Orientation and Surface Anchoring of Nematic Liquid Crystals on Linearly Polymerized Photopolymers

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The liquid crystal orientation on a poly(vinyl cinnamate) or poly(vinyl 4-methoxy-cinnamate) coated solid substrate exposed to linearly polarized UV light has been studied. The angular distribution of the polymer side chains and the photoreaction products was derived as a function of exposure time using a simple assumption about the probability for crosslinking of two side chains. The liquid crystal was assumed to be weakly anchored to the surface but have a degree of order and orientation determined from those of the polymer side chains. The polar and the azimuthal surface coefficients were estimated as a function of exposure time using the Landau–de Gennes theory and the behavior of a twist cell with polymer plates was studied for the values of the calculated surface coefficients. [S1063-651X(97)06802-5]

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I. INTRODUCTION

The ability of a liquid crystal to orient in a particular direction when in contact with a specially prepared surface is a phenomenon of major importance for the manufacturing process of liquid crystal displays. Homogeneous liquid crystal alignment, required for the proper operation of twisted and supertwisted nematic displays, is usually obtained by mechanically rubbing a polymer coated surface. In the last several years a different method for homogeneously aligning a liquid crystal has been discovered. Its main feature is the ability of some polymers to orient homogeneously a liquid crystal after being exposed to linearly polarized UV light. Two different groups of materials have been studied. In the case of poly(vinyl cinnamate) (PVCN) [1] and poly(vinyl 4-methoxy-cinnamate) (PVMC) [2] exposure to linearly polarized UV light results in crosslinking of polymer side chains, while in the case of polyimides (PI) [3–5] the exposure causes breaking of the polymer backbone.

In this work we concentrate on the liquid crystal alignment on PVCN and PVMC films. By using the model developed by Chen et al. [6] for the angular dependence of the probability for a photoreaction, we derive the angular distribution of the polymer side chains and photoreaction products, as well as a tensor order parameter describing their order. Using this order parameter to determine the boundary conditions for a liquid crystal in contact with the polymer film, we then use the Landau–de Gennes theory to calculate the azimuthal and polar surface coefficients as a function of exposure time. With the calculated values of the surface coefficients we study the behavior of a twist cell with polymer plates.

II. THEORY

Following the method of analysis developed by Egeron et al. [7], we describe the polymer film as a collection of reactivity sites, each consisting of a side chain together with its neighborhood surrounding. A site is reactive if in the neighborhood surrounding there is another side chain whose relative geometry is favorable for a photoreaction to occur. All other sites are considered to be nonreactive. The reactive sites can be further divided into two groups: head to head, which are usually formed from side chains belonging to the same macromolecule, and head to tail, formed from side chains belonging to different macromolecules. Since the sites contributing to the liquid crystal order are formed from head-to-tail reactive sites [1,2], we here neglect the contribution of the head-to-head reactive sites. We define the site orientation as the direction of elongation of the side chains in the head-to-tail reactive site or the direction of elongation of their photoreaction products.

Polymer films used for liquid crystal alignment are usually prepared by spin coating. This technique produces polymer films with chains preferentially lying in the plane of the film but with isotropic azimuthal distribution [8]. We assume that only side chains lying at the surface of the film and oriented parallel to it contribute to the liquid crystal alignment, and we use the term ordering sites to refer to both reacted and unreacted head-to-tail sites in the film top layer. In reality there is, of course, a distribution of orientations both for the direction of the ordering site relative to the surface normal and for the separation vector between the two side chains at a given ordering site (i.e., sometimes one side chain is beneath the other rather than beside it at the surface). The effect of both of these distribution effects is to reduce the orientational order in the polymer surface layer. It must be noted that in some cases the polymer film is found to consist of microdomains, each having polymer chains oriented along a particular direction [9]. The domains still lie in the plane of the film and each microdomain has a preferred azimuthal orientation, but the in-plane distribution of the domains is isotropic. In the case when the polymer film consists of such microdomains, the term ordering site introduced above can be thought to refer to a particular microdomain.

Before exposure to UV light the ordering sites are unreacted head-to-tail sites only and their azimuthal distribution is isotropic. When the polymer film is irradiated, crosslinking occurs between the two side chains in the reactive site. The photoreaction product lies in the plane determined by the orientation of the two side chains from which it was formed, and the site orientation changes to approximately perpendicular to its orientation before the photoreaction occurs (see Fig. 1 [1,10]). When the polymer film is exposed to normally propagating and unpolarized UV light, the resulting
The isotropic part of the probability for a photoreaction is proportional to \( \cos^2 \phi \sin^2 \theta \), where \( \phi \) and \( \theta \) are the azimuthal and polar angles in a reference frame where the \( \hat{x} \) axis coincides with the UV light polarization direction. Following this assumption for the probability for a photoreaction and approximating \( \theta \) with the UV polarization direction, which is in agreement with the experimental observation [1,2]. When the exposure time is increased, the anisotropy increases until a particular exposure time is reached and if the exposure time is increased further, the probability for finding an ordering site at azimuthal angles away from \( \phi = 90^\circ \) increases.

