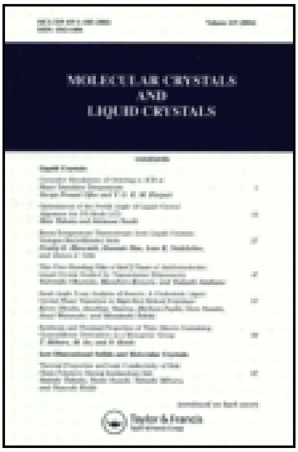


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Surface Nematic Order Induced by Silane Derivatives Studied by Second Harmonic Generation

S. Soria [a], D. Schuhmacher [a], G. Marowsky [a], R. Barberi [b], F. Ciuchi [b] & T. Rasing [c]

[a] Laser Laboratorium Goettingen e. V, Hans-Adolf-Krebs-Weg 1, Goettingen, 37077, Germany

[b] Dipartimento di Fisica, Università della Calabria, INFM Unità di Cosenza, Arcavacata di Rende (CS), 87036, Italy

[c] RIM, University of Nijmegen, P.O. Box 9010, Nijmegen, 6500 GL, The Netherlands

Version of record first published: 29 Oct 2010

To cite this article: S. Soria, D. Schuhmacher, G. Marowsky, R. Barberi, F. Ciuchi & T. Rasing (2002): Surface Nematic Order Induced by Silane Derivatives Studied by Second Harmonic Generation, Molecular Crystals and Liquid Crystals, 372:1, 291-303

To link to this article: http://dx.doi.org/10.1080/10587250127576

Mol. Cryst. and Liq. Cryst., 2001, Vol. 372, pp. 291-303

Surface Nematic Order Induced by Silane Derivatives Studied by Second Harmonic Generation

S. SORIA[1], D. SCHUHMACHER[1], G. MAROWSKY[1],
R. BARBERI[2], F. CIUCHI[2] and T. RASING[3]

[1]*Laser Laboratorium Goettingen e.V, Hans-Adolf-Krebs-Weg 1,*
37077 Goettingen, Germany,
[2]*Dipartimento di Fisica Università della Calabria, INFM Unità di Cosenza,*
87036 Arcavacata di Rende (CS), Italy and
[3]*RIM, University of Nijmegen, P.O.Box 9010, 6500 GL, Nijmegen,*
The Netherlands

Abstract We studied surface second-harmonic generation from thin layers of several silanes dipped on conductive glasses after the deposition of a thin film of 4‘-n-pentyl-4-cyanobiphenyl (5CB) nematic liquid crystal. The average orientation and surface order of the nematic were determined by using Fourier analysis of the second harmonic signal obtained by sample rotation in reflection geometry and by polarization rotation in transmission geometry.

The aim was to check the possible use of these materials as a control layer for the anchoring properties of nematics. The silane layer should passivate a conventional surface treatment mainly by changing the surface order properties.

Keywords second harmonic generation, nematic liquid crystals, silanes.

INTRODUCTION

Without special treatment at the surfaces the long axis of nematic molecules aligns spontaneously only over microscopic domains. Since macroscopic uniform alignment is a prerequisite for any liquid crystal device, suitable boundary conditions are crucial. Conventionally, the molecular alignment is achieved by putting the liquid crystal in contact with an anisotropic substrate. For commercial devices, the anisotropy is usually obtained by means of unidirectional mechanical rubbing of the polymer layer and the liquid crystal molecules point their long axes along the rubbing direction [1, 2].

Second Harmonic Generation (SHG) is a powerful technique for probing molecules adsorbed at an interface and it can be used to determine the orientational distribution of a surface monolayer of molecules [3,4]. In the electric-dipole approximation SHG is forbidden in centrosymmetric materials, but the inversion of symmetry is broken at surfaces and interfaces [5]. For this reason, SHG is suitable to probe also surface properties of liquid crystals.

Using Fourier analysis [6,7,8], we have evaluated the SH response of several silanes dipped on ITO (Indium Tin Oxide) coated glasses. ITO glasses are used because a conductive surface is necessary for electro-optic devices. We also evaluated the response of 5CB (4‘-n-pentyl-4-cyanobiphenyl, from Merck) liquid crystal monolayers deposited onto them under Fresnel reflection conditions at various polarization angles. Our aim is to check the intrinsic order properties that silane materials induce on 5CB at surfaces.

