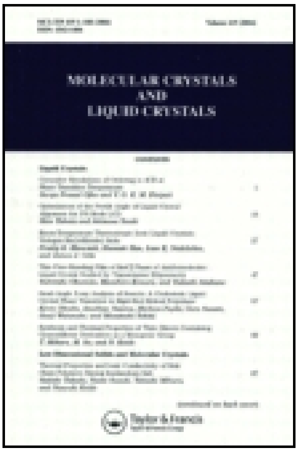

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dependence of Liquid Crystal Bulk Alignment on Its Surface Monolayer

X. Zhuang [a], L. Marrucci [a], D. Johannsmann [a b] & Y. R. Shen [a]

[a] Department of Physics, University of California, Berkeley, CA, 94720-7300

[b] Max-Planck-Institut fuer Polymer-forschung, Ackermannweg 10, D-55021, Mainz, Germany

To cite this article: X. Zhuang , L. Marrucci , D. Johannsmann & Y. R. Shen (1995): Dependence of Liquid Crystal Bulk Alignment on Its Surface Monolayer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 262:1, 35-43

To link to this article: http://dx.doi.org/10.1080/10587259508033510

Mol. Cryst. Liq. Cryst. 1995, Vol. 262, pp. 35–43
Reprints available directly from the publisher
Photocopying permitted by license only

DEPENDENCE OF LIQUID CRYSTAL BULK ALIGNMENT ON ITS SURFACE MONOLAYER

X. ZHUANG, L. MARRUCCI, D. JOHANNSMANN,* and Y.R. SHEN
Department of Physics, University of California, Berkeley, CA 94720-7300

Abstract Liquid crystal bulk alignment, including the pretilt angle, on rubbed polyimide is related, using a biaxial Landau-de Gennes model, to the orientational distribution of its surface monolayer. The predicted correlation can be experimentally verified, using optical second harmonic generation to probe the liquid crystal surface monolayer and linear optics to measure the bulk alignment.

INTRODUCTION

A variety of treatments of the substrates are routinely employed to impose a preferred bulk alignment in nematic liquid crystal (LC) cells. Nevertheless, a clear understanding of this surface-induced bulk alignment, or LC "anchoring", has not yet emerged.[1] Rubbed polyimide-coated substrates are commonly used to induce homogeneous alignment. For most polyimides, the induced bulk alignment is not exactly parallel to the substrate, but tilted at a small angle, called "pretilt", typically of a few degrees. This angle is an important design parameter for LC switch-devices and displays; some applications, such as supertwisted displays, could be substantially improved if complete control of its value by surface treatment were possible.[2] This would require an understanding of its origin, which is presently lacking.

Many rubbed substrates are known to align the LC bulk because of the rubbing-induced grooves.[3] The aligning effect of polyimides, however, seems to be qualitatively different. Recent experiments show that the LC monolayer adsorbed at the rubbed polyimide surface is oriented, which clearly indicates microscopic-scale anisotropy of the substrate.[4,5] Presumably rubbing stretches the polymer chains, inducing a surface anisotropic texture which is reflected in the orientational distribution of the adsorbed LC monolayer. The surface LC monolayer, in turn, can completely determine the alignment of the bulk via LC orientational correlation.[6] In this paper we describe this correlation in the framework of a Landau-de Gennes continuum theory, and discuss the experimental evidence in support of this picture.

THEORY

We consider the surface as a smooth plane. We choose a coordinate system with x along the rubbing direction, and z along the surface normal, pointing into the LC bulk. The nematic tensor order parameter is defined in the usual way as

$$Q_{ij} =< (3\zeta_i\zeta_j - \delta_{ij})/2 >, \tag{1}$$

where $\underline{\zeta}$ is a unit vector along the long molecular axis and δ_{ij} is the unit matrix. Because of the existence of an xz mirror plan in our case, Q_{ij} may be diagonalized by a rotation of angle α around the y axis, In the rotated system $x'yz'$, we can define the two "scalar" order parameters $S = Q_{x'x'}$ and $P = Q_{yy} - Q_{z'z'}$ describing in general the biaxial ordering. In the proximity of the surface, Q_{ij} or equivalently S, P, α are all functions of z. In the bulk limit, $z \to \infty$, Q_{ij} becomes uniaxial, with $P = 0$, and S and α approaching the bulk values S_b and α_b, respectively, where α_b is the pretilt angle. At $z = 0$, Q_{ij} is determined from Eq. (1) if the orientational distribution function $f(\underline{\zeta})$ of the surface LC monolayer is known. We assume that f can be expressed in the form

