RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 46, NUMBER 8 15 OCTOBER 1992

Correlations between surface and bulk liquid-crystal alignment observed with optical second-harmonic generation

M. Barmentlo, R. W. J. Hollering, and N. A. J. M. van Aerle
Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands

(Received 6 August 1992)

With the use of optical second-harmonic generation from liquid-crystal (LC) monolayers adsorbed on rubbed polymer surfaces, a close correlation between the rubbing-induced azimuthal orientational distribution of the LC monolayers and the resulting LC bulk pretilt angle has been observed. A simple model based on epitaxial growth of the bulk LC on top of the first LC monolayer is proposed to explain this correlation.

PACS number(s): 61.30.−v, 42.65.Ky, 68.35.Bs

Understanding the physical mechanisms involved in both *surface* and *bulk* liquid-crystal (LC) alignment is not only of fundamental interest but also finds its application in numerous electro-optic LC devices. Realization of a large-area monodomain LC layer sandwiched between two glass plates is a prerequisite for optimal performance of these devices. Homogeneous planar alignment (i.e., parallel to the surface along some easy axis) of a LC layer can be achieved in several ways [1]. The most widely used technique is the rubbing of polymer-coated glass substrates. In order to optimize the performance of the LC device, this planar alignment should be accompanied by a nonzero so-called pretilt (θ_p), defined as the angle between the average molecular orientation in the bulk (the director) and the surface.

Experimental realization and theoretical modeling of (high) pretilt angles with the use of rubbed polymer films has been reported frequently [2-5]. However, the generation of the pretilt on various substrates is not yet understood. Based on a theoretical model developed by Okano [6], Sugiyama *et al.* recently proposed a model for pretilted nematic LC layers on rubbed polyimide (PI) layers containing alkyl branches [5]. They correlated the polar θ_p to the azimuthal torsional surface coupling strength induced by the interaction of the bulk LC with the aligned alkyl branches at the surface.

As a result of the pioneering work of Shen and coworkers on the use of optical second-harmonic generation (SHG) for the study of molecular orientations, the technique recently has been exploited as a surface analytical tool to investigate the LC-interface alignment [7-14]. No direct correlation has been observed between the polar angle of the first LC monolayer adsorbed on surfactant-coated glass substrates and the bulk pretilt [8,9]. Additionally it was shown that at the LC-PI interface a polar ordered LC monolayer exists, with an anisotropic azimuthal distribution, preferentially along the rubbing direction, even at temperatures well above the bulk nematic-isotropic transition temperature [10,11]. It was also shown that both the LC monolayer and the LC director in the bulk are then aligned via short-range intermolecular interactions as opposed to long-range elastic interactions [10-12]. Combining these experimental results one concludes that the picture of a bulk LC, directly interacting with a flat polymer surface, with some distribution of aligned alkyl branches on top of it, seems no longer justified [5]. Instead, we have to consider the interaction of bulk LC with the first LC monolayer, which is oriented by the polymer surface.

In this Rapid Communication we report results from SHG experiments which provide insight into the LC bulk pretilt formation on rubbed polymer-coated glass substrates. We correlated the azimuthal orientational distribution of the LC monolayer, which can be determined with SHG, with the θ_p value of the LC layer in test cells made with these substrates. The results can be explained by considering the interaction of the LC bulk with the anisotropically aligned LC monolayer.

The theory of SHG, as a surface analytical tool, developed by Shen and co-workers, has been described elsewhere [15]. For LC molecules, where the molecular hyperpolarizability tensor ($\alpha^{(2)}$) is dominated by one single component ($\alpha^{(2)}_{\xi\xi\xi}$) along the molecular long axis (ξ), the measured nonlinear susceptibility ($\chi^{(2)}$) takes the form:

$$\chi^{(2)}_{ijk} = N_s \langle (\mathbf{i}\cdot\xi)(\mathbf{j}\cdot\xi)(\mathbf{k}\cdot\xi) \rangle \alpha^{(2)}_{\xi\xi\xi} .$$