THEORY

The monolayer characteristics are reflected in the surface nonlinear susceptibility $\chi^{(2)}$ of the monolayer. By measuring the individual components of the nonlinear susceptibility, it is possible to deduce information about the orientation and arrangement of molecules in a monolayer. We assume that there is only one dominant component of molecular hyperpolarizability β of the 5CB related to the long molecular axis $\hat{\xi}$: β_{333}. This approximation provides relatively simple relations between the macroscopic second-order nonlinear susceptibility components χ_{ijk} and the angular distribution of the molecules (Fig.1). For an isotropic distribution this yields [2,3]

$$\chi_{zzz} = N_s < \cos^3\theta > \beta_{333}$$

$$\chi_{zxx} = \chi_{zyy} = \chi_{xzx} = \chi_{yzy} = \frac{1}{2} N_S \langle \sin^2\theta \cos\theta \rangle \beta_{333}, \qquad (1)$$

where < > means averaging over the angular distribution, θ is the tilt angle describing the polar orientation, and N_s is the surface density of molecules.

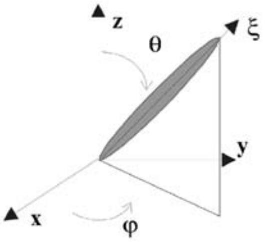


Figure 1- Long molecular axis $\hat{\xi}$ in relation to sample coordinates (x,y,z). θ and φ are polar angle and azimuthal angle of $\hat{\xi}$ respectively.

Eq. (1) yields

$$\frac{\langle \sin^2\theta \rangle}{\langle \cos^2\theta \rangle} = \frac{2\chi_{zxx}}{\chi_{zzz}} \tag{2}$$

By assuming a δ function distribution of the tilt angle, Eq. (2) can be used to determine the average tilt angle θ_0.

For an anisotropic distribution with two planes of symmetry, the nonlinear susceptibility tensor $\chi^{(2)}$ belongs to the C_{2v} group and can be described by three independent nonzero components [9]

$$\begin{aligned} \chi_{zzz} &= N_s < \cos^3\theta > \beta_{333}, \\ \chi_{zxx} = \chi_{xzx} &= N_s < \sin^2\theta \cos\theta \cos^2\varphi > \beta_{333}, \\ \chi_{zyy} = \chi_{yzy} &= N_s < \sin^2\theta \cos\theta \sin^2\varphi > \beta_{333}, \end{aligned} \tag{3}$$

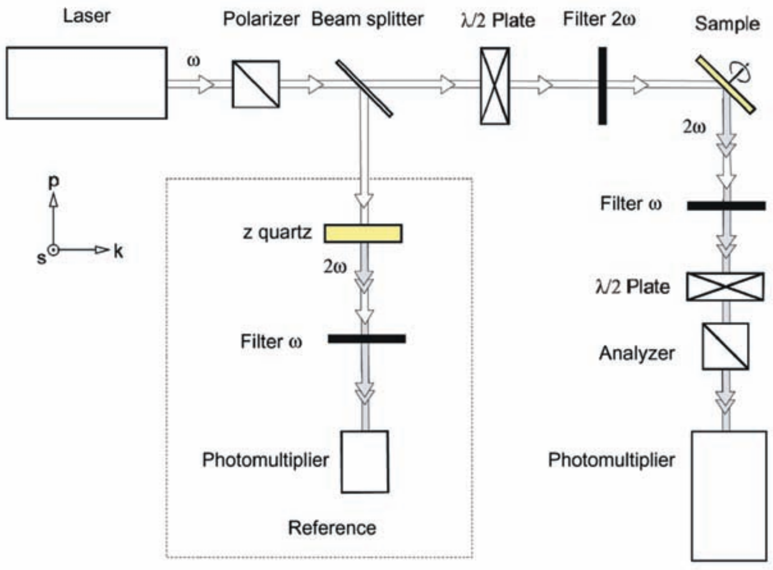
where φ is the azimuthal angle of the molecular long axis $\vec{\xi}$ with respect to the x axis. By assuming independent polar and azimuthal parts of the molecular orientational angular distribution function $f_s(\theta,\varphi) = \delta(\theta-\theta_0)g(\varphi)$, the in-plane surface orientational order parameter $Q_s = <\cos 2\varphi>$ of the 5CB monolayer can be calculated from Eq. (3) as [10]

