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Properties of liquid-crystal monolayers on silane surfaces

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Using optical second-harmonic generation, we have measured the surface coverage, binding energy, adsorption and desorption, and orientation of a liquid-crystal monolayer on clean glass and silane-treated glass. The results show that the short-range surface interaction does not necessarily dictate the bulk alignment of a liquid crystal.

It is well known that the bulk alignment of a liquid-crystal film can be controlled by surface treatment.[1] This is essential for the construction of liquid-crystal (LC) display devices. But the physical mechanisms for the surface-induced alignment are not yet clearly understood.[2] One would like to know how a surface interacts with and orients the first monolayer of LC molecules on the surface, and then through molecule-molecule interactions aligns the molecules in the bulk. For probing into the first part of this problem, the recently developed optical second-harmonic-generation (SHG) technique seems ideal.[3] Because it is forbidden in media with centrosymmetry, it is highly surface specific and sensitive. We report here our recent study with this technique on the interaction of LC monolayers with clean or surfactant-coated glass substrates. The surface coverage, polar arrangement, adsorption and desorption kinetics, adsorption energies, and orientations of LC molecules at different interfaces were measured. Our results indicate that the short-range interaction responsible for the orientation of the first monolayer of LC molecules at the surface may be overwhelmed by the long-range interaction in aligning the bulk LC.

The SHG technique for studies of adsorbed monolayers has been described elsewhere.[3] In the present experiment, a frequency-doubled Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser was used as the pump. The SH output from the LC monolayer on a substrate in the reflected direction was detected. The nonlinearities of the glass and the silane surfactants are relatively small so that their contributions to the SH output are negligible. Thus, from the SH signals with proper input-output polarization combinations, the nonlinear susceptibility $\chi_{ijk}^{(2)}$ for the LC monolayer can be derived. For isotropic molecular distribution in the surface plane, the nonvanishing elements of $\chi_{ijk}^{(2)}$ are $\chi_{zzz}^{(2)}$, $\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}$, and $\chi_{xzx}^{(2)}=\chi_{xxz}^{(2)}=\chi_{yzy}^{(2)}=\chi_{yyz}^{(2)}$, where $\hat{\mathbf{z}}$ is along the surface normal. They are related to the nonlinear polarizability $\overleftrightarrow{\alpha}^{(2)}$, per molecule via a geometric transformation connecting the molecular coordinate axes with the lab axes. In the simple case where $\overleftrightarrow{\alpha}^{(2)}$ is dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along the long molecular axis $\hat{\xi}$ and, where the local field correction due to intermolecular interaction can be neglected, we have

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

$$\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}=\chi_{xzx}^{(2)}=\chi_{yzy}^{(2)}=\tfrac{1}{2}N_s\alpha_{\xi\xi\xi}^{(2)}\langle\sin^2\theta\cos\theta\rangle\,, \quad (1)$$

where N_s is the surface density of molecules, θ is the angle between $\hat{\xi}$ and $\hat{z}$, and $\langle\ \rangle$ denotes an average over molecular orientations. Equation (1) is the basis of our data analysis.

We have studied monolayers of 4′-n-octyl-4-cyanobiphenyl (8CB) molecules on clean glass and on glass substrates coated with different silane surfactants: n,n-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilylchloride [DMOAP, $CH_3(CH_2)_{17}(Me)_2N^+(CH_2)_3$-$Si(OMe)_3Cl^-$, where Me denotes methyl], n-methylaminopropyltrimethoxysilane [MAP, $MeNH(CH_2)_3$-$Si(OMe)_3$], and octadecyltrichlorosilane [OTS, CH_3-$(CH_2)_{17}SiCl_3$]. These surfaces are known to yield different bulk LC alignments. DMOAP- and OTS-coated substrates lead to homeotropic alignment (perpendicular to the surface), while MAP-coated glass and often clean glass give planar alignment (parallel to the surface).[1,2] To prepare the samples, the glass substrates were first thoroughly cleaned. Surfactants were then chemisorbed and polymerized on the surfaces in accordance with the literature.[1,2] The 8CB monolayers were deposited on the substrates by an evaporation method. We heated a drop of 8CB held above the deposition surface. SHG was used an an *in situ* probe to monitor the deposition process. The absolute surface coverage of 8CB on the surface was determined by comparing the SH signal with that from a full monolayer of 8CB deposited on glass and on water.[4] Scanning the laser over the surface while monitoring SHG showed that the evaporation of 8CB on the surface was uniform to within 3%. Heating the newly 8CB-covered substrates caused thermal desorption of 8CB. Again, SHG was used to monitor the desorption process, from which the adsorption energy could be deduced.