To describe the degree of order of the ordering sites, we use a tensor order parameter analogous to the tensor order parameter describing liquid crystalline order [11]. We introduce \( Q^p \) such that

\[
Q^p_{ij} = \frac{1}{2} \langle \partial \delta_{ij} \rangle,
\]

where \( \xi_i \) is the component of the site long axis on the \( i \)th axis of the laboratory coordinate system, and the average is over the angular distribution of the ordering sites. In the case when the polymer film consists of isotropically distributed anisotropic microdomains, the distribution function in Eq. (5) describes the azimuthal distribution of the microdomains, and the average in Eq. (6) is taken over the microdomains. Assuming that the polarization direction of the UV light is along the \( \hat{x} \) axis of the laboratory reference frame and that the polar distribution is uniform with \( \theta = \pi/2 \), we obtain the following diagonal tensor order parameter:

\[
N_a(\phi, \tau) = N_0(\phi, \tau = 0) e^{-\alpha \cos^2 \phi},
\]

where \( \phi \) is the angle between the polarization direction of the UV light and the site orientation and \( \alpha \) is a measure of the probability for photoreaction between the two side chains in the reactive site.

At a particular exposure time the number of ordering sites, both crosslinked and not, at an angle \( \phi \) to the UV polarization direction is given by

\[
N(\phi, \tau) = N_a(\phi, \tau) + N_e(\phi, \tau),
\]

where

\[
N_e(\phi, \tau) = N_0(\phi - \pi/2, \tau = 0) (1 - e^{-\alpha \sin^2 \phi})
\]
is the number of reacted head-to-tail sites. Since the initial distribution of the sites is azimuthally isotropic, \( N_0(\phi, \tau = 0) = N_0(\phi - \pi/2, \tau = 0) \), and thus the number of ordering sites at an angle \( \phi \) to the UV polarization direction is

\[
N(\phi, \tau) = N_0(\phi, \tau = 0) (1 + e^{-\alpha \cos^2 \phi} - e^{-\alpha \sin^2 \phi}),
\]

and the angular distribution function is given by

\[
f(\phi, \tau) = \frac{1 - 2e^{-\alpha \tau^2 \sinh(\alpha \tau^2 \cos 2\phi)}}{\int_0^\infty (1 - 2e^{-\alpha \tau^2 \sinh(\alpha \tau^2 \cos 2\phi)}) d\phi}.
\]

The distribution function is isotropic at \( \tau = 0 \) and \( \tau \to \infty \) and its behavior at some intermediate exposure times is shown in Fig. 2. As can be seen in the figure, the distribution function is anisotropic in a direction perpendicular to the UV light polarization direction, which is in agreement with the experimental observation [1,2]. When the exposure time is increased, the anisotropy increases until a particular exposure time is reached and if the exposure time is increased further, the probability for finding an ordering site at azimuthal angles away from \( \phi = 90^\circ \) increases.

**Fig. 2.** Azimuthal distribution of ordering sites at different exposure times: (a) \( \alpha \tau = 1 \), and (b) \( \alpha \tau = 10 \). The magnitude of a radial vector from the origin is a measure of the probability of finding an ordering site at an angle \( \phi \).
FIG. 3. Eigenvalues of $Q^p$ as a function of exposure time.

\[
Q^p = \begin{pmatrix}
\frac{3}{2} \langle \cos^2 \phi \rangle_{\phi} & 1 & 0 & 0 \\
0 & \frac{3}{2} \langle \sin^2 \phi \rangle_{\phi} & 1 & 0 \\
0 & 0 & -\frac{1}{2} & 0 \\
0 & 0 & 0 & 1
\end{pmatrix},
\]

where $\langle \rangle_{\phi}$ is calculated by using the azimuthal distribution function in Eq. (5). The constant value of $Q_{33}^p = -1/2$, as well as the independence of $Q_{11}^p$ and $Q_{22}^p$ on the polar angle $\theta$, are both consequences of the assumptions that the ordering sites lie perfectly flat in the film top layer, and that only reactions of sites in that layer are relevant. As noted previously, real materials will not be perfectly flat in the surface layer but will have a distribution of orientations of the ordering sites. The effect produced by reactive sites not being parallel to the surface reduces the order so that a more realistic value of $Q_{33}^p$ might be $-0.4$. The fact that reacting chains may be positioned one below the other rather than beside each other on the surface leads to a decrease of $Q_{33}^p$, perhaps from $-0.4$ to $-0.3$, as a function of exposure time to the UV radiation. Calculations performed with $Q_{33}^p$ (and thus $Q_{22}^p$ and $Q_{11}^p$) smaller in magnitude did not change the qualitative nature of the results. Quantitatively, smaller $Q_{33}^p$ leads to a decrease in the calculated polar surface coefficient but the effect on the azimuthal surface coefficient is much weaker. These effects are secondary and for simplicity we present calculations where $Q_{33}^p$ is held at $-0.5$ for all exposure times.

