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Second-harmonic generation from rubbed ferroelectric liquid crystal mesogenic monolayer surfaces

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We have designed self-assembled monolayers of molecules containing a ferroelectric liquid crystal mesogen attached to a glass surface through an alkane chain. After mechanical rubbing these layers induce a single domain in a cell containing a high-polarization achiral liquid crystal in the smectic-*C* phase. We have used optical second-harmonic generation to demonstrate that this behavior is explained by rubbing-induced in-plane anisotropy of the angular distribution function that describes the ensemble of mesogenic units. The surface order parameter is 0.094, a substantial fraction of what has been observed for rubbed polymeric alignment layers.

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I. INTRODUCTION

Liquid crystal (LC) alignment (the control of macroscopic domain structure in LC samples) is the key to successful application of these materials in display devices. This is typically achieved through the interaction of the LC with specially treated solid surfaces. Among the LC alignment methods, Sagiv-type self-assembled monolayers (SAMs) [1–5] which produce stable and high-quality alignments have been widely studied for both homeotropic (molecules perpendicular to the surface) and homogeneous (molecules parallel to the surface) orientations. However, no systematic study has been done on different types of SAMs to find correlations between the molecular structure of the aligning layer and the macroscopic orientation of an adjacent LC. Recently, chiral smectic ferroelectric electric liquid crystal (FLC) alignment has been accomplished with a rubbed long-chain SAM [6]. The influence of the rubbing on these monolayers is not clear. It is tempting to suggest that the rubbing induces a tilt in what was originally a vertically oriented close-packed network of chains. However, investigation of the molecular conformation of this type of rubbed SAM using optical sum-frequency generation (SFG) has shown that rubbing actually straightens the chains while inducing anisotropy in only the orientation of the terminal methyl groups [7]. The subtlety of this influence is consistent with the fact that the free energies of different LC orientations can be separated by as little as 0.01 mJ/m^2 [8].

To design more effective alignment layers, it is advantageous to exploit short-range epitaxy between the oriented layer and the FLC. For this purpose, we sought to synthesize SAMs that contain FLC mesogenic units. In addition to efficient anchoring, such a layer may enable ferroelectric switching at high speeds and ultimately may provide a truly bistable FLC alignment surface. Polymeric films with liquid crystalline side chains have been synthesized and tested [9]. In these cases, significant rubbing-induced in-plane anisotropy was documented [10]. Monolayer-modified ‘‘command surfaces’’ that contain azobenzene components have also been reported [11]. These have been shown to regulate the direction of parallel alignment, depending on the characteristics of irradiation with visible light. However, no monolayer composed of FLC mesogens has yet been investigated. In addition to studying the new surface materials science that such systems represent, our program has been motivated by interest in developing a switchable alignment layer. This would lead to important photonic applications, particularly in the case where the mesogenic units have interesting optical properties of their own. In this paper we describe our initial study of FLC mesogenic SAMs. Of central interest is whether a monolayer of this type can be successfully attached to a glass surface and oriented by mechanical rubbing.

II. EXPERIMENTAL METHOD

A. Preparation of the FLC mesogenic SAM

We seek to exploit the favorable properties of *o*-nitroalkoxyphenyl biphenylcarboxylate (W314) (Fig. 1), which has been described previously [12]. This material was designed and synthesized specifically for nonlinear optical applications. It displays a large electroclinic effect and large nonlinear optical coefficients. To enable self-assembly, the C10 chain was modified with a terminal triethoxysilane group. We have previously demonstrated the utility of triethoxysilanes in forming high-quality SAMs [6]. The trialkoxysilanes are hydrolytically much more stable than their tricholorsilane counterparts, and the silane form is readily obtainable through hydrosilantion of the terminal alkene.

