

Optical second-harmonic-generation study of the interaction of silane-covered surfaces with liquid-crystal layers

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Optical second-harmonic generation has been used to determine the average molecular orientation of liquid-crystal (LC) molecules adsorbed on various silane-covered substrates. With the use of different preparation methods for the silane layers, considerable changes in molecular orientation of the polar-ordered part of the first LC monolayer were observed. Concomitantly, the number of polar-ordered LC molecules changed.

I. INTRODUCTION

Various types of bulk liquid-crystal (LC) alignment can be induced by specific surface treatments. However, the physical mechanisms which underlie the alignment are not completely understood.¹ One would therefore like to probe the interaction between the treated surface and the LC molecules close to it. Optical second-harmonic generation (SHG), which is intrinsically surface specific, seems an ideal tool for studying these interfaces.

The interface-specific character of the technique stems from the fact that, in the electric-dipole approximation, SHG is symmetry forbidden in the bulk of centrosymmetric media. Efficient generation of a polarization at the second-harmonic (SH) frequency is only possible at a surface or interface where this symmetry is broken. In recent publications, the use of SHG (Refs. 2 and 3) and sum-frequency generation⁴ (SFG) in studying liquid-crystal-surfactant interfaces has been successfully demonstrated. As a surprising result, it was found with SHG (Ref. 2) that the molecular orientation in the first LC monolayer adsorbed on glass was not affected by the presence of silane layers which yield different bulk LC alignments.

In this paper, we report that the molecular orientation strongly depends on the preparation of the silane layers.

II. THEORY

The SH intensity $I(2\omega)$ reflected from a monolayer of LC molecules adsorbed on a substrate is given by⁵

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

Here, ϕ is the angle of reflectance and $\chi^{(2)}$ the nonlinear susceptibility tensor. $\mathbf{e}_{2\omega}$ and \mathbf{e}_ω denote the products of Fresnel factors and the output- and input-polarization vectors at frequencies 2ω and ω , respectively,⁵ and $I(\omega)$ denotes the laser intensity at frequency ω . In this paper, the polarization directions are denoted by p , s , and q , where p and s are *in* the plane of incidence (x - z plane) and normal to it, respectively, while q refers to a mixed linear polarization with the polarizer set at 45° .

If the nonlinear susceptibility of the substrate is relatively small, the SH signal will be dominated by the ad-

sorbed LC molecules. Assuming the interaction between molecules to be negligible, $\chi^{(2)}$ takes the form

$$\chi_{ijk}^{(2)} = N_s \langle G_{ijk}^{\xi\eta\zeta} \rangle \alpha_{\xi\eta\zeta}^{(2)}, \quad (2)$$

where $\alpha^{(2)}$ is the nonlinear polarizability tensor of a molecule and N_s is the surface density of molecules. $\langle G_{ijk}^{\xi\eta\zeta} \rangle$ denotes an appropriate average over molecular orientation of the transformation matrix from the molecular coordinate axes $(\hat{\xi}, \hat{\eta}, \hat{\zeta})$ to the laboratory system $(\hat{i}, \hat{j}, \hat{k})$.

For SHG from an in-plane isotropic distribution of molecules where $\alpha^{(2)}$ is dominated by a single component, $\alpha_{\xi\xi\xi}^{(2)}$, along the long molecular axis $\hat{\xi}$, the only nonvanishing elements are

$$\chi_{zzz}^{(2)} = N_s \langle \cos^3 \theta \rangle \alpha_{\xi\xi\xi}^{(2)}, \quad (3)$$

$$\chi_{zii}^{(2)} = \chi_{izi}^{(2)} = (N_s/2) \langle \sin^2 \theta \cos \theta \rangle \alpha_{\xi\xi\xi}^{(2)} \quad (i = x, y), \quad (4)$$

where \hat{x} and \hat{y} are in-plane unit vectors, \hat{z} is taken as the surface normal, and θ denotes the tilt angle between the long molecular axis $\hat{\xi}$ and \hat{z} . It has repeatedly been shown that from appropriate input-output polarization combinations, the average molecular tilt angle θ can be determined, assuming some distribution of θ .⁶⁻¹⁰

III. EXPERIMENT

The experiments were performed using the 532-nm frequency-doubled output of a Nd:YAG laser (YAG denotes yttrium aluminum garnet) with a pulse duration of 30 ps and a pulse energy of 3 mJ. The unfocused beam was directed onto the sample at an angle of incidence of 45° . After appropriate spectral filtering of the specularly reflected beam, the SH output was detected using a photomultiplier and gated electronics. The SH wavelength (266 nm) is close to resonance for the 4-*n*-octyl-4'-cyanobiphenyl (8CB) molecules and therefore in all cases the SH background of the glass-silane substrates is negligible.

The silane layers were deposited onto chemically cleaned commercially available BK-7 glass prisms instead of glass plates in order to avoid interference of multiple reflections of the fundamental beam. The silanes we used were *N,N*-dimethyl-*N*-octadecylammoniumpropyltrimethoxysilane chloride (DMOAP), *N*-methyl-

aminopropyltrimethoxysilane (MAP), and octadecyltrichlorosilane (OTS). Trimethylsilyl diethylamine (TMSDEA) monolayers were used as a completely covered nonpolar reference.¹¹ DMOAP and MAP were used as received (Petrarch Systems). OTS and TMSDEA (Aldrich) were distilled before use. The liquid crystal which we used is 8CB, as obtained (British Drug Houses, Ltd.) without further purification.