$$f(\vartheta,\varphi) = Ne^{-\left(\frac{\vartheta-\vartheta_0}{\sigma}\right)^2}(1 + d_1\cos\varphi + d_2\cos 2\varphi + d_3\cos 3\varphi), \tag{2}$$

where ϑ and φ are the polar and azimuthal angles of $\underline{\zeta}$ with respect to the xyz axes. The φ dependence of f is shown schematically in figure 1. By using Eq. (2) to perform the average in Eq. (1), we obtain

$$Q_{ij}(0) = \begin{pmatrix} \gamma - \frac{1}{2} + \frac{\gamma d_2}{2} & 0 & \frac{3}{2}\delta d_1 \\ 0 & \gamma - \frac{1}{2} - \frac{\gamma d_2}{2} & 0 \\ \frac{3}{2}\delta d_1 & 0 & 1 - 2\gamma \end{pmatrix},$$

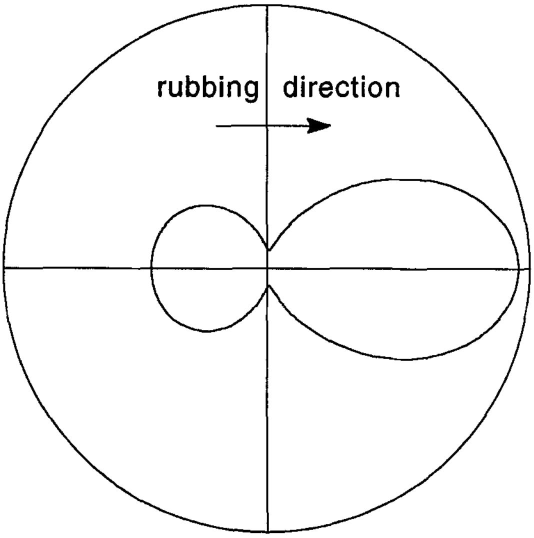

FIGURE 1. Azimuthal component of the orientational distribution f of liquid crystal monolayer on a rubbed polyimide.

with

$$\gamma = \frac{3}{4} < \sin^2\vartheta >_f \quad \text{and} \quad \delta = \frac{1}{2} < \sin\vartheta\cos\vartheta >_f . \tag{3}$$

Diagonalization of $Q_{ij}(0)$ then yields

$$\begin{aligned} S_s &= S(0) = \gamma - \frac{1}{2} + \frac{1}{2}\gamma d_2, \\ P_s &= P(0) = 3\gamma - \frac{3}{2} - \frac{1}{2}\gamma d_2, \\ \alpha_s &= \alpha(0) = \frac{\delta d_1}{S_s + P_s/3}, \end{aligned} \tag{4}$$

where, since we anticipate $\delta d_1 \ll 1$, we have neglected for simplicity terms quadratic or higher in δd_1.

To describe the transition region which connects the first monolayer to the bulk, we use a biaxial Landau-de Gennes theory[7]. The free energy density of a nematic film subject to a variation of Q_{ij} along z can be approximated by

$$F = \frac{1}{2}A_s(S - S_b)^2 + \frac{1}{2}A_p P^2 + \frac{1}{2}L_1 Q'_{ij}Q'_{ij} + \frac{1}{2}L_2 Q'_{iz}Q'_{iz}, \tag{5}$$

where the prime indicates the derivative with respect to z, and A_s, A_p, S_b, L_1, and L_2 are material constants which are functions of temperature. Notice that in Eq. (5) no direct substrate-LC interaction is included. The substrate effect is only in the boundary conditions, given by Eqs. (4). Expressing Q_{ij} in terms of S, P, and α, Eq. (5) can be rewritten as

$$\begin{aligned} F = \ & \frac{1}{2}A_s(S-S_b)^2 + \frac{1}{2}A_pP^2 + \left[\frac{3L_1}{4} + \frac{L_2}{8}(1+3\sin^2\alpha)\right] S'^2 \\ & + \left[\frac{L_1}{4} + \frac{L_2}{8}\cos^2\alpha\right] P'^2 + \frac{L_2}{4}\cos^2\alpha \ \ S'P' \\ & + \left(\frac{L_1}{4} + \frac{L_2}{8}\right)(3S+P)^2\alpha'^2 + \frac{L_2}{8}(3S+P)\sin^2 2\alpha(S'-P')\alpha'. \end{aligned}$$