In order to describe the liquid crystal order, we use the biaxial tensor order parameter [12]

\[
Q = \frac{1}{2} \begin{pmatrix}
-S + P & 0 & 0 \\
0 & -S + P & 0 \\
0 & 0 & 2S
\end{pmatrix},
\]

where $S$ is the usual uniaxial order parameter and $P$ is a measure of the biaxiality. For the free energy of the system we use the Landau–de Gennes free energy expansion [12] for the bulk part, and we introduce surface terms to describe the weak anchoring of the liquid crystal to the surface. For a semi-infinite sample of liquid crystal with the surface at $z=0$ and uniform order in all planes parallel to the surface, the free energy has the form

\[
\frac{F/A}{\mathcal{A}} = \int_0^\infty \left[ \frac{1}{4} A (\nabla Q_2) + \frac{1}{2} B (\nabla Q_3) + \frac{1}{2} C (\nabla Q_4)^2 + \frac{1}{4} L (\partial_\theta Q_{ij}) \right] \, dz + G_0 Q_{33}(0) + B_0 \left[ Q_{11}(0) - Q_{22}(0) \right],
\]

where $A$, $B$, $C$, $L_1$, $L_2$, are the Landau–de Gennes free energy parameters, and $\mathcal{A}$ is the surface area. The term in the total free energy involving the coefficient $G_0$ is a surface term corresponding to the polar anchoring energy. When $G_0$ is positive, this term favors a negative $Q_{33}$ at the surface, and thus it favors orientation in the plane perpendicular to the third axis of the coordinate system. Since the surface coincides with the $\mathbf{x}$-$\mathbf{y}$ plane, this term favors planar anchoring and the coefficient $G_0$ is a measure of its strength. We call the coefficient $G_0$ the polar surface coefficient. Similarly, the term with $B_0$, $B_0$ being positive, favors orientation along the $\mathbf{y}$ axis of the laboratory reference frame. The coefficient $B_0$ is a measure of the quality of alignment in the plane of the surface and we call it the azimuthal surface coefficient.

Rescaled to dimensionless units [13], the free energy has the form

\[
\mathcal{F} = \int_0^\infty \left[ \frac{1}{4} J \mu^2 + \frac{1}{4} \eta^2 + \mu (\eta^2 - \mu^2) + \mu^4 + \frac{1}{4} \eta^4 + \frac{1}{2} \left( 1 + \frac{1}{2} \rho \right) \mu^2 + \frac{1}{2} \eta^2 \right] \, dz + \nu \mu(0) + \chi \eta(0),
\]

where $1/4 \tau = (27C/4B^2)A$, $\rho = L_2/L_1$, $\mu = (9C/AB)S$, $\eta = (9C/AB)P$, $\nu = (81C^2/AB^2)G_0$, $\chi = (81C^2/AB^2)B_0$, $\xi = 27CL_1/4B^2$, $\zeta = \zeta/\xi$, and $\mathcal{F} = (3C/AB)F$. Minimizing the above free energy, we find the following system of ordinary differential equations

\[
\begin{align*}
&\frac{d}{dz} \left( \mu^2 + \frac{1}{4} \eta^2 + \mu (\eta^2 - \mu^2) + \mu^4 \right) + \frac{1}{2} \left( 1 + \frac{1}{2} \rho \right) \mu^2 + \frac{1}{2} \eta^2 = \frac{d}{dz} \mu(0) + \chi \eta(0), \\
&\frac{d}{dz} \mu = 0, \\
&\frac{d}{dz} \eta = 0.
\end{align*}
\]
with boundary conditions
\[\mu'(0) = \frac{2\nu}{2 + \frac{2}{3}\rho}, \quad \mu'(\infty) = 0, \quad \eta'(0) = 6\chi, \quad \eta'(\infty) = 0.\] (12)

To find the equilibrium state of the liquid crystal, we solve the equations above numerically utilizing the general purpose code COLNEW for systems of ordinary differential equations.