The modification reactions were performed in three different ways. A first batch of substrates was modified with DMOAP and MAP, according to Kahn.¹² A second batch of substrates was modified in a refluxing 2% solution of the appropriate silane (MAP, DMOAP, or OTS) in toluene and in the case of DMOAP, methanol, with the exclusion of moisture under an atmosphere of argon. In this way, polymerization of the silanes in solution is minimized yielding a better-defined monolayer.^{13,14} In order to obtain a higher density of the desired silane molecules (DMOAP and OTS), the reaction in batch 3 was catalyzed with a continuous flow of ammonia (NH₃), which deprotonizes the glass surface.^{14,15} It is known that afterwards no relevant fraction of NH₃ is left at the surface.^{14,15} The 8CB monolayers were deposited using an evaporation technique,² where SHG was used as an *in situ* deposition monitor.

IV. RESULTS AND DISCUSSION

In order to compare our results with those obtained by Mullin, Guyot-Sionnest, and Shen,² we first deposited 8CB onto clean glass and DMOAP- and MAP-coated glass substrates from the first batch (DMOAP-1, MAP-1). The variation in *p*-polarized SH intensity under *s* excitation (I_{ps}) obtained during adsorption of 8CB on the different substrates is shown in Fig. 1. The average molecular tilt angle $\theta = 67^\circ \pm 3^\circ$ was determined assuming a δ -function distribution. The other input- and output-polarization combinations showed the same SH response during deposition, which indicates that the orientation is independent of 8CB packing density. In all respects, these results agree with those reported by Mullin, Guyot-Sionnest, and Shen.² For adsorption of 8CB on OTS, prepared according to Kahn¹² (OTS-1), we refer to the data of Mullin, Guyot-Sionnest, and Shen.² They found the same tilt angle $\theta = 67^\circ$ and a reduction in SH intensity by more than an order of magnitude with respect to that of 8CB on clean glass.

The fact that no differences in θ are found for 8CB adsorption on the different silanes and clean glass is surprising, since these surfactant-coated substrates yield different *bulk* LC alignments. DMOAP-1 and OTS-1 lead to homeotropic alignment (perpendicular to the surface), while MAP-1 and often clean glass induce planar alignment (parallel to the surface).^{1,12} In addition, the SFG spectra of MAP and DMOAP behave differently upon adsorption of an 8CB monolayer.⁴ We believe that the anomalies mentioned above can be understood from an incomplete shielding of the glass substrates for small molecules, such as 8CB, by the silanes. Indeed it is known that formation of a layer of a multifunctional silane, such as MAP, DMOAP, and OTS, according to the procedure of

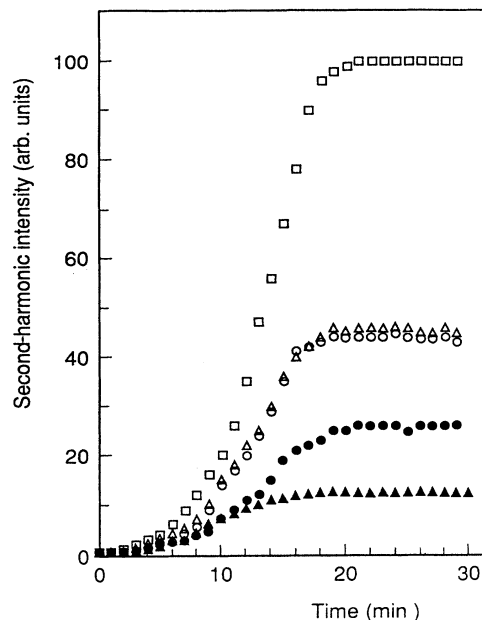


FIG. 1. Variation of the SH intensity (I_{ps}) during adsorption of 8CB on different substrates, MAP-1 (\square), DMOAP-1 (Δ), DMOAP-2 (\bullet), DMOAP-3 (\blacktriangle), and chemically cleaned glass (\square). I_{ps} denotes the *p*-polarized SH intensity for *s*-polarized excitation.

Kahn,¹² leads to polymerization during deposition and gives rise to the formation of a nonuniform multilayer.^{13,16} This means that, for instance, although no more DMOAP molecules can be attached to the surface, 8CB molecules can still penetrate the layer and a reasonably high packing density of 8CB molecules can be obtained.

