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

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We report a direct experimental observation of surface-induced liquid crystal (LC) monolayer orientation and its relation to the LC bulk alignment. Using optical second-harmonic generation from these LC monolayers, adsorbed on rubbed polymer surfaces, we determined both the polar and azimuthal orientation of the LC molecules. 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.

1. Introduction

Exploring 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. A prerequisite for an optimal performance of these devices is the realization of large area monodomain LC layers sandwiched between two glass plates. Homogeneous bulk alignment (*i.e.* parallel to the surface along some easy axis) of the LC layer can be achieved in several ways [1]. The most widely used technique for the production of today's LC devices, is the rubbing of polymer-coated glass substrates. In order to optimize the performance of the LC device the easy axis should be tilted away from the surface by a small angle, the so-called pretilt (Θ_p).

Although studies on the realization of (high) pretilt angles of LC layers by using rubbed polymer films have been reported frequently [2-5], a consistent model for the generation of the pretilt on various substrates is not yet available. Based on a theoretical model developed by Okano [6], Sugiyama *et al.* recently proposed a model for pretilted nematic LC layers on rubbed polyimide layers containing alkyl branches [5]. They correlated the measured polar Θ_p to the measured azimuthal torsional surface coupling strength induced by the interaction of the bulk LC with the aligned alkyl branches at the surface for a series of polyimide surfaces.

The use of optical second-harmonic generation (SHG) for the study of molecular orientations is well established [14]. Recently, the technique has been exploited as a surface analytical tool to investigate the LC interface alignment [7-12]. In the first experiments on LC monolayers adsorbed on various isotropic substrates, no direct correlation has been observed between the polar angle of the first LC monolayer adsorbed on surfactant-coated glass substrates and bulk alignment. Additionally, it was shown that the LC-polyimide interface consisted of a polar ordered LC monolayer. This monolayer exhibited 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

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intermolecular interactions as opposed to long range elastic interactions [10–12]. Combining these experimental results one can conclude that the model 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 paper the results from SHG experiments which provide insight into the LC bulk pretilt formation on rubbed polymer-coated glass substrates are presented. We measured the SH response of cyano-biphenyl monolayers adsorbed on various rubbed polymers, which can be determined from the SHG data, with the Θ_p -value of the LC layer in test cells made with these substrates. The results can be understood by considering the interaction of LC bulk with the anisotropically aligned LC monolayer, which is aligned by the rubbed polymer surface.

2. Theory

For surface SHG, the signal at the second-harmonic frequency 2ω is generated by the induced surface nonlinear polarization

$$\mathbf{P}^{(2)}(2\omega) = \chi^{(2)}(-2\omega; \omega, \omega) : \mathbf{E}(\omega) \mathbf{E}(\omega).$$

Here, $\mathbf{E}(\omega)$ denotes the excitation field at the fundamental frequency ω and $\chi^{(2)}$ is the surface nonlinear susceptibility tensor. Starting from this expression, it can be derived that the SH intensity $I(2\omega)$ reflected from a surface is given by [14]

$$I(2\omega) \propto \sec^2 \Omega | \mathbf{e}_{2\omega} \cdot \chi^{(2)} : \mathbf{e}_\omega \mathbf{e}_\omega |^2 I^2(\omega). \quad (1)$$

Here, Ω is the angle of reflectance, which equals the angle of incidence and $\mathbf{e}_{2\omega}$, \mathbf{e}_ω denote the output- and input-polarization vectors at frequency 2ω and ω respectively, which contain products of linear Fresnel factors [14], and $I(\omega)$ symbolizes the laser intensity at frequency ω . In this paper, the polarization directions are denoted by \hat{p} and \hat{s} , which are in the plane of incidence and normal to it, respectively.

