Rubbing-induced anisotropy of long alkyl side chains at polyimide surfaces

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ABSTRACT

Molecular organization at polyimide surfaces used as alignment layers in liquid crystal displays was investigated using vibrational Sum Frequency Generation (SFG) Spectroscopy. We focus on the orientation of the long alkyl side groups at the polymer surface using polarization-selected SFG spectra of the CH3- and CH2-stretch modes of the side chain. Mechanical rubbing and baking, an accepted industrial procedure used to produce pretilt of the liquid crystal, was found to induce pronounced azimuthal anisotropy in the orientational distribution of the alkyl side chains. Orientational analysis of the SFG vibrational spectra in terms of the azimuthal and tilt angles (in- and out-of-plane, respectively) of the alkyl side chains shows their preferential tilt along the rubbing direction, with the azimuthal distribution narrower for stronger rubbed polymer samples.
INTRODUCTION

The numerous modern applications of polymers often depend on their interfacial properties, which are determined by the surface molecular structure, i.e., orientation and conformation of molecular units at the polymer surface. One example is rubbed polymer films, which have long been used in the liquid crystal (LC) display industry as substrates for obtaining bulk liquid crystal alignment parallel to the substrate plane. There are two main schools of thought for the alignment mechanism: Alignment is induced by the surface topography, as suggested by Berreman, or it comes about by epitaxial growth of liquid crystal alignment from the polymer backbone, which has been extended unidirectionally during the rubbing process. The latter mechanism is more broadly accepted, although it is clear that grooves alone (created lithographically) can induce good planar alignment of the liquid crystal. Other methods exist for inducing planar alignment, most notably irradiation by polarized ultraviolet light on a photosensitive polymer alignment layer. Homeotropic (vertical) LC alignment, on the other hand, generally involves deposition of a long chain surfactant or silane material at the substrate. More recently, interest has grown in obtaining LC orientation that is tilted (often referred to as "pretilt") by a significant polar angle from the normal to the surface. A particularly attractive method to achieve this controllable and robust pretilt involves rubbing of polyimide that contains a long alkyl side chain. Until now the rubbing-induced orientations of the different moieties were inferred from the resulting liquid crystal alignment. In this paper we examine the structure of the rubbed side chains directly.
In the past, several analytical techniques have been employed to study polyimide surfaces, including ellipsometry,\textsuperscript{11} optical retardation,\textsuperscript{3,12} infrared (IR) spectroscopy,\textsuperscript{13} and atomic force microscopy.\textsuperscript{14} However the image of a rubbed polymer surface obtained using atomic force microscopy often is not sufficient to resolve the surface molecular structure.\textsuperscript{14} Second Harmonic Generation (SHG) also has been used to study the rubbed polymer surfaces although the structural information that can be obtained is rather limited.\textsuperscript{15}

Recently, Sum Frequency Generation (SFG) vibrational spectroscopy has been developed as a useful surface analytical technique.\textsuperscript{16,17} It has been successfully applied to study the structure of rubbed polymer surfaces by several researchers during the past decade.\textsuperscript{18-28} The technique is highly surface selective because the SFG signal is forbidden in media with inversion symmetry under the electric dipole approximation, but allowed at interfaces where the inversion symmetry is broken. This allows quantitative determination of molecular orientation and alignment of polymer at a surface. The technique involves three optical waves (IR, visible, SFG), with the infrared input beam providing resonant enhancement by spectrally overlapping with the interfacial vibrational modes. Thus the vibrational spectrum of the interface is obtained. The surface vibrational spectra with different input/output polarization combinations can be used to determine the orientation of selected molecular groups at the surface, providing information on surface structure and composition of polymer.

Several reports can be found in the literature that discuss applications of SFG spectroscopy to investigate the molecular structure at rubbed polymer surfaces, such as
polyvinyl alcohols (PVA), polyimides (PI), polystyrene (PS), and nylon-11. In particular, the question of whether mechanical rubbing induces molecular-level anisotropy has been addressed. In general, the results indicate that rubbing aligns the polymer backbones. This was found for several rubbed polymers, including polyimide, as well as PVA and nylon.

