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Dependence of threshold behavior upon surface distribution of polymer chains in a twisted nematic liquid crystal

Jin Seog Gwag,[1] Gi-Dong Lee,[2] Tae-Hoon Yoon,[1,3] and Jae Chang Kim[1,3]
[1]*Department of Electronics Engineering, Pusan National University, Pusan 609-735, Korea*
[2]*Division of Electronics Engineering, Dong-A University, Busan 604-714, Korea*
[3]*Research Institute of Computer, Information and Communication, Pusan National University, Pusan 609-735, Korea*

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On the basis of a general Rapini and Papoular equation and a unified surface anchoring energy theory, dependence of the threshold behavior of the liquid crystal director upon the statistical distribution of polyimide chains is theoretically investigated for a twisted nematic liquid crystal cell. We assumed that the anisotropy distribution of polyimide chains induced by the rubbing can be dominated by a Gaussian distribution around the rubbing direction. Our results show that the threshold behavior of a twisted nematic liquid crystal is affected strongly by the surface distribution of polymer chains.

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The director distribution of liquid crystal (LC) molecules in the bulk and at the surfaces of the twisted nematic liquid crystal (TNLC) cell has caused considerable interest in both basic and applied science. Behavior of the director distribution is affected by the surface distribution of solid substrate materials such as polymer chains, as well as by the interfacial anchoring strength between LC molecules and solid substrate, and by external fields such as magnetic and electric fields. Interactions between the LC molecules and solid substrate determine the orientational order of the LC molecules in the monolayer that comes across solid substrate. This monolayer orients in turn with LC molecules in bulk because of the tendency of intermolecular interaction to align molecules parallel to each other [1–5].

The solid surface treated by the conventional rubbing method, which has been widely used to obtain a uniform director alignment in liquid crystal cells, orients the LC direction, **L** along the easy axis (rubbing direction). Rubbing breaks the symmetry by reorienting polyimide (PI) chains used as solid substrate material. Then the anisotropic distribution of PI chains is responsible for the LC alignment. Surface molecular distribution of PI film treated by rubbing or photoexposure has been revealed through prominent experiments by several scientists [5–13]. Despite such experimental results, LC anchoring properties on rubbed surfaces that were considering surface distribution of PI molecules was reported by Baharat R. Acharya *et al.* [14]. Moreover, reports on deformation of LC directors in bulk, including surface distribution of PI chains, are still few.

In models for director deformation [15–19], many authors assumed that all PI chains in a surface are aligned with the easy axis because of the difficulty of mathematical analysis in weak anchoring boundaries. Actually, although the microscopic origin of LC alignment has not yet been perfectly revealed, according to rubbing strength, these distributions should be different.

The surface effect has been demonstrated by the Rapini and Papoular equation [20], a simple expression for the interfacial surface anchoring energy per unit area, which illustrates the anisotropic interaction between liquid crystal and solid substrate. A unified surface anchoring energy has been proposed by Akiko Sugimura *et al.* who studied director deformation of a twisted chiral nematic liquid crystal cell (TCNL) [18].

In this paper, on the basis of a general Rapini and Papoular equation and a unified surface anchoring energy, a threshold field of the LC director depending on Gaussian statistical distribution of PI chains is researched for TCNL.

For a twisted nematic LC sample, the extended anisotropic energy density of director orientation described by Sugimura is as follows:

$$f_s = -\tfrac{1}{2}A(L\cdot u)^2, \tag{1}$$

which is a nonlinear combination of the azimuthal and polar angles, where A means the anisotropic anchoring strength determined by the distribution of PI chains, and $\boldsymbol{L}$ and $\boldsymbol{u}$ express the LC director along a particular orientation and the distribution of PI chains per unit area, respectively. For PI chains treated by the rubbing it can be approximated by a Gaussian distribution centered around the easy axis with $\Theta=0$ and $\Phi=0$. A_0 represents the pure strength of interfacial interaction between LC molecules and PI chains per unit area. Here Θ and Φ denote the azimuthal and polar angles of PI chains with respect to the easy axis (rubbing direction). If PI surfaces have strong anchoring, i.e., all PI chains are aligned along the same direction, the width of the PI chain distribution $\sigma_\Theta \to 0$ and $\sigma_\Phi \to 0$ and the probability distribution function $P(\Theta,\Phi)$ exists only at $\Theta=\Theta_0$ and $\Phi=\pi/2$, where these are units, then $A=A_0$. If $\sigma_\Theta \to \infty$ and $\sigma_\Phi \to \infty$, i.e., in the weak anchoring limit, PI chains randomly distribute, which means isotropic alignment, then anisotropic anchoring strength $A\to 0$. The total free energy density in the bulk defined by Frank and Oseen is given by the following expression:

