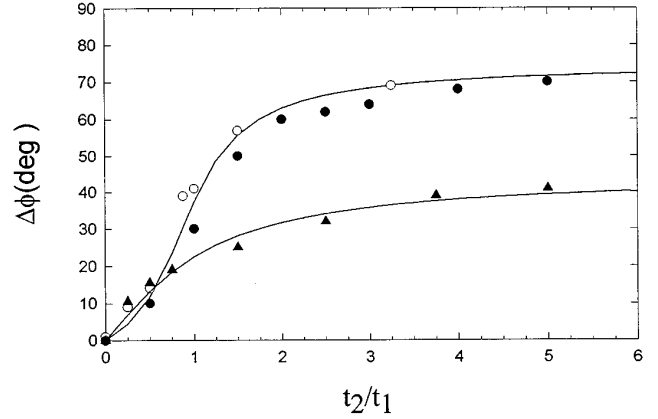

FIG. 4. Experimental results and model prediction for double linearly polarized UV exposure. The open dots are for $\phi_0 = 75°$ and $t_1 = 1$ h. The solid dots are for $\phi_0 = 75°$ and $t_1 = 2$ h. The solid triangles are for $\phi_0 = 45°$ and $t_1 = 2$ h. The PI material used is Dupont PI2555. The solid lines are calculated from Eq. (3).

which can continually vary from zero to ϕ_0, depends solely on ϕ_0 and the ratio of the two exposure times. Figure 4 shows the experimental results of a double linearly polarized UV exposure for the Dupont PI2555 system at $\phi_0 = 75°$ and 45°. The first UV exposure time t_1 was purposely set differently, and equal to 1 and 2 h for $\phi_0 = 75°$, while t_1 is equal to 1 h for $\phi_0 = 45°$. The solid lines are calculated from Eq. (5). We did the same experiment for the Nissan PI610, and set t_1 equal to 1 h with $\phi_0 = 75°$. For comparison, we put the experimental result of the Dupont PI2555 together with that of the Nissan PI610 in Fig. 5. All experimental results quantitatively match our universal Eq. (5) very well, which quite accurately and unambiguously confirms the theoretical model.

How to generate the LC pretilt angle on the UV exposed LC alignment film is essential for its practical application. It is clearly shown from our model that the LC easy axis has a twofold degeneracy (θ and $\pi - \theta$) (see Fig. 6) in the yz
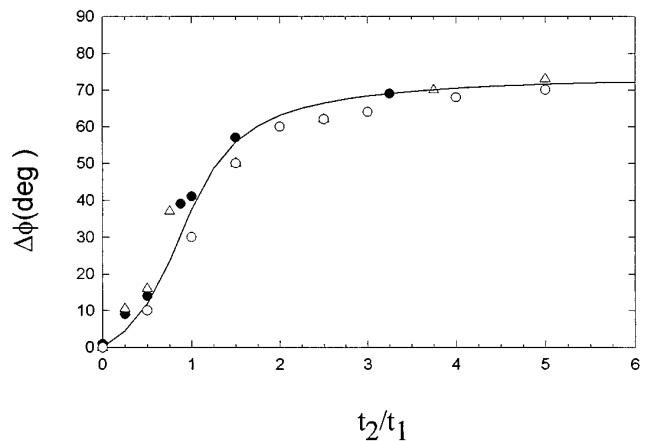

FIG. 5. Experimental results and model prediction for double linearly polarized UV exposure for different PI materials The solid dots are for Dupont PI2555, $\phi_0 = 75°$ and $t_1 = 2$ h. The open dots are for Dupont PI2555, $\phi_0 = 75°$, and $t_1 = 1$ h. The open triangles are for Nissan PI610, $\phi_0 = 75°$, and $t_1 = 1$ h. The solid lines are calculated from Eq. (3).
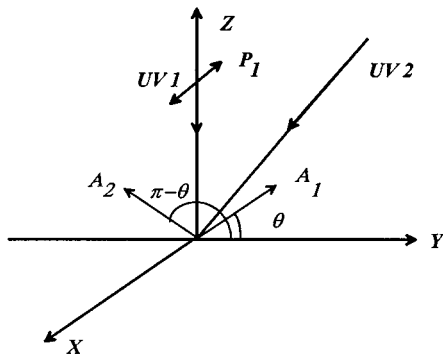
FIG. 6. The geometry of a double UV exposure process to generate a controllable LC pretilt angle on UV-exposed PI films. The polarization for the first UV exposure is along the x direction. A_1 and A_2 are the two degeneracy LC easy axes after the first UV exposure. They are in the yz plane. UV2 represents the second oblique UV exposure. It is in the yz plane.

plane for the LC alignment obtained by a normally incident linearly polarized UV exposure, whose polarization is in the x direction. The desired LC pretilt angle can be generated by removing this degeneracy; for example, another obliquely UV irradiation process is added to realize this purpose. The geometry of the double UV exposure to create a finite LC pretilt angle is shown in Fig. 6. For oblique UV exposure, unpolarized UV light can be used. These expectations are all confirmed by recent experimental results [17,18,27]. It is worth mentioning here that if the molecules on the spin coated polymer surface all lie flatly on the surface, it is impossible to generate a LC pretilt angle even if another oblique UV exposure process is added.