$$Q_s = (\chi_{zxx} - \chi_{zyy}) / (\chi_{zxx} + \chi_{zyy}) \tag{4}$$

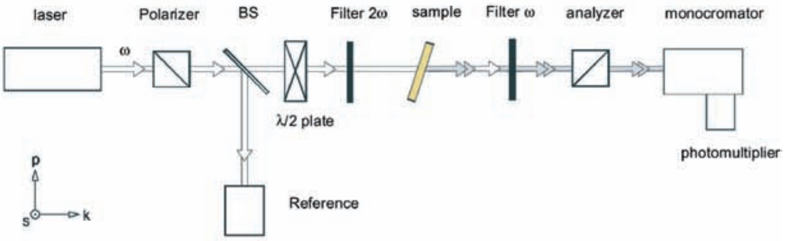
This parameter describes the surface anisotropy between **x** and **y**.

EXPERIMENTAL SET-UP

The experimental set-up in reflection geometry is shown in Fig.2.a. The linearly polarized radiation from a Nd:YAG laser pumped Optical Parametric Oscillator (OPO) (4 ns, 10 Hz, 420-1600 nm) was used as light source to generate SH radiation. The angle of incidence of the laser beam was kept constant at 45°. The sample was mounted on a rotation stage in air. A polarizer in front of the multiplier allows polarization-sensitive SH detection by setting the polarization angle to p-polarization (0°) and s-polarization (90°). We also measured the SH spectrum of the films in the visible range of the OPO in this geometry.



a)



b)

Figure 2- Experimental set-up for SHG a) in reflection, b) in transmission.

The fundamental wavelength was filtered out from SH signal by using appropriate colour filters and a grating monochromator. We also placed colour filters in front of the sample in order to filter out the second harmonic signal. The transmission configuration (Fig.2.b) facilitates the identification of the anisotropic tensor components since normal incidence delivers SH signals only from these components, and the isotropic components can be gradually introduced by rotating the sample around **y**. We rotated the polarization of the fundamental radiation by rotating the λ/2 plate. Also for transmission the detection of SH signal was done for p and s polarizations.

MATERIALS AND SAMPLES

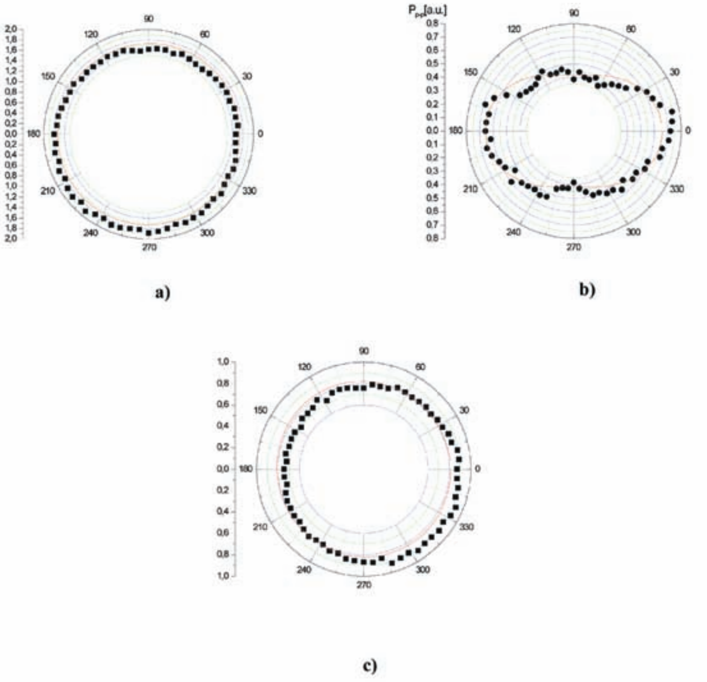
We used three surfactants as alignment layers: methyltrimethoxysilane (MMS), methylpropoxysilane (MPP) and methyltriethoxysilane (MES) from Fluka and we used them without any further purification. These materials were dissolved in isopropanol and demineralized water (10%) at 1‰ in volume. The used materials have been chosen because they present different lengths of their saturated hydrocarbon chains. Molecular layers have been deposed on each substrate by dipping the plate in the silane solution. The low concentration of silane materials has been chosen because we are interested on the modification that they can induce on the alignment properties of a standard anisotropic surface treatment. The role of silanes, which are use like dopants for the surface, should be to perturbate the contact properties of 5CB for instance on the usual alignment layers of a rubbed polymer. Some samples have been analysed just after the coating by dipping; other samples have been observed after a rubbing procedure. In this case the rubbing process was carried out by translating a substrate at constant speed while it was in contact with a rotating wheel of velvet.