The FLC mesogenic silane (W399) was synthesized as shown in Fig. 1 by heating the known FLC compound W324 with octadecyltriethoxysilane ($(\mathrm{EtO})_3\mathrm{SiC}_{18}\mathrm{H}_{34}$) in the presence of a catalytic amount of cyclo-octadiene platinum (II) chloride. While W324 has only a limited solubility in triethoxysilane, the product W399 is completely soluble, giving brown oil on completion of the reaction. Due to the stability

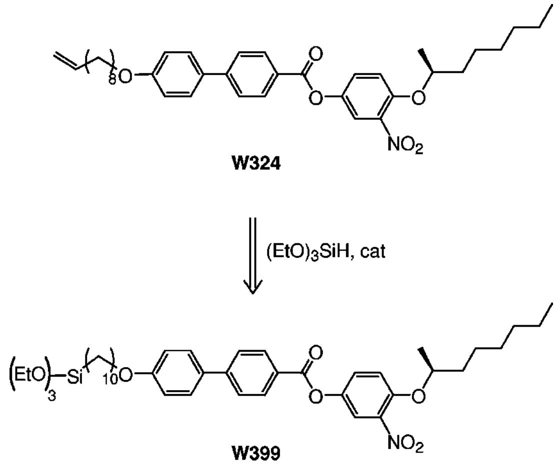

FIG. 1. Molecular structure of ferroelectric liquid crystal molecules cited in this study.

of the resulting silane, the compound can readily be purified on a column of silica gel without decomposition. Attempts at carrying out hydrosilation at room temperature with platinum on carbon as a catalyst were also successful if the reaction mixture was agitated in an ultrasonic cleaning bath. In this case, however, significant amounts of the isomerized double bond were obtained, which were difficult to remove by column chromatography.

Using W399, SAMs on float glass microscope slides were prepared using a procedure described in the literature [5]. Float glass microscope slides were dipped into a solution of FLC mesogenic silane (2% by weight) and *n*-butylamine (0.5% by weight) in toluene. After 10 min the slides were removed from the solution and baked in a 100 °C oven for two days without rinsing. Finally, the excess material was removed by cleaning with acetone to leave a hydrophobic surface. The bake after removal from the solution without rinsing is a critical step in the preparation of a fully reacted polysiloxane network on the surface.

Rubbed W399 SAMs were obtained with a homemade rubbing machine. The rubbing machine was composed of a substrate translation stage below a rotating drum covered with cloth. The device was adjusted to simulate the extent of rubbing that is typically employed in LC display manufacturing.

B. Second-harmonic generation experiments

Optical second-harmonic generation (SHG) is more appropriate than SFG to characterize the orientation of the biphenyl core of the mesogen. This molecular group possesses a dominant hyperpolarizability element along its symmetry axis, as has been shown in SHG experiments involving *n*-cyanobiphenyl nematics [13,14]. In the SHG phenomenon, two incident photons from the same laser beam combine in the sample to produce a single outgoing photon with twice the energy of those in the incident beam. The lowest-order effect is forbidden in media with inversion symmetry, but allowed at an interface where inversion symmetry is broken. The technique has been productively applied to characterize anchoring of LC molecules [13–17], but has only recently been used to directly examine surface alignment layers [10,18].

To discuss the orientation of the mesogenic core in the molecules of the FLC SAM, we introduce a sample coordinate system. The x-y plane is the surface, with x parallel to the rubbing direction. The inward surface normal is parallel to z. An azimuthal angle ϕ is defined in the surface plane so that $\phi=0$ corresponds to the x axis. The polar angle θ describes inclination away from the surface normal. In these terms, the population of mesogenic units in the sample is characterized by an angular distribution function $g(\theta,\phi)$. We are primarily concerned with anisotropy in the surface plane. This can be revealed by measuring the SHG signal while rotating the sample about its surface normal. The sample rotation angle Φ is defined so that $\Phi=0$ when the rubbing direction is parallel to the projection of the direction of propagation of the incident light onto the surface.

The second-harmonic signal S can be described through a model involving the way in which the nonlinear surface susceptibility $\boldsymbol{\chi}^{(2)}$ is sampled through the configurations of the optical fields [13],

$$S\propto|\mathbf{e}_{2\omega}\cdot\boldsymbol{\chi}^{(2)}:\mathbf{e}_{\omega}\mathbf{e}_{\omega}|^{2}, \tag{1}$$

where $\mathbf{e}_{2\omega}$ and $\mathbf{e}_{\omega}$ describe the outgoing and incident optical polarization vectors at 2ω and ω, respectively. These vectors contain corrections for the Fresnel reflection effect due to the glass substrate and the rotation of the sample, which changes the projection of the optical fields onto the sample coordinate system.