For LC molecules adsorbed on clean centrosymmetric substrates often the nonlinear susceptibility is dominated by the polar ordered molecules. Assuming the interaction between molecules to be negligible, the $\chi^{(2)}$ tensor can be related to the hyperpolarizability tensor of the adsorbed molecules $\alpha^{(2)}$, which is dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along the long molecular axis ξ , by:

$$\chi_{ijk}^{(2)} = N_s \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\xi})(\hat{k} \cdot \hat{\xi}) \rangle \alpha_{\xi\xi\xi}^{(2)}. \quad (2)$$

Here N_s is the surface density of polar-ordered molecules, $(\hat{i}, \hat{j}, \hat{k})$ refer to the unit vectors $(\hat{x}, \hat{y}, \hat{z})$, which are in the plane of the sample (\hat{x}, \hat{y}) and normal to it (\hat{z}) , respectively. For surfaces exhibiting C_{1v} -symmetry along \hat{x} , with independent polar Θ and azimuthal ϕ distributions of ξ , we find the following non-vanishing elements of $\chi^{(2)}$

$$\left. \begin{aligned} \chi_{xxx}^{(2)} &= -N_s \langle \sin^3 \Theta \rangle \langle \cos^3 \phi \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{xyy}^{(2)} &= \chi_{yxy}^{(2)} = \chi_{yyx}^{(2)} = -N_s \langle \sin^3 \Theta \rangle \langle \cos \phi \sin^2 \phi \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{xzz}^{(2)} &= \chi_{zxx}^{(2)} = \chi_{zzx}^{(2)} = -N_s \langle \sin \Theta \cos^2 \Theta \rangle \langle \cos \phi \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{zxx}^{(2)} &= \chi_{zxx}^{(2)} = \chi_{xzz}^{(2)} = N_s \langle \cos \Theta \sin^2 \Theta \rangle \langle \cos^2 \phi \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{zyy}^{(2)} &= \chi_{yyz}^{(2)} = \chi_{yzy}^{(2)} = N_s \langle \cos \Theta \sin^2 \Theta \rangle \langle \sin^2 \phi \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{zzz}^{(2)} &= N_s \langle \cos^3 \Theta \rangle \alpha_{\xi\xi\xi}^{(2)}. \end{aligned} \right\} \quad (3)$$

The angular brackets denote an average over all molecular orientations within the (macroscopic) probed area. The six independent elements of $\chi^{(2)}$ are determined by measuring the SH response in reflection from the LC monolayer as a function of sample rotation about its surface normal (\hat{z}) for four different polarization combinations I_{ss} , I_{sp} , I_{ps} , I_{pp} . Here, I_{sp} denotes the \hat{s} -polarized SH signal under \hat{p} -polarized excitation. According to equation (3) the elements of $\chi^{(2)}$ contain information on both the polar and azimuthal distribution functions of the adsorbed LC molecules.

If we assume the polar molecular orientation function to be represented by a Gaussian distribution centred at Θ with standard deviation σ , these two values can be deduced from the following linear combinations of $\chi^{(2)}$ -elements:

$$\left. \begin{aligned} \frac{\chi_{xxx}^{(2)} + \chi_{xyy}^{(2)}}{\chi_{xxx}^{(2)} + \chi_{xyy}^{(2)} + \chi_{xzz}^{(2)}} &= \frac{\langle \sin^3 \Theta \rangle}{\langle \sin \Theta \rangle}, \\ \frac{\chi_{zxx}^{(2)} + \chi_{zyy}^{(2)} + \chi_{zzz}^{(2)}}{\chi_{zzz}^{(2)}} &= \frac{\langle \cos \Theta \rangle}{\langle \cos^3 \Theta \rangle}. \end{aligned} \right\} \quad (4)$$

The azimuthal ϕ -distribution function $f(\phi)$ can be built up from a Fourier series $f(\phi) = \sum_n a_n \cos n\phi$. From the remaining independent combinations of the elements of $\chi^{(2)}$ the Fourier coefficients a_n can be determined up to the third order.