The Euler-Lagrange equations for minimization of the total free energy are

$$\frac{d}{dz}\frac{\partial F}{\partial S'} - \frac{\partial F}{\partial S} = 0, \quad \frac{d}{dz}\frac{\partial F}{\partial P'} - \frac{\partial F}{\partial P} = 0, \tag{6}$$

and

$$\frac{d}{dz}\frac{\partial F}{\partial \alpha'} - \frac{\partial F}{\partial \alpha} = 0. \tag{7}$$

This results in a set of coupled nonlinear equations for $S(z), P(z)$, and $\alpha(z)$, to be solved with the boundary conditions given by Eqs. (4) and $S'(\infty) = P'(\infty) = \alpha'(\infty) = 0$. Since α is usually small, we can limit ourselves to a linearized theory in α. Eq. (7) is then reduced to

$$\alpha'' + a(z)\alpha' + b(z)\alpha = 0, \tag{8}$$

where

$$a(z) = \frac{6S_0'(z) + 2P_0'(z)}{3S_0(z) + P_0(z)} \text{ and}$$

$$b(z) = \frac{L_2\left[S_0''(z) - P_0''(z)\right]}{(2L_1 + L_2)\left[3S_0(z) + P_0(z)\right]}.$$

$S_0(z)$ and $P_0(z)$ are the solution to the equations

$$(6L_1 + L_2)S_0'' + L_2P_0'' = 4A_s(S_0 - S_b),$$

$$(2L_1 + L_2)P_0'' + L_2S_0'' = 4A_pP_0, \tag{9}$$

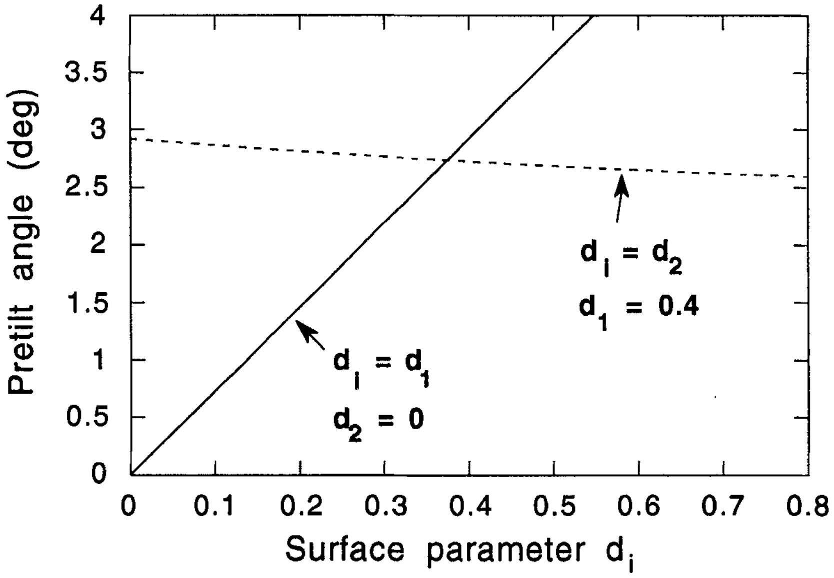

FIGURE 2. Correlation between bulk pretilt angle and surface parameters d_1 (for $d_2 = 0$) and d_2 (for $d_1 = 0.4$), setting all the other parameters to typical values.

obtained by setting $\alpha = 0$ in Eqs. (6). Equation (8) can be solved analytically with an iterative procedure, if $S(z) - S_b$ and $P(z)$ are small. To first order, we find

$$\alpha(z) = \alpha_s \left\{ 1 - \frac{L_2[S(z) - S_s - P(z) + P_s]}{3(2L_1 + L_2)S_b} \right\}.$$

With $S(\infty) = S_b, P(\infty) = 0$, and the expression of S_s and P_s in Eqs. (4), we obtain the bulk pretilt angle $\alpha_b = \alpha(\infty)$ as

$$\alpha_b = \frac{\delta d_1}{2\gamma - 1 + \gamma d_2/3} \left[1 - \frac{L_2(S_b + 2\gamma - 1 - \gamma d_2)}{3(2L_1 + L_2)S_b} \right]. \tag{10}$$

Equation (10) describes the correlation of α_b with the four surface parameters d_1, d_2, ϑ_0, and σ that characterize the orientational distribution of the surface monolayer. Notice that within our approximation α_b does not depend on the intermediate values of $S_0(z)$ and $P_0(z)$, but only on their boundary values.