Finally, we coated the prepared substrates with 5CB. Adsorbed 5CB monolayers on substrates were prepared by evaporation, using SHG as an in situ probe of the deposition [10]. In all cases, the signal increased quadratically with time and then saturated, indicating that the molecules have been adsorbed uniformly onto the substrate until a full monolayer has been formed. Evaporation of 5CB onto all substrates under investigation exhibited similar temporal behaviour [11].

EXPERIMENTAL RESULTS.

The SH spectra from the ITO coated glasses both cleaned or coated by a silane are practically the same. None of these silanes generated a significant SHG signal before deposition of 5CB. Hence we can assume that the isotropic SHG background comes only from the ITO layer.

We monitored SH signal from 5CB deposited onto the different silanes as a function of the rotation angle of the sample. We deduce from our measurements the surface in-plane order parameter Q_s of the 5CB monolayer on top of the substrate as well as its average tilt angle.



a) b)

c)

Figure 3 - Azimuthal dependencies of the pp second-harmonic power: a) rubbed MMS film, b) rubbed MES film, c) rubbed MPP film.

For unrubbed silanes the output power of the SH signal for the p-in-s-out and s-in-s-out combinations was very low compared to that for the s-in-p-out and p-in-p-out case (i-in-j-out indicate the polarizations of the fundamental and SH beams, respectively) in accordance to the $C_{\infty\upsilon}$ surface symmetry of a 5 CB monolayer on an isotropic substrate. As expected, the signal from these unrubbed substrates is azimuthally isotropic. The tilt angle of the 5CB molecules in the monolayer is $\theta \approx 65$ °, for all the unrubbed silanes [11]. This means that the 5CB molecules are arranged conically. The surface nematic director has moved towards the magic angle (~54.7°), which is typical of disordered substrates [12].

Figure 3 shows these azimuthal dependences of SH signals for a p-in-p-out polarization combination. Three cases are shown: MMS (a), MES (b) and MPP (c), all of them rubbed. In these cases, the molecules could have a preferred alignment along the rubbing direction (**x** axis). For both rubbed and unrubbed MMS (Fig.3.a) and MPP (Fig.3.c) coated substrates, the SHG signal shows an isotropic dependence on sample rotation around the surface normal for s-in-p-out and p-in-p-out polarizations, indicating that there is no detectable anisotropy in the distribution of the 5CB monolayer. These results are in agreement with the experiments made by Chen and coworkers[3]: they have shown that a rubbed surfactant-coated substrate cannot orient the adsorbed first LC monolayer while it can induce a macroscopic alignment in a cell. Furthermore some authors [13] stress that the orientation of the monolayer depends on the preparation method. Our results indicate that the LC molecules in the monolayer are not aligned in the surface plane.

From the measured values of the susceptibility components, we found that the tilt angle for the rubbed MPP and MMS is 72° ± 3°.

The third material, MES, behaves differently. In this case the rubbed MES layer shows an anisotropy (Fig.3.b): the chromophores of 5CB molecules follow the direction of the rubbing strokes. The surface alignment is characterized by $Q_s \approx 0.3$ and $\theta \approx 71°$. The value of the surface in-plane order parameter is quite small in the lowest range of the usual values for rubbed polymeric surfaces: $Q_s \approx 0.3 - 0.5$ [14-16]. The observed tilt angle is comparable with alignment angles of cyano-biphenyl monolayers usually found on substrates that induce a planar macroscopic alignment [2,10].