3. Experimental

The experiments were performed using the frequency-doubled output at a wavelength of 532 nm of a Q-switched Nd:YAG laser producing pulses of 12 ns duration at a repetition rate of 10 Hz with a pulse energy of 25 mJ. The unfocused beam with a diameter of approximately 8 mm was directed on to the sample at an angle of incidence of 45°. After blocking the reflected 532 nm beam, the SH output was selected with the use of a home-built prism monochromator with a high transmission for UV light. The SH output was detected for both \hat{p} and \hat{s} polarization using an analyser, a solar-blind photomultiplier and gated electronics.

The polymer films were made by spincoating polymer solutions on to quartz substrates and subsequent curing. The preferential orientation of the polymer surfaces was effectuated by rubbing the surface on a home-built rubbing machine, enabling a high reproducibility of the rubbing conditions [12]. LC monolayers were deposited on to the samples with the use of an evaporation technique, using SHG as a monitor [9]. Cells were made by sandwiching the LC between two antiparallel rubbed polymer coated substrates with 4 μm spacers. The effective Θ_p was measured using a phase-rotation method [15].

The SH wavelength (266 nm) is close to resonance for the 8CB molecules and therefore in all cases the SH background of the glass-polyimide substrates is negligible.

4. Results

The anisotropic SH response under rotation of the sample over an angle ψ about its surface normal directly reflects the symmetry properties of the LC monolayers under investigation [10, 12]. Figure 1 shows for different polarization combinations the normalized SH response obtained from 5CB monolayers evaporated on a rubbed polyimide substrate 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

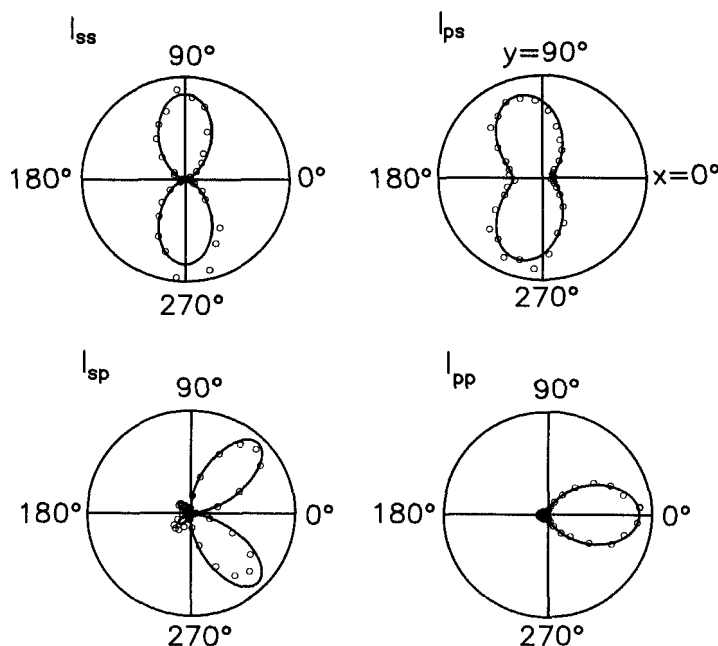


Figure 1. Polar plots of the second-harmonic intensity as a function of the rotation about the surface normal for a 5CB monolayer adsorbed on a rubbed polyimide substrate. $\Psi = 0^\circ$ corresponds to the rubbing direction.

mirror symmetry in the plane perpendicular to the rubbing direction (\hat{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. 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. We refer to such a distribution as oriented. Recall that similar symmetry conditions are present in a LC cell. In the nematic bulk of an LC cell, the molecules are symmetrically aligned along the rubbing direction, however, in this case the presence of a non-zero Θ_p , removes the mirror symmetry in the plane perpendicular to the rubbing direction.