Polymers with alkyl side chains are attractive for LC alignment applications because of their potentially favorable interactions with the similar alkyl side-groups of LC molecules, which may facilitate homotropic (vertical) alignment. However, the question of whether mechanical rubbing can induce side-chain anisotropy at polymer surfaces has not been fully resolved. Studies of polyimides with short side chains (m=1-7 carbon atoms) concluded that rubbing does not induce any appreciable azimuthal (in-plane) anisotropy. The chains were found to project out normally from the surface with a broad orientational tilt distribution (out-of-plane), which is made even broader but still azimuthally isotropic after rubbing. In addition, the authors detected the changes of the structure after adsorption of a (partially deuterated) LC monolayer onto the rubbed polymer surface, which resulted in considerable anisotropy in the spectra of long (m=7) alkyl chains. The proposed interpretation of this observation suggested that the LC monolayer is itself aligned in some way by the rubbed surface, and then the LC in turn aligns the alkyl side chains of the polyimide. Although this result gives indirect evidence of rubbing-induced anisotropy of the polyimide alkyl side chains, the measurement was complicated by the fact that the LC monolayer was only 70% deuterated, and thus the aligned LC molecules significantly contributed to the observed C-H vibrational spectra of the polymer side chains. In another study, it was found that the orientation of phenyl
side groups of polystyrene is affected by rubbing, which aligns them perpendicular to the rubbing direction, with the phenyl planes inclined towards the surface with a rather broad distribution.\textsuperscript{23}

In this work, we investigate orientation of long alkyl side-chains (m>16) at the air/polymer interface of polyamic acid SE-1211 (Nissan Chemical Industries, Ltd.). For the first time, to our knowledge, azimuthal alignment of the alkyl side chains is demonstrated by SFG spectroscopy.

EXPERIMENTAL METHODS

A. Sample Preparation

The polyamic acid SE1211 used in this study was provided by the Nissan Chemical Industries, Ltd. The chemical structure is illustrated in Scheme 1. The exact chain length and the structure of the linker group X is proprietary information of Nissan Chemicals Industries, but the chain is all-alkyl and m is greater than 16 carbon atoms.
Scheme 1. Structure of polyimide S1211 (Nissan Chemicals) used in this study. The side chain length is $m>16$.

In this experiment we have studied three types of polyimide samples: unrubbed, weakly rubbed, and strongly rubbed. All samples were deposited by spin coating the polyamic acid at a spin rate of 2000 rpm for 9 s on CaCl$_2$ substrates; the layer thickness was approximately 100 nm. For the imidization reaction, all three samples were baked at 200$^\circ$C for one hour. Rubbing was performed in order to align the polyimide surface. The rubbing machine involved passing the slide under a roller covered with a woven cloth (Yoshikawa Chemical Co., model YA-20-R) having a fiber density $\sigma_f = 1330$ thread cm$^{-2}$. The rubbing strength was changed by changing the distance between the surface of the cloth and the sample surface. The weakly rubbed samples were prepared under conditions known to produce nearly no pretilt of alkylcyanobiphenyls (nCB) liquid crystals, whereas strongly rubbed samples correspond to conditions producing moderate pretilt.$^{30}$
B. SFG spectroscopy

A detailed description of our experimental setup has been presented elsewhere. Briefly, the Sum Frequency Generation (SFG) spectroscopy set-up is based on a high power amplified femtosecond Ti-Sapphire laser system (Spectra Physics Spitfire sub-50 fs HP). 50% of the 2 mJ fundamental output pulse (800 nm, FWHM < 35 fs measured using a home-built noncollinear single-shot autocorrelator) is used to pump an Optical Parametric Amplifier (OPA) followed by the signal–idler difference frequency mixing in a 0.5 mm thick AgGaS$_2$ crystal producing 75 fs IR pulses (300 cm$^{-1}$ spectral FWHM) centered at 2900 cm$^{-1}$. Spectra of the IR pulses were measured using an IR grating (blazed at 5 µm) in the monochromator and a liquid nitrogen (LN2) cooled MCT detector (IR Associates).