To check the macroscopic alignment induced by the investigated substrates, we prepared thin cells with rubbed and unrubbed silane-coated substrates. The cells were observed by means of an optical microscope between crossed polarizers. The cells made with unrubbed plates were inhomogeneous, with only small domains randomly oriented, whereas all the rubbed substrates have shown cells with a homogeneous alignment along the rubbing direction. This behaviour confirms that a macroscopic alignment of nematics does not depend on an uniform alignment of the first monolayer in contact with the substrate.

To obtain more information we have performed SHG experiment in transmission geometry at two angles of incidence, 0° and 45°. As expected, for an isotropic distribution and a C_{2v} distribution no signal could be observed at normal incidence. At 45° all Fresnel factors are different from zero and SH signal could be detected: a small anisotropy has been observed also in the case of rubbed MMS and MPP (about 2% of the total signal). For these silanes we have found a very low order parameter $Q_s \approx 0.02$, in the limit of the experimental accuracy of our set-up.

DISCUSSION AND CONCLUSIONS

The results presented in this paper were planned to determine the orientational distribution of a monolayer of NLC molecules adsorbed on a substrate by SHG. We used reflection and transmission geometry to obtain the tilt angle and the order parameter induced by three different silanes. None of these silanes generated a significant SHG signal before deposition of 5CB.

In all analysed cases, we found comparable tilt angles. This result implies that the rubbing of silanes does not affect the polar orientation of the 5CB molecules; only the azimuthal orientation can be influenced. This is expected since the polar angle distribution of LC molecules at the surface is mainly determined by molecule-surface bonding, and therefore is not likely influenced by rubbing.

We found that on MPP and MMS rubbed surfaces, the LC molecules are practically in an isotropic conical state. Only in the case of the MES coated substrate a clear influence of rubbing on the molecular alignment has been observed. There is an uncertainty (≤ 10 %) in the values of the χ_{ijk} mainly due to a 10 % uncertainty in the index of refraction of the monolayers at the SH frequency.

We underlined the apparent disagreement between the optical microscope observation of NLC thick layers and SHG measurements of the first LC monolayer. This result indicates that the surface induced homogeneous bulk alignment is not strictly connected with the order and anisotropy of the NLC first layer. The low surface order parameter is suitable to use these surfactants as surface perturbators. They could screen the strong order imposed by usual surface treatment, favouring the control of weak anchoring conditions. Measurements to check the validity of this hypothesis are in progress.

ACKNOWLEDGEMENTS

We thank Dr. O. Roders for his helpful discussions. Financial support from the European network grant no. ERB FMRXCT 980209 (SILC) is gratefully acknowledged.

REFERENCES

[1] D.W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972); Mol. Cryst. Liq. Cryst. **23**, 215 (1973).

[2] M.B. Feller, W.Chen, Y.R. Shen: Phys. Rev. A **43** (12), 6778 (1991).

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

[4] G. Marowsky, G. Luepke, R. Steinhoff, L.F. Chi, and D. Moebius, Phys. Rev. B **41**, 4480 (1990).

[5] Y. R. Shen, Annu. Rev. Phys. Chem. **40**, 327 (1989); R.M. Corn and D.A. Higgins, Chem. Rev. **94**, 107 (1994).

[6] B.U. Felderhof, A. Bratz, G. Marowsky, O. Roders, F.Sieverdes: J. Opt. Soc. Am. B **10**, 1824 (1993).

[7] A.Bratz, G. Marowsky: Mol. Eng. **1**, 59 (1991).

[8] O. Roders, O. Befort, G. Marowsky, D. Moebius, A. Bratz: Appl. Phys. B. **59**, 537 (1994).

[9] J.R. Dennis and V. Vogel, J. Appl. Phys. **83**, 5195 (1998).

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

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

[12] G.Barbero, I.Dozov, J.F.Palierne, G.Durand Phys.Rev.Lett. 56, 2056 (1986).

[13] Barmentlo, Hoekstra, Willard, Hollering Phys. Rev. A **43**, N.10 5740

[14] X.Wei, X. Zhuang, S.C. Hong, T. Goto, and Y.R. Shen, Phys. Rev .Lett. **82**, 4256 (1999).

[15] R. Meister and B. Jerome, Macromolecules **32**, 480 (1999).

[16] T. Sakai, J.G. Yoo, Y. Kinoshita, K.Ishikawa, H. Takezoe, A. Fukuda, T. Nihira, and H. Endo, Appl. Phys. Lett. **71**, 2274 (1997).