We expect the surface order of a linearly polarized UV induced PI alignment layer to be much lower than that of unidirectionally buffed PI systems. The reasons are that the quantity of photoreaction products is very small in the PI systems after linearly polarized UV exposure, and that anisotropic distribution of reaction products spreads in a large azimuthal angle instead of in a narrow one like a buffed PI film in which polymer chains align well along the buffing direction [10].

The pretransitional birefringence measurement can give us information about surface order [28]. The experimental results are shown in Fig. 7. For comparison, we also present the pretransitional birefringence data taken from a LC cell with buffed Dupont PI2555 alignment layers. The geometry of all three LC cells is the same. The thickness is 50 μm and the nematic LC 5CB purchased from Emerck was used. No detectable pretransitional enhancement was found even after 9 h of linearly polarized UV exposure. This result means that the surface order induced by linearly polarized UV exposure on a PI surface is very small.

It is worthwhile comparing our microscopic model to existing models describing the photoinduced optical anisotropy effect [12,14]. The model we present here describes the photoinduced optical anisotropy effect induced by irreversible photochemical reactions, and it assumes no rotation of the molecules. However, in the models of Janossy [12] and Palto and Durand [14], the photoinduced optical anisotropy effect is induced by the electric torque on a molecule during the reversible trans-cis conformation transition. Molecular
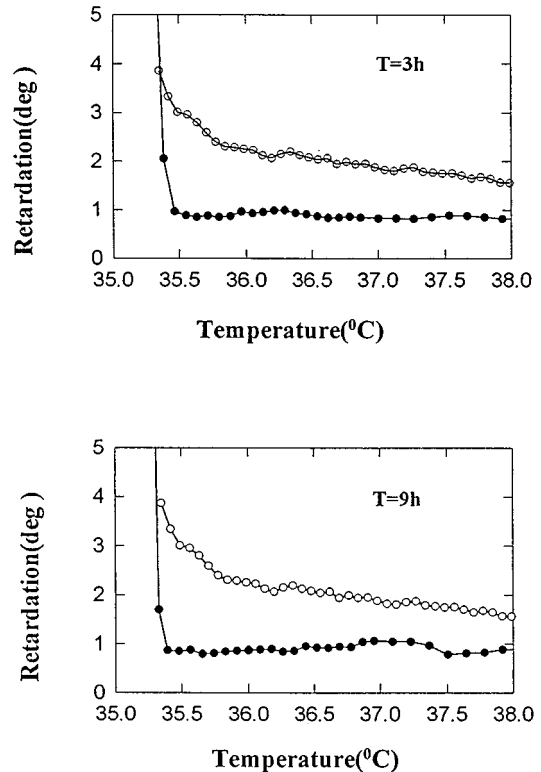

FIG. 7. Pretransitional birefringence behavior of LC cells assembled with linearly polarized UV induced PI (Dupont PI2555) alignment films (●). The UV exposure times are 3 and 9 h, respectively. We shifted the 9-h curve (●) down by 1° on purpose to avoid the overlap. The open dots are the data measured from LC cells assembled with unidirectional buffed PI (Dupont PI2555) films. The geometry of all cells is the same.

rotation must be introduced. Furthermore, the thermal fluctuation plays an essential role in their models. The behavior of optical birefringence versus the irradiation dosage is also different. Contrary to their models, our model predicts that the optical birefringence is not a monotonic function of irradiation dosage, and that LC alignment ability as well as birefringence finally will be lost after a high enough dosage. It is clearly shown from Eq. (3) that a bistable anchoring surface for LC orientations cannot be achieved by a double UV exposure process whether or not the polarizations are perpendicular to each other. This is consistent with experimental results in PI systems. However, a bistable anchoring state was realized in LB films containing azobenzene by double irradiation, and it can be explained by their model [13]. Finally, it is almost impossible for their models to elucidate quantitatively our results of a double UV exposure. Our model predicts the change of easy axis after the second UV exposure is determined by ϕ_0 and exposure time ratio t_2/t_1 instead of ϕ_0 and t_2, as predicted by Palto and Durand's friction model [14]. Relationship (5) in this paper and (21) in Ref. [14] can be used as a criterion to compare the two different photoalignment mechanisms.

V. CONCLUSIONS

In summary, the mechanism of surface induced alignment by linearly polarized UV exposure arises from the angular

dependence of the probability of photoreactions. The resulting anisotropy of the photosensitive bond distribution results in an anisotropic interaction with LC's, which induces an easy axis. The experimental results of double linearly polarized UV exposure experiments quantitatively verify the above statement. Our model clearly shows that the anisotropic distribution of photoreaction products can be strictly controlled by UV exposure dosage and polarization. Our model makes it possible, given a molecular interaction model, to calculate the anchoring strength from a microscopic model, and compare with experimental results. The pretransitional birefringence measurement shows that the linearly polarized UV exposed PI films have a much lower surface order than unidirectionally buffed PI films.

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