For the frequency-domain spectroscopy, the broad-band SFG scheme was employed that uses spectrally broad IR and narrow visible pulses to obtain the spectrum by frequency-dispersing the SFG signal. A zero-chirp 4-f design pulse stretcher was used to narrow the spectrum of the visible pulse from 430 cm$^{-1}$ of the Spitfire output down to the desired spectral width. The pulse shaper consists of a grating, collimating lens and a mirror equipped with a tunable slit that allows us to control the bandwidth of the visible beam making the spectrum as narrow as necessary. Since the full width at half maximum (FWHM) of the spectral features of the polyimide samples was determined to be greater than 20 cm$^{-1}$ (vide infra), we selected the visible pulse spectral width to be less than 15 cm$^{-1}$ Gaussian FWHM.
The IR and visible beams were spatially and temporally overlapped at the horizontal sample surface. The incidence angle for both beams is 65° from surface normal. The beam diameter at the sample is ~150 µm for both visible and IR beams. The laser power at the sample is 4 µJ/pulse for IR and up to 17-18 µJ/pulse for the visible at 1 kHz repetition rate. The SFG signal reflected from the sample surface was recollimated, spatially and frequency filtered passed through a 300 mm monochromator (Acton Spectra-Pro 300i), and detected using a LN2-cooled CCD (Princeton Instruments Spec-10:100B, 100x1340 pixels). Five pixel binning along the horizontal axis was performed to reduce noise. With this binning, the spectrometer resolution is 2.7 cm⁻¹. The SFG spectrum was obtained by vertical integration of the CCD image. The signals were averaged over many laser shots by using the CCD as the integrator, with acquisition time typically 20-30 min per spectrum. The CCD image was processed using a LabView program to correct for the floating background (typically a few counts per hour) and cosmic X-rays. The background correction was performed by subtracting from the signal region of interest (e.g., horizontal strips 40-45), a non-illuminated region of the CCD of the same size (e.g., horizontal strips 80-85). Spikes due to the cosmic X-rays were eliminated using a differential discriminator program.

The IR frequencies are calculated by subtracting the central frequency of the narrow visible pulse (measured using the same monochromator) from the SFG frequency, \( \omega_{IR} = \omega_{SFG} - \omega_{vis}^o \). In addition, we calibrate the IR frequency scale using a known SFG surface spectrum of dimethyl sulfoxide (DMSO). We estimate our IR frequency calibration accuracy to be ±3 cm⁻¹.
Polarization of the visible beam is controlled by using a zero-order half-wave plate, while the IR beam polarization can be made either horizontal or vertical by using a periscope before the sample. The polarization combination used in these experiments is PPP (SFG-vis-IR).

RESULTS

The experimental geometry and the definition of the surface coordinate system are illustrated in Figure 1. Because we are interested in the azimuthal (in-plane component) orientation of the polymer side chains, we recorded SFG spectra at different azimuthal angles ($\Psi$), defined as the angle between rubbing direction and the plane of incidence of beams. Figure 2 (a-c) shows SFG spectra of unrubbed sample for $\Psi$=0°, 90°, and 180°. Figures 3 and 4 show the series of the SFG spectra of the weakly rubbed (Figure 3) and strongly rubbed (Figure 4) polyimide samples as they are rotated azimuthally with respect to the incidence plane of the laser beams. While the unrubbed sample spectra show little variation as a function of the azimuthal angle $\Psi$, both weakly and strongly rubbed samples show measurable anisotropy which is more pronounced in the case of strongly rubbed samples.

The SFG spectra were recorded at PPP (SFG-vis-IR) polarization combination at room temperature. They cover the CH vibrational stretch region from 2800 cm$^{-1}$ to 3000 cm$^{-1}$, thus focusing on the C-H stretch transitions. As typical for surfaces with oriented alkyl chains, several SFG transitions are expected (and indeed observed) in the spectra,
namely CH$_2$ symmetric stretch (d$^+$) at 2850 cm$^{-1}$, CH$_3$ symmetric stretch (r$^+$) at 2880 cm$^{-1}$, Fermi resonance of CH$_2$ symmetric stretch with CH$_2$ antisymmetric bending overtone (d$^+_{FR}$) at ~2900 cm$^{-1}$, CH$_2$ antisymmetric stretch (d$^-$) at ~2925 cm$^{-1}$, Fermi resonance of CH$_3$ symmetric stretch with CH$_3$ antisymmetric bending overtone (r$^+_{FR}$) 2940-2950 cm$^{-1}$, and CH$_3$ antisymmetric stretch (r$^-$) at 2960-2975 cm$^{-1}$.\textsuperscript{32,35-39}