Here, N_s is the surface density of LC molecules, **i**,**j**,**k** refer to the sample coordinates, and the brackets denote an appropriate average over all molecular orientations. For LC molecules with a C_{1v}-symmetric arrangement along **x** with **z** as the surface normal, we find the following nonvanishing elements of $\chi^{(2)}$:

$$\begin{aligned}
&\chi^{(2)}_{xxx} = -N_s \langle \sin^3\theta \rangle \langle \cos^3\phi \rangle \alpha^{(2)}_{\xi\xi\xi} ,\\
&\chi^{(2)}_{xyy} = \chi^{(2)}_{yxy} = \chi^{(2)}_{yyx} = -N_s \langle \sin^3\theta \rangle \langle \cos\phi \sin^2\phi \rangle \alpha^{(2)}_{\xi\xi\xi} ,\\
&\chi^{(2)}_{xzz} = \chi^{(2)}_{zxz} = \chi^{(2)}_{zzx} = -N_s \langle \sin\theta \cos^2\theta \rangle \langle \cos\phi \rangle \alpha^{(2)}_{\xi\xi\xi} ,\\
&\chi^{(2)}_{zxx} = \chi^{(2)}_{xzx} = \chi^{(2)}_{xxz} = N_s \langle \cos\theta \sin^2\theta \rangle \langle \cos^2\phi \rangle \alpha^{(2)}_{\xi\xi\xi} ,\\
&\chi^{(2)}_{zyy} = \chi^{(2)}_{yzy} = \chi^{(2)}_{yyz} = N_s \langle \cos\theta \sin^2\theta \rangle \langle \sin^2\phi \rangle \alpha^{(2)}_{\xi\xi\xi} ,\\
&\chi^{(2)}_{zzz} = N_s \langle \cos^3\theta \rangle \alpha^{(2)}_{\xi\xi\xi} .
\end{aligned} \tag{1}$$

Here, θ denotes the polar angle between $\hat{\mathbf{z}}$ and $\hat{\xi}$ and ϕ is the azimuthal angle of the LC molecular orientation with respect to $\hat{\mathbf{x}}$ [10–12]. It has been shown that by measuring the SH response for four different input-output polarization combinations as a function of the sample rotation ψ about its surface normal, all six independent elements of $\chi^{(2)}$ can be determined [10–12]. From the resulting values of $\chi^{(2)}$ we determine both the polar (θ) and azimuthal (ϕ) orientational distribution of the LC molecules [10–12]. For the rubbed surfaces the ϕ distribution can be determined up to third order as

$$f(\phi)=\frac{1}{2\pi}(1+a_1\cos\phi+a_2\cos2\phi+a_3\cos3\phi)\,. \qquad (2)$$

The SHG experiments were carried out with use of the 532-nm output of a frequency-doubled Q-switched neodymium-doped yttrium aluminum garnet laser with a pulse duration of 15 ns and a pulse energy of 25 mJ. The unfocused beam was directed onto a rotation stage, on which the samples were mounted, at an angle of incidence of 45°. After blocking the excitation beam, the reflected SH output was detected with a photomultiplier and gated electronics. The polymer films were made by spincoating polymer solutions onto quartz substrates and subsequent curing. The preferential orientation of the polymer surfaces was effectuated by rubbing the surfaces on a home-built rubbing machine, enabling a high reproducibility of the rubbing conditions [12]. LC monolayers were deposited onto the samples with an evaporation technique, using SHG as a monitor [9]. The liquid crystals which we used are 4-n-octyl-4′-cyanobiphenyl (8CB), and 4-n-pentyl-4′-cyanobiphenyl (5CB). Cells were made by sandwiching the LC between two antiparallel rubbed polymer-coated substrates with 4-μm spacers. The effective θ_p of the nematic LC was measured using a phase-rotation method [16].

Figure 1 shows the measured SH response of an adsorbed 8CB monolayer on one of the rubbed polyimides, for different input and output polarizations as a function of the angle ψ between the rubbing direction and the plane of incidence. In agreement with expectations the data clearly show a mirror symmetry about the rubbing direction (C_{1v} symmetry). But more important here, we observe the absence of mirror symmetry in the plane perpendicular to the rubbing direction ($\hat{\mathbf{x}}$). From the fit to the data, represented by the solid lines, we derived the $\chi^{(2)}$ values, which subsequently give the Fourier coefficients a_1, a_2, and a_3 of the in-plane orientational distribution [Eq. (2)]. The magnitude of the coefficient a_1 directly reflects the parallel-antiparallel asymmetry. Interpretation of the data allows us to conclude that rubbing clearly forces more molecules to lie parallel than antiparallel to the rubbing direction. In this paper we refer to this parallel-antiparallel asymmetry (a_1) as the *orientation* along the rubbing direction of the azimuthal distribution; such a distribution is referred to as *oriented.* Recall that similar symmetry conditions are present in a LC cell. In the nematic bulk of a LC cell, the molecules are symmetrically aligned along the rubbing direction; however, in this case the presence of a nonzero θ_p, removes the mirror symmetry in the plane perpendicular to the rubbing direction.