Equation (10) describes the role of the surface parameters in determining the pretilt angle. The average polar angle ϑ_0 is related to δ and γ by Eqs. (3). With ϑ_0 close to 90°, we have $\delta \approx (90° - \vartheta_0)/2$ and $\gamma \approx 3/4$. In this limit, α_b is simply proportional to $90° - \vartheta_0$, which is the average angle of inclination the adsorbed LC molecules make with the surface (notice that, in our conventions, α_b is measured from the surface while θ_0 is measured from the surface normal). The pretilt angle is also linearly proportional to the parameter d_1, describing the surface forward-backward azimuthal asymmetry along the rubbing direction. The dependence on the xy-anisotropy d_2 is more complex, but is rather weak, as shown in figure 2.

DISCUSSION

The theory leading to Eq. (10) is a simple application of biaxial Landau-de Gennes formalism, but its validity relies on several important assumptions. The first and perhaps most important one is the use of the Landau-De Gennes theory itself to describe the interface. This assumption implies two essential points: first, the surface monolayer orientational distribution is continously connected to the bulk orientational distribution, as described by the tensor order parameter; second, the transition region is smooth enough on the molecular scale to allow the use of a linearized free energy density, such as that given by Eq. (5). Another assumption of our model is that liquid crystal properties other than the tensor order parameter can be ignored. Specifically, the other variables which could eventually play a role are the mass density and the molecule polarization, i.e., the first moment of the orientational distribution, which is known to vanish in the bulk but not necessarily at the surface monolayer. A third important assumption implicit in the theory is that long-range interactions between LC molecules and the substrate can be neglected. It is a consequence of the last two assumptions that the free-energy density F depends on z only through the order parameter $\overleftrightarrow{Q}$, and that its functional dependence on $\overleftrightarrow{Q}$ is spherically symmetric. Finally, in using expression (2) for the monolayer distribution f, we made the assumption that the polar and azimuthal distributions are not correlated.

It is very difficult to justify these assumptions theoretically by means of a mechanical-statistical theory of the interface. We therefore rely on the comparison with experiment to test the validity of Eq. (10), in the specific case of rubbed-polyimide surfaces. It is also important to recall the existence of these assumptions when trying to extend this approach to a more generale case.

EXPERIMENTAL VERIFICATION

We briefly outline the results of our recent experimental studies aimed at testing the theory described above.[6,8] The parameters ϑ_0, σ, d_1, and d_2 for the surface monolayer orientational distribution on rubbed polyimide were obtained by measuring optical second harmonic generation (SHG) from the surface monolayer, in reflection geometry.[5] The LC bulk tilt angles were measured using the crystal rotation method.[9] The LC used was the 4'-n-octyl-4-cyanobiphenyl (8CB). The polyimides were poly-n-alkyl-pyromellitic imides $-(N-(CO)_2-C_6H_2-(CO)_2-N-(CH_2)_n-)$, with n=3,4,5,6 (P3,P4,P5,P6). In order to change systematically the surface properties, the rubbing strength and the homologous series of polyimide were varied. The theoretical and experimental comparison of the bulk pretilts at various rubbing strengths is shown in figure 3.[8] In this figure, for the sake of clarity, the full surface-parameter space is projected onto the axis of d_1, which is the dominant parameter affected by rubbing. In the calculations, the bulk constants S_b, L_1, and L_2 were taken from Ref. 10, and no adjustable parameter was used. The agreement is also observed with different polyimides but the same rubbing strength.[6] In the polyimide series P3-P6, the varying length of the flexible $(CH_2)_n$ spacer between the aromatic cores affects the rigidity and the microscopic texture of the polyimide. A longer spacer makes the polyimide more flexible and easier to be aligned by the rubbing process. Moreover, an even number of spacer units favors parallel orientation of neighboring aromatic cores, yielding smoother surfaces and better crystallization than for an odd number of units.[11] Odd-even behavior is observed in the surface monolayer parameters, and is reflected in the bulk tilt angles predicted using Eq. (10), $\alpha_b = 1.9°, 2.2°, 1.6°$, and 2.7°. These values compare well with the measured