In order to investigate a possible correlation between the orientation of the LC monolayer azimuthal distribution (a_1), and the Θ_p in a cell, we prepared a series of polymer orienting layers, which were known to yield different Θ_p values. In the inset of figure 2 we show the azimuthal distribution functions of 5CB monolayers adsorbed on three different polymers, as determined from the SHG data. It can clearly be seen that the anisotropy in the azimuthal distribution function of these 5CB monolayers greatly differs. We observe a positive correlation between a_1 and Θ_p . In figure 2 this correlation is plotted for the complete series of investigated samples. For this series the polar distribution of the 5CB molecules was nearly identical; the assumed gaussian distribution is centred around $\Theta = 77^\circ$ with a standard deviation $\sigma = 4^\circ$. This observation is in agreement with recently published results for 8CB monolayers [11, 12]. Note that the polar angle Θ 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 Θ_p and a_1 equal zero is obtained for 5CB on rubbed bare glass substrates. In this case all Fourier components in $f(\phi)$ were found to be zero.

5. Discussion

In order to understand the relation between the interfacial ordering and the resulting bulk LC orientation we next discuss the orientational mechanism. 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 (a_2), as can be seen in the inset of figure 2, already leads to a macroscopic bulk alignment. On basis of this observation and the correlation observed in figure 2, it is realistic to expect that a_1 , although small, determines the macroscopic Θ_p . Furthermore it was reported by Shen and co-workers that 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 interactions of the LC-bulk with the well characterized, LC monolayer. The occurrence of a non-zero Θ_p is then assumed to stem from the steric interactions of the rod-like LC molecules in the bulk with those at the interface, firmly attached to the orienting polymer surface. The given interfacial in-plane orientational spread of LC molecules gives rise to a competition between the orienting forces of neighbouring LC molecules with a different azimuthal angle ϕ . As pointed out by Ong *et al.* [16] 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.

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

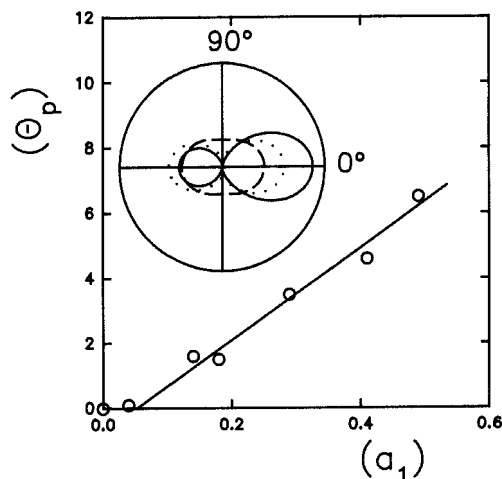


Figure 2. Bulk pretilt angle (Θ_p) of liquid crystal cells filled with 5CB as a function of the orientation of the azimuthal distribution (a_1) of 5CB molecules adsorbed on the rubbed surfaces. The solid line is merely a guide to the eye. The inset shows polar plots of the azimuthal distribution functions of 5CB monolayers adsorbed on rubbed polymer surface which yield bulk pretilt angles of 0.2° (dashed), 1.5° (dotted), and 6.5° (solid), respectively.



Figure 3. Illustrative drawing of the bulk pretilt Θ_p formation in the case of zero orientation ($a_1 = 0$) (a) and non-zero orientation ($a_1 \neq 0$) (b) of the azimuthal distribution function of the monolayer.

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 . Different pretilt angles are now thought to be tuned by changing the orientation of the azimuthal distribution of the LC monolayer. The average polar angle of the interfacial molecules is not tuned, as we determined with SHG. In figure 3 an illustrative drawing of the pretilt formation is shown.

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 8CB monolayers on the same series of polymer surfaces. The alkyl tail of an 8CB molecule is longer than that of an 5CB molecule. Thus, the chain–chain interaction would differ. In our case this should result in an even more oriented distribution of the 8CB molecules at the surface under identical rubbing conditions. We found that for all polyimide surfaces the 8CB monolayers are approximately 20 per cent more oriented than 5CB monolayers adsorbed on identically rubbed substrates, however the similar correlation between a_1 and Θ_p is observed. 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 [13]. A 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 on to an anisotropically distributed LC monolayer.

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