In order to investigate a possible correlation between a_1, determined for a LC monolayer, and θ_p measured in a LC cell, a series of polymer orienting layers, which were known to yield different θ_p values when identical rubbing conditions were applied, was prepared and studied. The azimuthal distribution functions $f(\phi)$ of 8CB monolayers adsorbed on three different polymers, as determined from the SHG data, are plotted in Fig. 2. It can clearly be seen that the anisotropy in $f(\phi)$ of these 8CB monolayers greatly differ. We observe a positive correlation between a_1 and θ_p. In Fig. 3 this correlation is plotted for the complete series of investigated samples. For this series the polar distribution of the 8CB molecules was nearly identical;

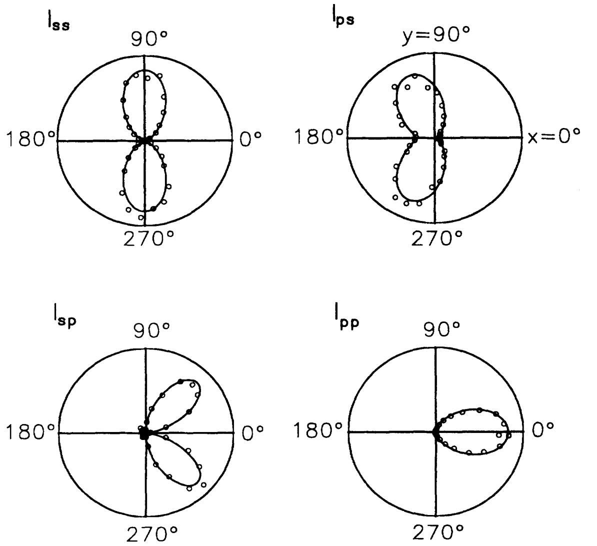

FIG. 1. Polar plots of the SH signal as a function of the rotation about the surface normal of an adsorbed 8CB monolayer on rubbed polyimide, which yield a high bulk pretilt angle. I_{ps} denotes the p-polarized SH intensity under s-polarized excitation. $\Psi=0°$ corresponds to the rubbing direction.

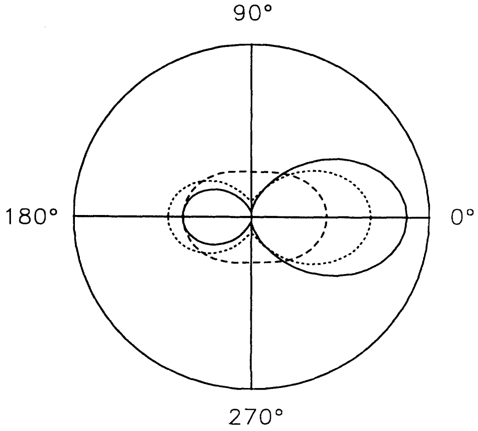

FIG. 2. Polar plots of the azimuthal distribution functions $f(\phi)$ of 8CB monolayers adsorbed on rubbed polymer surfaces which yield bulk pretilt angles of 0.2° (dashed line), 1.5° (dotted line), and 6.5° (solid line). $\phi=0°$ corresponds to alignment parallel to the rubbing direction $\hat{\mathbf{x}}$.