The nonlinear susceptibility of the surface is related to the hyperpolarizability of the molecule, which is defined with respect to the molecular coordinate system a,b,c. In the case where one hyperpolarizability element β_{ccc} is larger than all the rest, a monolayer with a surface number density N_s leads to

$$\chi^{(2)}_{ijk}=N_s\langle(\hat{\boldsymbol{\imath}}\cdot\hat{\boldsymbol{c}})(\hat{\boldsymbol{\jmath}}\cdot\hat{\boldsymbol{c}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{c}})\rangle\beta_{ccc} \tag{2}$$

for the elements of $\boldsymbol{\chi}^{(2)}$. Here, $\hat{\boldsymbol{\imath}}$ is a unit vector along the ith sample coordinate direction and $\hat{\boldsymbol{c}}$ is a unit vector that identifies the orientation of the dominant axis of the molecule. The angular brackets designate an ensemble average over the population of molecules in the sample using the orientation distribution function $g(\theta,\phi)$. If the orientation distribution is isotropic in the sample (x,y) plane, only seven susceptibility elements are nonzero. Of these, only two are unique: $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}=\chi^{(2)}_{xzx}=\chi^{(2)}_{xxz}=\chi^{(2)}_{zyy}=\chi^{(2)}_{yzy}=\chi^{(2)}_{yyz}$. This would be the characteristic of an unrubbed surface. A rubbed surface has mirror (C_{1v}) symmetry, which is associated with the x-z plane. For a sample of this type, there are 14 nonzero susceptibility elements, of which six are unique: $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxx}$, $\chi^{(2)}_{zxx}=\chi^{(2)}_{xzx}=\chi^{(2)}_{xxz}$, $\chi^{(2)}_{zyy}=\chi^{(2)}_{yzy}=\chi^{(2)}_{yyz}$, $\chi^{(2)}_{xzz}=\chi^{(2)}_{zxz}=\chi^{(2)}_{zzx}$, and $\chi^{(2)}_{xyy}=\chi^{(2)}_{yxy}=\chi^{(2)}_{yyx}$.

Anisotropy in the surface plane can be detected by using s-polarized incident light and by measuring the p-polarized second-harmonic signal. For a sample bearing C_{1v} symmetry which is rotated by Φ, Eq. (1) becomes

$$S_{s\rightarrow p} \propto |\chi^{(2)}_{\mathrm{eff}}|^2, \tag{3}$$

where the effective susceptibility includes the influence of the sample rotation and the specific optical polarizations,

$$\begin{aligned}\chi^{(2)}_{\mathrm{eff}} &= a(\chi^{(2)}_{zxx}+\chi^{(2)}_{zyy})+b(\chi^{(2)}_{xxx}+\chi^{(2)}_{xyy})\cos(\Phi)\\ &\quad -a(\chi^{(2)}_{zxx}-\chi^{(2)}_{zyy})\cos(2\Phi)-b(\chi^{(2)}_{xxx}-3\chi^{(2)}_{xyy})\cos(3\Phi).\end{aligned} \tag{4}$$

The coefficients a and b depend upon the angle of incidence and the indices of refraction of the glass at ω and 2ω [13]. In our calculation of a and b we follow the common approximation that the monolayer does not influence the surface fields, which is equivalent to setting the index of refraction for the monolayer equal to unity. From the sample rotation data one can extract the relative magnitudes of the susceptibilities. These are related to the orientation distribution of the molecule through Eq. (2).

To perform the experiment we used a 10 Hz, a Q-switched Nd-YAG (yttrium aluminum garnet) 6-nsec pulsed laser with an output wavelength of 1064 nm. The beam diameter at the sample was ≈ 0.5 cm with the angle of incidence at 45°. The single-pulse energy was kept below 5 mJ. The incident polarization was set by the orientation of a half-wave plate. A long-pass filter placed immediately before the sample blocked any foreign light at the second-harmonic wavelength, 532 nm. After the sample an infrared-blocking filter and a narrow band interference filter removed the light at the incident frequency leaving only the second-harmonic light generated by the sample. A dichroic polarizer in the detection branch of the optical system was set for p polarization. The processed optical signal was detected with a photomultiplier, which was coupled through a preamplifier to a boxcar integrator. The sample was mounted on a stepping-motor equipped stage that enabled it to be rotated about the surface normal. This was controlled by a computer, which also received the output of the boxcar integrator. This enabled improvement of the signal-to-noise quality through the accumulation of data during multiple rotations.