$$f_b = \frac{1}{2}\left[k_1(L_{i,i})^2 + k_2\left(L_iL_{k,j}\varepsilon_{ijk} + \frac{2\pi}{p}\right)^2 + k_3L_iL_jL_{k,i}L_{k,j}\right] + f_e, \tag{2}$$

where k represents the elastic constants; k_1, k_2 and k_3 are the splay, twist, and bend elastic constants, respectively; p is the pitch of LC material by a chiral dopant; and ε_{ijk} is the Levi-Civita symbol ($\varepsilon_{123}=\varepsilon_{231}=\varepsilon_{312}=1, \varepsilon_{132}=\varepsilon_{213}=\varepsilon_{321}=-1$, all other $\varepsilon_{ijk}=0$). f_e. The electric free energy density which represents interaction energy between the LC molecule and an electric field is given by $f_e=-\frac{1}{2}\varepsilon_0\Delta\varepsilon(E\cdot L)^2$, where ε_{o} is the dielectric constant in the space and $\Delta\varepsilon$ is the dielectric anisotropy.

A director configuration at which total free energy is minimized can maintain the stable state. The total free energy, which is the sum of the bulk and the surface free energy, can be expressed as the following integral form:

$$F=\int f_s^b da+\int f_s^t da+\int f_b dv, \tag{3}$$

where da is the surface area element and dv is the bulk volume element. Here, the variational approach using the unit step function and the Dirac function proposed by Akiko Sugimura *et al.* to solve Eq. (3), which induces more complicated equilibrium condition forms under a weak boundary, can make Eq. (3) reduce to the unified integral. As a result, more simple equilibrium conditions were obtained as the followings [18]:

$$\frac{\partial f_b}{\partial L_i}-\frac{\partial}{\partial k_j}\left[\frac{\partial f_b}{\partial L_{i,j}}\right]=\vartheta L_i(0\leqslant z\leqslant d)(k_1=x,k_2=y,k_3=z),$$

$$\frac{\partial f_b}{\partial L_{i,3}}=-A_b(\boldsymbol{L_b}\cdot\boldsymbol{u_b})u_i^b-\alpha_b L_i^b(z=0),$$

$$\frac{\partial f_b}{\partial L_{i,3}}=A_t(\boldsymbol{L_t}\cdot\boldsymbol{u_t})u_i^t+\alpha_i L_i^t(z=d), \tag{4}$$

where A_b, $\boldsymbol{L_b}$, and $\boldsymbol{u_b}$ represent the anisotropic anchoring strength, the direction of LC director, and the distribution of PI chains per unit area at the bottom substrate surfaces, respectively. A_t, $\boldsymbol{L_t}$, and $\boldsymbol{u_t}$ represent the anisotropic anchoring strength, the direction of LC director, and the distribution of PI chains per unit area at the top substrate surfaces, respectively, and ϑ, α_b, and α_t are Lagrange multipliers to be determined by the constraint $\boldsymbol{L}\cdot\boldsymbol{L}$ in the bulk and at the surfaces and $L_{ij}=\partial L_i/\partial k_j$. The distribution of PI chains per unit area at $z=0$ could be given by

$$\boldsymbol{u}(\Theta,\Phi)=(U(c,c),U(c,s),U(s,)), \tag{5}$$

where

$$U(c,c)=\int_{-\pi/2}^{\pi/2}\int_0^{\pi}\times\frac{e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta}{\int_{-\pi/2}^{\pi/2}\int_0^{\pi}e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta\,d\Theta\,d\Phi}\times\cos\Theta\cos\Phi\,d\Theta\,d\Phi,$$

$$U(c,s)=\int_{-\pi/2}^{\pi/2}\int_0^{\pi}\times\frac{e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta}{\int_{-\pi/2}^{\pi/2}\int_0^{\pi}e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta\,d\Theta\,d\Phi}\times\cos\Theta\sin\Phi\,d\Theta\,d\Phi,$$

$$=\int_{-\pi/2}^{\pi/2}\int_0^{\pi}\times\frac{e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta}{\int_{-\pi/2}^{\pi/2}\int_0^{\pi}e^{[-(\Theta-\Theta_o)^2/2\sigma_\Theta^2-(\Phi)^2/2\sigma_\phi^2]}\sin\Theta\,d\Theta\,d\Phi}\times\sin\Theta\,d\Theta\,d\Phi.$$