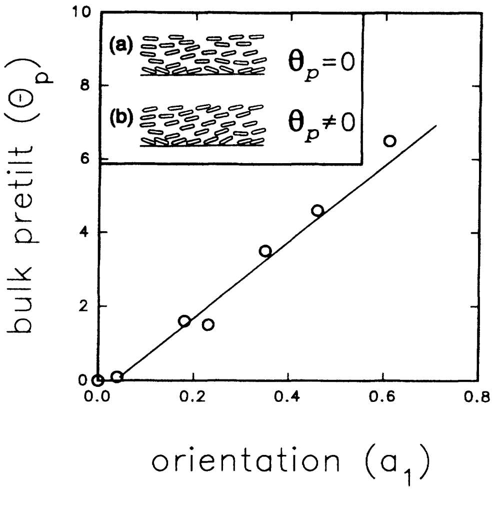

FIG. 3. Bulk pretilt angle (θ_p) of LC cells filled with 5CB as a function of the *orientation* of the azimuthal distribution (a_1) of 8CB molecules adsorbed on the rubbed surfaces. The solid line is merely a guide to the eye. Inset: An illustrative drawing of the bulk pretilt θ_p formation in the case of zero *orientation* ($a_1=0$), which yields $\theta_p=0$ (a) and nonzero *orientation*, of the azimuthal distribution function of the LC monolayer, resulting in a finite θ_p (b).

the assumed Gaussian distribution is centered around $\theta=77°$ with a standard deviation $\sigma=4°$. This observation is in agreement with the results published by Feller, Chen, and Shen [11]. On several isotropic surfaces this polar angle θ is approximately the same and not directly correlated with θ_p [8,9]. Note that the polar angle of 8CB molecules is defined as the angle between the surface normal $\hat{z}$ and the long molecular axis $\hat{\xi}$, whereas θ_p is defined as the complementary angle. The point at the origin, where both θ_p and a_1 equal zero is obtained for 8CB on rubbed bare glass substrates. In this case all Fourier components in $f(\phi)$ were found to be zero.

In order to understand the relation between the interfacial ordering and the resulting bulk LC orientation we next discuss the orientational mechanism. As already reported by Shen and co-workers the orientational distribution of the interfacial monolayer is practically not affected by the presence of a LC bulk, up to temperatures of 20 K above the nematic-isotropic transition temperature [10, 11]. Or, in other words, the interaction energy of the LC molecules with the rubbed polymer substrate is significantly larger than the interactions between LC molecules. Thus for an understanding of the magnitude of θ_p it suffices to consider the interaction of the bulk LC with the well-characterized LC monolayer. Since *all* LC cells constructed from our polymer covered substrates showed perfect, homogeneous bulk alignment, we conclude that even a small alignment along the rubbing direction of the LC monolayer (a_2), as can be seen in Fig. 2, already leads to a macroscopic bulk alignment. On the basis of this observation and the correlation observed in Fig. 3, it is realistic to expect that a_1, although small, determines the macroscopic θ_p. The occurrence of a nonzero θ_p is then assumed to stem from the steric interactions of the rodlike LC molecules in the bulk with those at the interface, firmly attached to the orienting polymer surface. In the case all LC molecules in the first monolayer would be aligned parallel to the rubbing direction $\hat{x}$, the bulk pretilt would correspond to the average tilt angle of the first monolayer. The given interfacial in-plane orientational spread of LC molecules, however, will give rise to a competition between the orienting forces of neighboring LC molecules aligned parallel or antiparallel to $\hat{x}$. As pointed out by Ong, Hurd, and Meyer [17] this spatial variation fades away in the interior of the sample with a characteristic length equal to that of the spatial variation at the surface, and finally leads to a macroscopic mean orientation of the bulk LC. Both the monodomain homogeneous alignment and pretilt angle of the LC bulk can be explained in this way. Different pretilt angles are now thought to be tuned by changing the *orientation* of the azimuthal distribution of the LC monolayer a_1. In the inset of Fig. 3 the pretilt formation is shown for the case of zero *orientation*, yielding $\theta_p=0°$ and for an *oriented* distribution yielding $\theta_p\neq0°$. The average polar angle of the interfacial molecules is not tuned, as we determined with SHG.

An alternative microscopic picture of the formation of pretilted nematic LC was proposed by Okano [6] and further developed by Sugiyama *et al.* [5]. They attribute θ_p to the interaction of the LC bulk, as rodlike molecules, with alkyl branches, present at the surface. This low-density, fully *oriented*, distribution of alkyl tails at the polymer surface is tilted from the surface with an angle corresponding to θ_p. In our model, however, we consider a less *oriented*, high density distribution of polar ordered LC molecules, which are tilted from the surface at an angle bigger than θ_p.