To check whether the quality of the silane layers can be held responsible for the surprising results, we prepared the silane layers under various conditions. We will first discuss the results for OTS. It is known that formation of OTS-2 in batch 2 ensures polymerization of OTS only along the surface, thus yielding a better-defined monolayer.^{13,14} Deposition of 8CB on OTS-2 reduced the tilt angle to $\theta = 52^\circ \pm 3^\circ$, while the SH intensity was reduced by a factor of 10 with respect to 8CB on clean glass. By catalyzing the chemisorption (OTS-3), the packing density of the OTS monolayer is improved.^{15,17} θ was further reduced to $39^\circ \pm 3^\circ$, and concomitantly the SH intensity was further decreased. In Fig. 2 the SH intensities of 8CB molecules adsorbed on differently covered OTS substrates for different input- and output-polarization combinations are shown. The decrease in overall SH intensity and the change in relative SH intensities (I_{ps} , I_{sq} , I_{pp} , and I_{pq}) for 8CB adsorbed on differently prepared substrates is clear, indicating the sensitivity of SHG to changes in the preparation method of the silane layer. The significant change in θ is not affected by introducing Gaussian distribution functions for the molecular orientation. Assuming, for instance, a standard deviation $\sigma = 10^\circ$, the peak positions only change from 67° to 73° , from 52° to 54° , and from 39° to 37° , respectively.

The results can be interpreted as follows. The SH signal is dominated by those molecules that are attached to

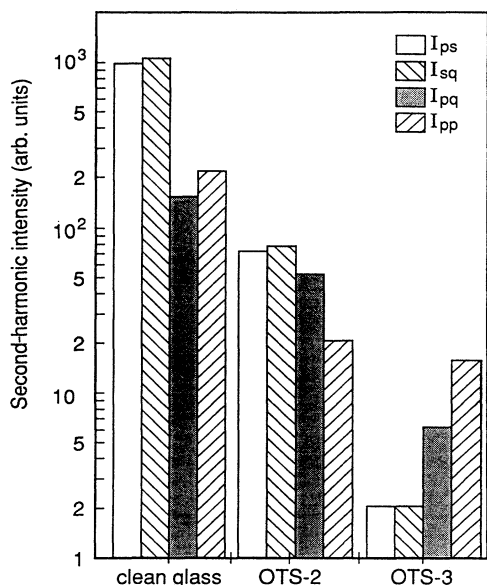


FIG. 2. p - and s -polarized SH intensities for different polarizations of the excitation beam for 8CB adsorbed on clean glass and two differently prepared OTS-covered substrates (OTS-2 and OTS-3).

polar glass sites and therefore have polar ordering. The remaining 8CB molecules presumably form electric quadrupolar pairs and contribute negligibly to the SH intensity.² The OTS-1 layer is known to be nonuniform. Therefore patches of unshielded glass are present and the polar-ordered 8CB molecules have enough freedom to align just as on clean glass. The OTS-2 layer has an improved uniformity. The polar-ordered 8CB molecules are now more closely surrounded by OTS molecules and their alignment is affected accordingly ($\theta \approx 52^\circ$). On the OTS-3 surface, the distance between the OTS molecules is reduced. The influence on the alignment is therefore enhanced¹⁸ ($\theta \approx 39^\circ$). Concomitantly, the number of free glass sites for the 8CB molecules to attach to is reduced, which leads to a reduction of the SH intensity.

This interpretation is further supported by the results for DMOAP. The SH intensity (I_{ps}) of 8CB on DMOAP-2 was reduced by a factor of 2 with respect to the first batch and no significant change in θ was found. However, adsorption of 8CB on DMOAP layers, chemisorbed in the presence of NH_3 (DMOAP-3), yielded a tilt angle $\theta = 52^\circ \pm 3^\circ$ and a SH intensity (I_{ps}) reduced

by a factor of 9 with respect to 8CB on clean glass (see Fig. 1).

The fact that the DMOAP-2 surface did not influence the alignment is not surprising, since the DMOAP head group covers more space than the OTS group and therefore the distance between the alkyl chains is greater. Since DMOAP-3 did, in fact, influence θ , we conclude that the DMOAP packing density must have been improved. In order to test the DMOAP layers, cells have been produced from these substrates. They showed regular homeotropic alignment of the bulk LC.

Adsorption of 8CB on MAP-2 and DMOAP-2, which differ only in the presence of an alkyl chain, yielded the same results, supporting the idea that the alkyl chains of DMOAP-2 do not yet play a role in the alignment of the first polar-ordered LC monolayer. Catalyzing the chemisorption of MAP with NH_3 is not possible.

Finally, adsorption experiments carried out on trimethylsilyl-covered glass substrates, which were used as a completely covered nonpolar reference,¹¹ yielded very weak SH signals. Here, the 8CB molecules are unable to find polar sites. Also for glass substrates, which were not chemically cleaned, we found that the polar character of the surface is greatly reduced. This indicates that the SH intensity can be used as a gauge of the surface density of polar sites at a surface. Adsorption of 5CB, 6CB, and 7CB (predecessors of 8CB in the homologous series) on clean glass yielded virtually the same results as for 8CB.

V. CONCLUSIONS

We were able to prepare various surfactant layers of OTS and DMOAP, which yielded a measurable change in the molecular orientation of the first LC monolayer as measured by SHG. A change in θ up to approximately 30° towards the bulk alignment could be induced, depending on the amount and structure of the silane. It is concluded that the SHG data yield information only on LC molecules attached to polar glass sites. Such molecules may constitute only a (minor) fraction of the first LC monolayer.

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