III. RESULTS AND DISCUSSION

Glass slides coated with rubbed W399 monolayers were assembled into cells with the rubbing directions antiparallel. We filled the cell with an achiral high-polarization LC, ZLI3234B, in the nematic phase. This resulted in homeotropic alignment that is very similar to what is achieved with C18 surfactant coated windows. Under a polarizing microscope the cell displayed no observable birefringence in the nematic phase and, upon cooling, was completely black in the smectic-A phase. However, upon further cooling into the smectic-C condition, the LC demonstrated a uniform tilt that was inclined toward the rubbing direction. This implies that the rubbing successfully established an anisotropic surface.

A possible interpretation of the LC cell test results is that the rubbing produced grooves in the surface. These would then promote alignment in the smectic-C phase as the LC organized to minimize the elastic energy. To investigate this hypothesis we performed atomic force microscopy (AFM) on bare glass and glass coated with the W399 SAM before and after rubbing. The SAMs were smooth on the scale of several angstroms and did not show rubbing-induced grooves. Bare glass was similar in smoothness to the SAM and, on this scale, gave AFM images identical to those obtained from the monolayer. We conclude that the surface anisotropy was attained through rubbing-induced changes in the conformations of the molecules in the SAM and that the observed LC alignment was achieved through a short-range template effect.

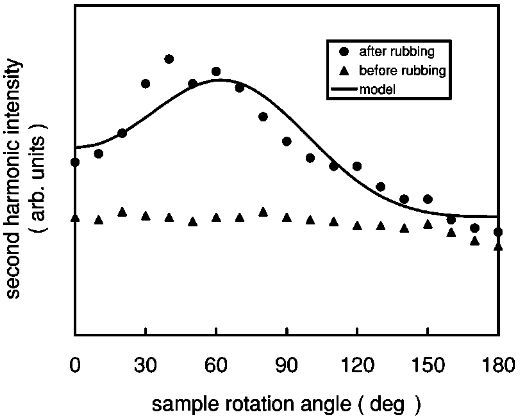

FIG. 2. The SHG intensity obtained from the FLC mesogenic SAM W399 as a function of the angle of rotation of the sample about the surface normal. Data were acquired for a full rotation of 360°. The results from an angle Φ were averaged with those from $(360° - \Phi)$ to minimize the influence of optical misalignment.

The SHG experiment helps to understand the nature of the anisotropy. The SHG results in Fig. 2 show that prior to rubbing, the SHG intensity does not depend on the orientation of the sample. This indicates that the W399 SAM was polar, but that the distribution of the orientations of the mesogenic cores was isotropic in the surface plane. The polar nature of the SAM implies that the cores were organized with a preferential inclination with respect to the surface normal.

After a rubbing treatment, the SHG intensity from the W399 SAM displayed a pronounced dependence on the sample orientation, as indicated by the circles in Fig. 2. The magnitude of this effect depended on the rubbing strength. The result shown in the figure was a characteristic of fairly hard rubbing. The general form of the anisotropy seen in Fig. 2 is similar to what has been reported about SHG analyses of mechanically rubbed mesogenic side-chain polymers [10].