The natural question that arises is: What determines the in-plane distribution of the first LC monolayer? Alkyl branches, if present at the surface, can still be important in aligning the interfacial monolayer. After rubbing, both the polymer and the alkyl tails, present at the surface, will be aligned to a great extent. The molecular orientation of the rubbed polyimides has been verified with the use of birefringence measurements [12]. The polar ordered LC monolayer at the surface is then aligned via short-range intermolecular interactions [10–12]. Chain-chain interactions between a highly *oriented* distribution of the alkyl tails at the polymer surface and the adsorbed LC molecules may be responsible for the *orientation* of the azimuthal LC monolayer alignment. To investigate this effect we studied 5CB monolayers on the same series of polymer surfaces. The alkyl tail of a 5CB molecule is shorter than that of an 8CB molecule. Thus, the chain-chain interaction would differ. In our case this should result in a less *oriented* distribution of the 5CB molecules at the surface under identical rubbing conditions. We found that for all polyimide surfaces the 5CB monolayers are less oriented than 8CB monolayers adsorbed on identically rubbed substrates ($\approx 20\%$ less). The polar distribution is approximately the same for all LC monolayers. This is in line with the model of chain-chain interaction. As has been shown by Shen and co-workers it is possible to detect interaction effects between alkyl chains directly with the use of infrared-visible sum-frequency spectroscopy (SFG) [18]. An SFG study on these rubbed polymer surfaces might elucidate the role of the alkyl tails at the surface.

In conclusion, we have observed a correlation between the rubbing-induced azimuthal *orientation* of LC monolayers and the bulk pretilt angle. This correlation can be understood by epitaxial growth of the bulk LC layer onto an anisotropically distributed LC monolayer.

The authors gratefully acknowledge Dr. M. P. C. M. Krijn, Dr. C. J. Gerritsma, and Professor Dr. Q. H. F. Vrehen for their contributions to this work.

---

[1] See, for example, J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon and Breach, London, 1982).

[2] S. Kuniyasu, H. Fukuro, S. Maeda, K. Nakaya, M. Nitta, N. Ozaki, and S. Kobayashi, Jpn. J. Appl. Phys. **27**, 827 (1988).

[3] H. Fukuro, and S. Kobayashi, Mol. Cryst. Liq. Cryst. **163**, 157 (1988).

[4] K. Yoshida, H. Kukuro, and S. Kobayashi, Proc. SID **28**, 755 (1988).

[5] T. Sugiyama, S. Kuniyasu, D. Seo, H. Fukuro, and S. Kobayashi, Jpn. J. Appl. Phys. **29**, 2045 (1990).

[6] K. Okano, N. Matsuura, and S. Kobayashi, Jpn. J. Appl. Phys. **21**, L109 (1982); K. Okano, *ibid.* **22**, L343 (1983).

[7] P. Guyot-Sionnest, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. **57**, 2963 (1986).

[8] C. S. Mullin, P. Guyot-Sionnest, and Y. R. Shen, Phys. Rev. A **39**, 3745 (1989).

[9] M. Barmentlo, F. R. Hoekstra, N. P. Willard, and R. W. J. Hollering, Phys. Rev. A **43**, 5740 (1991).

[10] W. Chen, M. B. Feller, and Y. R. Shen, Phys. Rev. Lett. **63**, 2665 (1989).

[11] M. B. Feller, W. Chen, and Y. R. Shen, Phys. Rev. A **43**, 6778 (1991).

[12] M. Barmentlo, N. A. J. M. van Aerle, R. W. J. Hollering, and J. P. M. Damen, J. Appl. Phys. **71**, 4799 (1992).

[13] W. Chen, Y. Ouchi, T. Moses, Y. R. Shen, and K. H. Yang, Phys. Rev. Lett. **68**, 1547 (1992). Y. Ouchi, M. B. Feller, T. Moses, and Y. R. Shen, Phys. Rev. Lett. **68**, 3040 (1992).

[15] See, for example, Y. R. Shen, Annu. Rev. Phys. Chem. **40**, 327 (1989).

[16] H. A. van Sprang, Mol. Cryst. Liq. Cryst. **199**, 19 (1991).

[17] H. L. Ong, A. J. Hurd, and R. B. Meyer, J. Appl. Phys. **57**, 186 (1985).

[18] J. Y. Huang, R. Superfine, and Y. R. Shen, Phys. Rev. A **42**, 3660 (1990).