In all cases, the SH signal was dominated by adsorbed 8CB molecules with their polar head groups facing the substrate. Measuring the ratio $\chi_{zyy}^{(2)}/\chi_{zzz}^{(2)}$ allowed us to find the tilt angle θ of such molecules away from the surface normal if we assumed a sharp orientational distribution.[3] We obtained from our experiment a most unexpected result: While different surfaces may align the bulk LC in such different ways, they appeared to orient the adsorbed 8CB molecules with nearly the same tilt angle, $\theta \sim 67°$. This orientation also did not vary significantly with the surface coverage of 8CB or with temperature between room temperature and desorption temperature at $\sim 70\,°C$.

Adsorption of 8CB on clean, DMOAP-coated, and

MAP-coated glass substrates, as monitored by SHG, is shown in Fig. 1. Since the molecular orientation was the same in all cases, the data in Fig. 1 with $N_s \propto S^{1/2}$ directly reflect the surface density of adsorbed molecules in the polar arrangement as a function of time. The absolute surface coverage was obtained by calibration against a known amount of 8CB spread on glass and on water. We found that the SH signal from 8CB on glass in Fig. 1 has a saturation value corresponding to $N_s \simeq 3\times10^{14}$ cm^{-2}, which is about 0.45 times the number of molecules per cm^2 in a smectic layer (a bilayer with molecules in an antiparallel arrangement). This value is the same as that of a full monolayer of 8CB on water, indicating that the first monolayer of 8CB on glass has a completely polar arrangement. The SH signal from 8CB on DMOAP- and MAP-coated glass, however, saturates at a lower value, corresponding to a smaller number of 8CB molecules in the polar arrangement ($N_s \simeq 2\times10^{14}$ cm^{-2}). In the case of 8CB on OTS-coated glass, the results were drastically different. The SH signal saturates at $N_s \simeq 0.5\times10^{14}$ cm^{-2}, even though the rate approaching saturation was nearly the same as in the other cases. Reevaporation of the deposited 8CB on a clean glass showed that at saturation, the number of 8CB molecules on the OTS-coated glass was close to that of a full monolayer on clean glass. Thus most of the 8CB molecules on the OTS surface must be in the antiparallel arrangement.

The above results can be qualitatively understood by examining a model structure of various surfaces. The strongly hydrophilic glass surface behaves like the water surface and allows the binding of 8CB to the oxygen on the surface to form an almost fully packed polar monolayer. In preparing an MAP-coated glass surface by adsorption from a solution, the MAP molecules are hydrolyzed in solution (with OMe replaced by OH). Upon adsorption and curing, the molecules form a polymerized monolayer on the surface. Each molecule is attached to the surface at both the Si and the N end, and is linked to two neighboring molecules by releasing H_2O and establishing the Si—O—Si bonds.[5] To form a closely packed monolayer and keep the tetragonal bonding symmetry of Si, the silances may have locally a row structure with the —Si—O—Si—O— chain acting as the backbone. The MAP-coated surface now has nearly the same density of oxygen binding sites for the 8CB along the chains as the clean glass surface, but less across the chains. Since the distance between neighboring chains is about 0.7 nm, which is larger than the transverse dimension of 8CB (0.35 nm), we estimate that the 8CB coverage on an MAP-coated surface is about half that of a clean glass as observed. The DMOAP-coated glass surface is expected to be the same except that the molecules have a long alkane chain at the nitrogen end oriented along the surface normal. This alkane chain is presumably responsible for the homeotropic 8CB alignment in the bulk when the LC film is sandwiched between DMOAP-coated substrates. That the binding sites of 8CB on these different surfaces are similar may be responsible for the observation of the same tilt angle of 8CB on such surfaces.

The OTS monolayer on glass is much more tightly arranged. Each molecule is bound to the surface with a single Si—O bond, and the closely packed long alkane chains of the molecules are normal to the surface, resulting in a hyrdrophobic overlayer on the surface. Consequently, the adsorbed 8CB molecules unable to find polar adsorption sites tend to form quadrupole pairs on the surface. Our experimental finding of the presence of a fractional polar monolayer (20%) of 8CB on the OTS-coated surface is presumably due to imperfect OTS covering of the glass surface. The OTS-coated surface also led to a homeotropic bulk alignment presumably because of the vertically aligned long alkane chains of OTS on the surface.