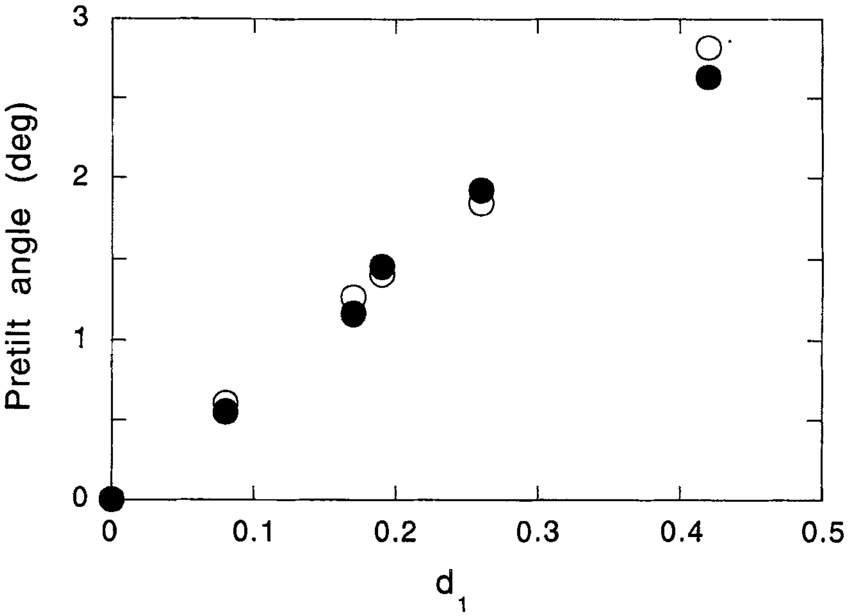

FIGURE 3. Correlation between orientational distribution of surface 8CB monolayers and bulk pretilt angles at different rubbing strengths on the polyimide P6. Solid circles are bulk pretilt angles measured by crystal rotation method and open circles are predictions from Eq. (10) using the measured monolayer distribution parameters. Data points from left to right correspond to increasing rubbing strength.

ones, $\alpha_b = 1.5°, 3.5°, 1.9°$, and $2.6°$.

CONCLUSION

We show that in the case of rubbed polyimides the nematic LC bulk homogeneous alignment including the bulk pretilt angle is correlated to the orientational distribution of the surface LC monolayers. The correlation can be described by means of a biaxial Landau-de Gennes model, and is well confirmed by the experiment.

Acknowledgments

D.J. gratefully acknowledges financial support from Alexander-von-Humboldt Foundation. L.M. is grateful to Stiftelsen Blanceflor Boncompagni-Ludovisi, Född Bildt, and Fondazione Angelo della Riccia for fellowship support. This work was supported by NSF Grant No. DMR-9025106.

REFERENCES

*. Permanent address: Max-Planck-Institut fuer Polymer-forschung, Ackermannweg 10, D-55021 Mainz, Germany.

1. For a recent review see, for example, B. Jérôme, Rep. Prog. Phys., 54, 391 (1991).
2. V. G. Chigrinov, V. V. Belyaev, S. V. Belyaev, and M. F. Grebenkin, Sov. Phys. JEPT, 50, 994 (1979).
3. D. W. Berreman, Phys. Rev. Lett., 28, 1983 (1972); S. Faetti, Phys. Rev. A, 36, 408 (1987).
4. W. Chen, M. B. Feller, and Y. R. Shen, Phys. Rev. Lett., 63, 2665 (1989).
5. M. B. Feller, W. Chen, and Y. R. Shen, Phys. Rev. A, 43, 6778 (1991).
6. D. Johannsmann, H. Zhou, P. Sonderkaer, H. Wierenga, B. O. Myrvold, and Y. R. Shen, Phys. Rev. E, 48, 1889 (1993).
7. P. Sheng and E. B. Priestley in Introduction to liquid crystals, edited by E. B. Priestley, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1974), Chap. 10.
8. X. Zhuang, L. Marrucci, and Y. R. Shen, to be published.
9. G. Baur, V. Wittwer, and D. W. Berreman, Phys. Lett., 56A, 142 (1976).
10. N. V. Madhusudana and R. Pratibha, Mol. Cryst. Liq. Cryst., 89, 249 (1982).
11. B. O. Myrvold, Liq. Cryst., 10, 771 (1991); H. Yokokura, M. Oh-E, K. Kondo, and S. Oh-Hara, Mol. Cryst. Liq. Cryst., 225, 253 (1993).