The direction of LC molecules in the z axis can be described as

$$\boldsymbol{L}(\theta,\phi)=(\cos\theta\cos\phi,\cos\theta\sin\phi,\sin\theta). \tag{6}$$

When the polar and the azimuthal deviations of LC directors with respect to the z layer is only considered and an electric field is applied to the cell parallel to the z axis, then the free energy density in the bulk formulated in Eq. (2) is reduced to

$$\begin{aligned}f_b=\frac{1}{2}\Bigg[&k_1L_{3,3}^2+k_2\left(L_2L_{1,3}-L_1L_{2,3}+\frac{2\pi}{P}\right)^2+k_3(L_1L_3L_{1,3}L_{1,1}\\&+L_1L_3L_{2,3}L_{2,1}+L_1L_3L_{3,3}L_{3,1}+L_2L_3L_{1,3}L_{1,2}\\&+L_2L_3L_{2,3}L_{2,2}+L_2L_3L_{3,3}L_{3,2}+L_3L_3L_{1,3}L_{1,3}\\&+L_3L_3L_{2,3}L_{2,3}+L_3L_3L_{3,3}L_{3,3})\Bigg]+f_e\\=\frac{1}{2}\Bigg[&k_1L_{3,3}^2+k_2\left(L_2L_{1,3}-L_1L_{2,3}+\frac{2\pi}{P}\right)^2+k_3(L_3L_3L_{1,3}L_{1,3}\\&+L_3L_3L_{2,3}L_{2,3}+L_3L_3L_{3,3}L_{3,3})\Bigg]-\frac{1}{2}\varepsilon_0\Delta\varepsilon(\boldsymbol{E}\cdot\boldsymbol{L})^2.\end{aligned} \tag{7}$$

In order to conduct the torque balance equation, which means minimization of the free energy and the stable director state in the bulk, variational calculus is applied to Eq. (7). From it, the torque balance equation in the bulk is given by

$$(k_1\cos^2\theta+k_3\sin^2\theta)\left(\frac{d\theta}{dz}\right)^2+\left[\frac{1}{(k_2\cos^2\theta+k_3\sin^2\theta)\cos^2\theta}\times\left(B+\frac{2\pi k_2}{p}\cos^2\theta\right)\right]^2-\Delta\varepsilon E^2\sin\theta\cos\theta=I, \tag{8}$$

where B and I are integration constants. Here the polar angle θ and azimuthal angle ϕ are the functions of z. We now find B using the boundary condition at the surface. Using Eqs. (5) and (6), the third equation of Eq. (4) is given as follows:

$$\frac{\partial f_b}{\partial L_{i,3}} = -A_b(\boldsymbol{L_b}\cdot\boldsymbol{u_b})u_i^b - \lambda_b L_i^b(z=0)$$

$$= \begin{cases} \dfrac{\partial f_b}{\partial L_{1,3}} = -A[U(c,c)\cos\,\theta\cos\,\phi + U(c,s)\cos\,\theta\sin\,\phi + U(s,)\sin\,\theta]U(c,c) - \lambda_b\cos\,\theta\cos\,\phi, \\ \dfrac{\partial f_b}{\partial L_{2,3}} = -A[U(c,c)\cos\,\theta\cos\,\phi + U(c,s)\cos\,\theta\sin\,\phi + U(s,)\sin\,\theta]U(c,s) - \lambda_b\cos\,\theta\sin\,\phi, \\ \dfrac{\partial f_b}{\partial 3_{1,3}} = -A[U(c,c)\cos\,\theta\cos\,\phi + U(c,s)\cos\,\theta\sin\,\phi + U(s,)\sin\,\theta]U(s,) - \lambda_b\sin\,\theta. \end{cases} \quad (9)$$