To interpret these data we compare the sample rotation dependence of the SHG signal ($S(\Phi)$) with the prediction from Eqs. (3) and (4). The optical coefficients a and b are known. So the relative magnitudes of the susceptibility elements in Eq. (4) can be extracted through a linear regression fit. This yields $\chi^{(2)}_{xxx}=1.00$, $\chi^{(2)}_{xyy}=0.200$, $\chi^{(2)}_{zxx}=1.73$, and $\chi^{(2)}_{zyy}=1.43$, where χ_{xxx} was arbitrarily set equal to unity. Of particular interest are parameters that describe the anisotropy induced by rubbing. We follow the common approximation that the polar and azimuthal dependencies of the angular distribution function are independent $(g(\theta,\phi)=g_1(\theta)g_2(\phi))$

and that the azimuthal factor can be modeled with a truncated Fourier series,

$$g_2(\phi)=(d_0+d_1\cos(\phi)+d_2\cos(2\phi)+d_3\cos(3\phi)). \quad (5)$$

Using this expression in Eq. (2) for the ensemble averaged surface susceptibility leads to the following associations:

$$\frac{\chi^{(2)}_{xxx}}{\chi^{(2)}_{xyy}}=\frac{\langle\cos^3\phi\rangle}{\langle\cos\phi\sin^2\phi\rangle}=\frac{3+(d_3/d_1)}{1-(d_3/d_1)} \quad (6)$$

and

$$\frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zyy}}=\frac{\langle\cos^2\phi\rangle}{\langle\sin^2\phi\rangle}=\frac{2+(d_2/d_0)}{2-(d_2/d_0)}. \quad (7)$$

From Eq. (6), and the experimental surface susceptibilities, we find that $d_3/d_1=0.337$. Both of these terms contribute to asymmetry in the angular distribution with respect to $+x$ versus $-x$. The ratio of 0.337 is realistic for an asymmetry contribution with an angular half-width of $\approx 45°$. The d_1 and d_3 parameters can be determined independently as can the characteristics of $g_1(\theta)$. However, this requires data obtained from other optical polarization combinations. At this early stage in our study of W399 SAMs, these experiments have not yet been performed.

The primary anisotropy information comes from Eq. (7), which tells us that $d_2/d_0=0.187$. This shows a small but significant preference for the FLC mesogenic core of the molecules in the SAM to be oriented along the rubbing direction. This preference can be characterized by a surface in-plane order parameter Q_s [19], which in our case can be defined as

$$Q_s=\frac{\chi^{(2)}_{zxx}-\chi^{(2)}_{zyy}}{\chi^{(2)}_{zxx}+\chi^{(2)}_{zyy}}=\langle\cos 2\phi\rangle. \quad (8)$$

For an isotropic distribution $Q_s=0$, while complete ordering along the rubbing direction would be associated with $Q_s=1$. Using the data from our experiment, we find that the rubbed W399 SAM is characterized by $Q_s=0.094$. This can be compared to the recently reported results of $Q_s=0.31$ for the in-chain structural units in the surface of rubbed polyimide [18], an alignment layer that is commonly used in commercial LC display technology, and of $Q_s=0.25$ for rubbed mesogenic side-chain polymers, an advanced alignment layer that was synthesized with a similar objective as has motivated our work. Although our surface in-plane order parameter is smaller than that achieved on the rubbed polymers, our system retains the advantage of a monomolecular alignment layer, whereby the separation between a control electrode and the aligned liquid crystal is minimized.

IV. CONCLUSION

As a first step in the design and synthesis of an FLC mesogenic SAM as a switchable alignment layer, we have prepared W399, a triethoxysilane modified variant of the *o*-nitro-1-methylheptyloxyaryl systems. This was successfully assembled onto a glass substrate using a catalyzed dehydration and polysiloxane formation reaction. Our objective at this stage in the program was to determine if mechanical rubbing of this SAM would lead to effective homogeneous alignment of a LC through the molecular template mechanism. We have shown that the system does align an achiral LC in the smectic-*C* phase and that this alignment is not caused by grooves. On the contrary, our optical SHG experiments have shown that the mesogenic core of the FLC SAM adopts an orientation along the rubbing direction with a suface order parameter that is nearly one-third that of the molecules in the surface of rubbed polyimide. We are encouraged by this result and will be performing additional characterization of this promising system. For example, a more complete understanding of the orientation distribution function can be obtained through SHG experiments involving different combinations of the optical polarizations. Surface anchoring of both achiral and chiral LC molecules can be investigated through resonant SHG studies of single-layer and multilayer interactions with the mesogenic SAM. Finally, the response of these phenomena to applied electric fields will reveal whether or not the polar nature of the mesogenic SAM leads to a switchable alignment layer.

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