The adsorption data in Fig. 1 cannot be fit by a simple Langmuir-type exponential. This is because the adsorption of 8CB does not limit to a single monolayer; after the first monolayer, the adsorbed 8CB molecules should appear in the antiparallel arrangement and contribute only little to the SH signal.

Upon heating the 8CB-monolayer-covered substrates, the 8CB molecules would be desorbed. Figure 2 shows the thermal desorption of 8CB from clean, DMOAP-coated, and MAP-coated glass surfaces during a linear temperature ramp as monitored by SHG. The desorption curves for samples prepared at different times could vary somewhat, either steeper or more gradual in their decay with temperature, but the inflection points always occurred at nearly the same temperature. It is seen that molecules are

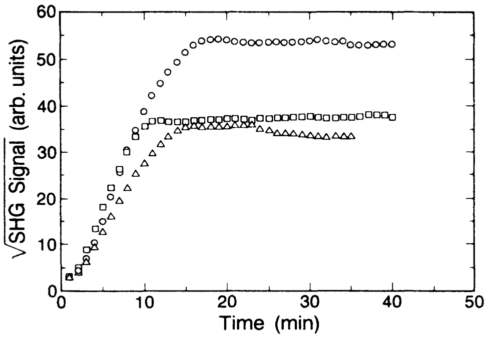

FIG. 1. Adsorption of 8CB on clean glass (○), DMOAP-coated (□), and MAP-coated (△) surfaces as a function of evaporation time.

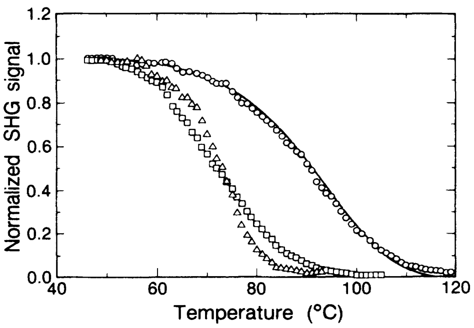

FIG. 2. Thermal desorption of an 8CB monolayer from clean glass (○), DMOAP-coated (□), and MAP-coated (△) surfaces. The temperature was ramped at 1 °C/min.

desorbed from the surfactant-coated surfaces at ~20° lower than those from the clean surface. This indicates that 8CB has lower binding energies on the surfactant-coated surfaces. Following the usual equation for thermal desorption,[6] $d\theta/dt = -\nu\theta\exp(-E_{\mathrm{des}}/k_B T)$, we have

$$\theta(T) = \exp\left[\int_{T_0}^{T(t)} \frac{\nu}{dT/dt} e^{-E_{\mathrm{des}}/k_B T'} dT'\right] , \tag{2}$$

where θ is the surface coverage normalized against the adsorbed 8CB full monolayer, ν is a preexponential factor, E_{des} is the desorption energy, and k_B is the Boltzmann constant. Knowing that the 8CB molecules are immobile on the surface, we expect $\nu \sim 10^{16}\ \mathrm{sec}^{-1}$ (Ref. 6). We can then derive from Eq. (2) the temperature at which $d\theta/dt$ is maximum and compare it with experiment to deduce E_{des}. We find that $E_{\mathrm{des}} = 1.3 \pm 0.005$ eV for 8CB on DMOAP and MAP-coated substrates and $E_{\mathrm{des}} = 1.38 \pm 0.005$ eV for 8CB on glass. For 8CB on OTS-coated glass, the thermal desorption curve could be obtained by monitoring the reevaporation of the desorbed 8CB on another glass substrate using SHG. We estimated a desorption energy of $E_{\mathrm{des}} \simeq 1.24$ eV.

In conclusion, we have shown that optical SHG can be used to study quantitatively the adsorption and arrangement of 8CB monolayers on substrates with different surface treatments. A clean glass surface displays a strong polarity for 8CB to form a strong polar layer on it, while an OTS-coated substrate has a densely packed surface layer of alkane chains that tends to forbid 8CB from forming a polar layer on it. Intermediate to these two cases lie the DMOAP- and MAP-coated surfaces. The similar orientations of 8CB monolayers on clean glass and MAP- and DMOAP-coated surfaces, coupled with dissimilar bulk alignments caused by these surfaces, suggest that the bulk LC alignment relies heavily on long-range interactions.[7] However, the short-range interactions may still be important for setting a boundary condition.

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[7] Results in Ref. 4 show that the orientation of the first monolayer at the LC-glass interface is not affected appreciably by the presence of the bulk LC film.