III. RESULTS AND DISCUSSION

The eigenvalues of the tensor order parameter \(Q^p\) [Eq. (6)] describing the order of the ordering sites are shown in Fig. 3 as a function of \(\alpha \tau\). We associate the average orientation of the sites to be along that eigenvector of \(Q^p\) which corresponds to the eigenvalue of the largest magnitude. As can be seen in Fig. 3, for small and large exposure times, the eigenvalue of the largest magnitude is \(Q_{22}\) and it is negative, showing that the predominant order of the ordering sites is in the plane of the film but there is no in-plane easy axis. For intermediate exposure times \((1.5 < \alpha \tau < 10)\), the eigenvalue of the largest magnitude is \(Q_{22}\), showing that the sites are on average oriented along a direction perpendicular to the UV light polarization direction. This result is in agreement with the experimental observation \([1,2]\). The in-plane anisotropy of the ordering sites is shown in Fig. 4 as a function of \(\alpha \tau\). It exhibits the main feature of the optical retardation measurements \([2]\), that is, with switching the UV light on, the anisotropy increases rapidly, then peaks at certain exposure time, and afterwards decreases slowly.

Liquid crystal in the nematic phase exhibits planar, polydomain order when in contact with a nonexposed film \([1]\). To see the behavior of the liquid crystal on a surface favoring planar alignment, we calculated the eigenvalues of the liquid crystal order parameter \(Q\) as a function of the distance from the surface for a set of different values of the scaled polar anchoring \(\nu\) and keeping \(\chi = 0\). Figure 5 shows the eigenvalues at the surface as a function of the polar anchoring at the supercooling limit \((\tau = 0)\) and setting \(\rho = 1\). It can be seen that at this temperature the liquid crystal is uniaxial only for \(\nu = 0\) (bulk limit), and for \(\nu \to \infty\), which corresponds to infi-
nite polar anchoring. Thus at any intermediate \( \nu \) the liquid crystal is biaxial and some anisotropy will be present in the plane of the surface. This anisotropy, however, is completely symmetric with respect to the interchanging of \( Q_{11} \) and \( Q_{22} \). In the case when the polymer film consists of isotropically distributed microdomains, this symmetry will be broken according to the orientation of the microdomains, and when no microdomains exist in the plane of the film, the symmetry between \( Q_{11} \) and \( Q_{22} \) will be spontaneously broken. In both cases a polydomain structure will result—the liquid crystal will have different orientation at different surface regions.

At an exposed film the symmetry between \( Q_{11} \) and \( Q_{22} \) is broken; in this case larger \( Q_{22} \) is favored. We assume that apart from giving a preferred direction, the polymer film in contact with the liquid crystal enhances the inherent in-plane anisotropy of the liquid crystal by an amount equal to the anisotropy of the film. We also assume that the amount of order in a direction perpendicular to the film plane is the same for both the side chains and the liquid crystal. Thus we calculate the values of the scaled polar anchoring \( \nu \) and the scaled azimuthal anchoring \( \chi \) required to obtain values of \( Q_{11}^{-1}(\tau) = -1/2 \) and \( \Delta Q''(\tau) = \Delta Q''(\tau=0) + \Delta Q''(\tau) \), where \( \Delta Q = Q_{22} - Q_{11} \). The results for \( \nu \) and \( \chi \) as a function of exposure time are shown in Fig. 6. It can be seen that both \( \nu \) and \( \chi \) follow a behavior similar to that of the anisotropy of the polymer film; they exhibit a maximum at the same exposure time as the anisotropy of the film. However, the relative change in the polar surface coefficient \( \nu \) is much smaller than the change in the azimuthal surface coefficient \( \chi \), and the value of \( \chi \) is always at least one order of magnitude weaker than \( \nu \). Rescaling back \( \nu \) and \( \chi \), for the anchoring of 5CB [13] to PVCN or PVMC film, we obtain maximum values of \( G_0 \sim 10^{-3} \text{ J/m}^2 \) and \( B_0 \sim 10^{-4} \text{ J/m}^2 \) which are associated with strong anchoring.

In order to compare our results with experimental observations, we have calculated the behavior of the twist angle in a twist cell of thickness \( d = 10^5 \zeta \). (For 5CB the value of \( \zeta = 8 \) nm.) The cell is composed of two identical polymer plates but oriented in such a way that a 90° twist is favored. The behavior of the twist angle as a function of the distance between the plates is shown in Fig. 7(a) for three different values of \( \chi \), and the total twist in the cell as a function of \( \chi \) is shown in Fig. 7(b). It can be seen that for a value of \( \chi = 0.1 \) there is practically a full twist. In terms of the polymer film this result means that even a film exposed for very short or very long time would strongly anchor the liquid crystal. Experimental observations [6] show that the quality of alignment is decreased on film exposed for a long time. However, no quantitative results are available. If we have a systematic study of the behavior of a twist cell with polymer plates exposed for different periods of time, we can compare our calculations with experimental results and see how our assumption about the degree of order at the surface should be modified.

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