Using Eqs. (2) and (6), $\partial f_b/\partial L_{i,3}$ can be expressed in the following forms:

$$\frac{\partial f_b}{\partial L_{1,3}} = \begin{cases} \dfrac{\partial f_b}{\partial L_{1,3}} = -k_3\sin^3\,\theta\cos\,\phi\dfrac{\partial\theta}{\partial z} - (k_2\cos^2\,\theta + k_3\sin^2\,\theta)\cos\,\theta\sin\,\phi\dfrac{\partial\phi}{\partial z} + k_{22}\cos\,\theta\sin\,\phi, \\ \dfrac{\partial f_b}{\partial L_{2,3}} = k_3\sin^3\,\theta\sin\,\phi\dfrac{\partial\theta}{\partial z} + (k_2\cos^2\,\theta + k_3\sin^2\,\theta)\cos\,\theta\cos\,\phi\dfrac{\partial\phi}{\partial z} + k_{22}\cos\,\phi\cos\,\phi, \\ \dfrac{\partial f_b}{\partial L_{3,3}} = (k_1 + k_3\sin^2\,\theta)\cos\,\theta\dfrac{\partial\theta}{\partial z}, \end{cases} \quad (10)$$

where $k_{22}=2\pi k_2/p$. From Eqs. (9) and (10), the torque balance equations at the surface, $z=0$, can be expressed as follows:

$$(k_1\cos^2\,\theta + k_3\sin^2\,\theta)\left.\frac{d\theta}{dz}\right|_{z=0} = A[U(c,s)\sin\,\phi + U(c,c)\cos\,\phi][U(c,c)\cos\,\phi + U(c,s)\sin\,\phi]\sin\,\theta\cos\,\theta + AU(s,) \times(\cos^2\theta - \sin^2\,\theta)[U(c,s)\sin\,\phi - U(c,c)\cos\,\phi] + AU^2(s,)\sin\,\theta\cos\,\theta, \quad (11)$$

$$(k_2\cos^2\,\theta + k_3\sin^2\,\theta)\cos^2\,\theta\left.\frac{d\phi}{dz}\right|_{z=0} = A[U(c,c)\cos\,\theta\cos\,\phi + U(c,s)\cos\,\theta\sin\,\phi + U(s,)\sin\,\theta][U(c,c)\sin\,\phi - U(c,s)\cos\,\phi]\cos\,\theta + \frac{2\pi k_2}{p}\cos^2\,\theta. \quad (12)$$

From Eq. (12) and the boundary condition at the surface, B is found as follows;

$$B = A[U(c,c)\cos\,\theta_o\cos\,\phi_o + U(c,s)\cos\,\theta_o\sin\,\phi_o + U(s,)\sin\,\theta_o][U(c,c)\sin\,\phi_o - U(c,s)\cos\,\phi_o]\cos\,\theta.$$

Also, from midplane condition defined as

$$\left.\frac{d\theta}{dz}\right|_{z=d/2} = 0, \quad \theta = \left.\theta_m\right|_{z=d/2}, \quad \phi = \left.\frac{1}{2}\phi_t\right|_{z=d/2}, \quad (13)$$

I is solved simply as follows:

$$I = \left[\frac{1}{(k_2\cos^2\,\theta_m + k_3\sin^2\,\theta_m)}\left(B + \frac{2\pi k_2}{p}\cos^2\theta_m\right)^2 + \varepsilon_o\Delta\varepsilon E^2\sin^2\theta_m\right].$$

Then, from Eq. (8), we can obtain

$$\frac{d\theta}{dz} = \left\{\frac{1}{(k_1\cos^2\,\theta + k_3\sin^2\,\theta)}\left[\frac{1}{(k_2\cos^2\,\theta_m + k_3\sin^2\,\theta_m)\cos^2\,\theta_m} \times\left(B + \frac{2\pi k_2}{p}\cos^2\,\theta_m\right)^2 - \frac{1}{(k_2\cos^2\,\theta + k_3\sin^2\,\theta)\cos^2\,\theta} \times\left(B + \frac{2\pi k_2}{P}\cos^2\,\theta\right)^2 + \Delta\varepsilon E^2(\sin^2\,\theta_m - \sin^2\,\theta)\right]\right\}^{1/2}. \quad (14)$$

We assume that $\theta_o = \theta_m \rightarrow 0$ at the threshold condition. Then, B is reduced as

$$B = A[U(c,c)\cos\,\phi_0 + U(c,s)\sin\,\phi_0] \times[U(c,c)\sin\,\phi_0 - U(c,s)\cos\,\phi_0]. \quad (15)$$

Here θ_0 and ϕ_0 are polar and azimuthal angles of LC at $z=0$ or $z=d$ with respect to easy axis, respectively. From Eqs. (13)–(15), this very important equation, related between the azimuthal anchoring strength and the azimuthal deviation angle of the surface LC directors concerning the distribution of polymer chains, is defined as

$$
\begin{aligned}
(Ad/k_2) &= [U(c,c)\cos\phi_0 + U(c,s)\sin\phi_0][U(c,c)\sin\phi_0 \\
&\quad - U(c,s)\cos\phi_0] \\
&= \phi_{\mathrm{t}} - 2\phi_0 - (2\pi d/p). \qquad (16)
\end{aligned}
$$

For simplicity of calculation, we suppose that PI molecules at the surface have only azimuthal distribution. Applying Eq. (14) to Eq. (11) and using Eqs. (13) and (16) at threshold condition leads to the relationship between the threshold field and anchoring strength as the follows:

$$(1/\lambda)U^2(,c)\cos^2\phi_0 = (1/a\pi)\sqrt{q}\tan\left(\tfrac{1}{2}\sqrt{q}\right), \qquad (17)$$

where $a=k_2/k_1$, $b=k_3/k_1$, and the dimensionless coupling parameter

$$\lambda = (\pi k_2/Ad),$$

$$q = \Delta\varepsilon E_t^2\frac{d^2}{k_1} + (2a-b)(\phi_{\mathrm{t}}-2\phi_0)^2 - 4\pi ac(\phi_{\mathrm{t}}-2\phi_0), \qquad (18)$$

where $c=d/p$. For convenience, we use the reduced voltage, $v=V_t/V_{th}$, where V_{th} is the Fréedericksz threshold votage for $\phi_{\mathrm{t}}=0$, defined as

$$V_{th} = \pi\sqrt{k_1/\Delta\varepsilon}. \qquad (19)$$

From Eqs. (18) and (19), the general reduced voltage v is given by

$$v = \frac{1}{\pi}\sqrt{q - (2a-b)(\phi_{\mathrm{t}}-2\phi_0)^2 + 4\pi ac(\phi_{\mathrm{t}}-2\phi_0)}. \quad (20)$$

From Eqs. (17) and (20), we look into the distribution width σ_ϕ dependence with the λ dependence of the threshold voltage for twisted cells and untwisted cells ($\phi_{\mathrm{t}}=\pi/2$ and $\phi_{\mathrm{t}}=0$ with $\sigma_\phi=0$, 0.8 and 1.2 for $a=k_2/k_1=0.6$, $b=k_3/k_1$, and $c=d/p=0$) as shown in Fig. 1. As depicted in Fig. 1, in the strong anchoring of $\lambda\to 0$, our results agree well with the results of previous studies. For an isotropic surface of $\lambda\to\infty$ and $\sigma_\phi\to\infty$, our model shows more reasonable results because the threshold voltage approaches zero voltage, which means that the Fréedericksz transition does not exist. The most important difference between our model and Becker's model [17] is the existence of threshold voltage inversion between the twisted state and the untwisted state in weak anchoring. The existence of threshold voltage inversion between the twisted state and the untwisted state was not noted in Becker's model, but it was noted in our model. This could mean that under the surface with weak anchoring the threshold voltage is principally affected by the interaction of LC molecules in bulk, namely, under weak anchoring, free energy of the twisted state which has worse ordering is higher than that of the untwisted state which has better ordering. In addition, an increase of the distribution width σ_ϕ leads to threshold voltage inversion under stronger anchoring and decreases threshold voltage in both the twisted state and untwisted state. This obviously shows that the configuration and the threshold behavior of directors in bulk is affected by distribution of surface polymer chains.

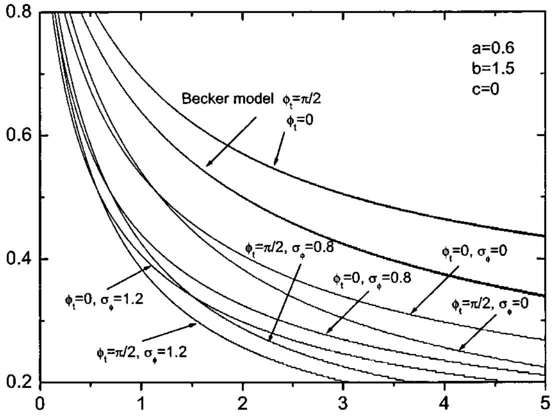

FIG. 1. When the widths of distribution are 0, 0.8, and 1.2 for the twisted state of $\pi/2$ and the untwisted state, the dimensionless coupling parameter λ and the width of the distributions σ_ϕ dependence on the threshold voltage is shown with Becker's model for comparison. The ratios of the elastic constants a and b are 0.6 and 1.5, respectively. Here, the pitch of LC material p is infinite.

In this paper, we assumed that anchoring strengths are the same as $A=A_t=A_b$ and pretilt angles at both surfaces are the same as $\theta_0=\theta(0)=\theta(d)$.

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