In our analysis below, we focus on the spectral peaks in the 2850-2880 cm$^{-1}$ range, namely, the CH$_3$ symmetric stretch (r$^+$) of the terminal methyl group of the side chain at 2880 cm$^{-1}$ and the CH$_2$ symmetric stretch (d$^+$) of the chain at 2850 cm$^{-1}$. The reasons for this choice are: (1) the symmetry and the molecular hyperpolarizability tensor elements for the r$^+$ and d$^+$ transitions are well-known\textsuperscript{17,40} and (2) this region is free of contributions from the polymer backbone CH-stretch vibrations, thus allowing us to make unambiguous conclusions pertaining only to the side chain alignment. The lone CH-stretch vibration of the substituted cyclobutane ring of the polyimide backbone is expected above 2900 cm$^{-1}$, based on vibrational spectra of structurally similar compounds. Methylocyclobutane,\textsuperscript{41} ethynylmethyl cyclobutane,\textsuperscript{42} cyclobutylsilane,\textsuperscript{43} and cyclobutyl trifluorosilane\textsuperscript{44} all show the lone CH-stretch frequency in the 2900-2950 cm$^{-1}$ range. Aromatic CH-stretch modes of the backbone are expected above 3000 cm$^{-1}$.

All the spectra were fitted to a series of Lorentzian functions (solid lines passing through the experimental data points in Figures 2, 3 and 4) according to the following expression:

$$I_{SFG-PPS}(\omega_{ir}) \propto \left| X_{PP}^{(2)} (\omega_{ir}) \right|^2 I_{ir} (\omega_{ir}) I_{vis} (\omega_{vis})$$  \hspace{1cm} (1)
where, $I_{IR}$ and $I_{vis}$ are the intensities of IR and visible pulses and $X_{ppp}^{(2)}$ is the macroscopic second order nonlinear susceptibility tensor

$$X_{ppp}^{(2)}(\omega_{IR}) \propto A_{NR}e^{i\phi} + \sum_{j=1}^{N} \frac{B_j \Gamma_j}{(\omega_{IR} - \omega_j) + i\Gamma_j}$$  \hspace{1cm} (2)

The first term in the equation (2) accounts for the nonresonant (instantaneous) part of the response with amplitude $A_{NR}$ and phase $\phi$ with respect to the vibrationally resonant part of the response. The second part of the equation describes the addition of several vibrational resonances with Bloch-type dephasing, with amplitudes of $B_j$ line widths $\Gamma_j$, and transition frequencies $\omega_j$.

The fitting results for the two modes under analysis, $r^+$ (CH$_3$ symmetric stretch) and $d^+$ (CH$_2$ symmetric stretch), are collected in Table 1. In order to analyze the azimuthal dependence of the SFG spectra, we define the intensity of the vibrational mode $j$ as

$$|X_{ppp,j}^{(2)}|^2 \equiv |B_j|^2$$  \hspace{1cm} (3)

The azimuthal dependence of the observed intensity $|X_{ppp,r,c}^{(2)}|^2$ of the terminal methyl $r^+$ band is plotted as a function of the azimuthal angle $\Psi$ for the weakly rubbed (Figure 5) and strongly rubbed polyimide sample (Figure 6). The intensity of the $d^+$ (CH$_2$ symmetric stretch) mode for the strongly rubbed polyimide is shown in Figure 7. All intensities are normalized to the $\Psi=0$ spectrum of that sample. The observed changes in
the methyl and methylene SFG peak intensities are a clear indication of anisotropy in the alkyl side chains at the surface produced by rubbing.

We note that the $d^+$ and $r^+$ modes of the unrubbed sample (Figure 2) do not show any azimuthal dependence, which is an important calibration since it is nearly impossible to rotate the sample with the laser spot exactly on axis, therefore different spots on the surface are sampled by the $\Psi$-dependence measurement.

Due to the SFG propensity rules, the appearance of CH$_2$ vibrational modes in SFG spectra is an indication of symmetry-breaking gauche-defects of the alkyl chain. In other words, the relative intensities of the CH$_2$ vs. CH$_3$ modes in SFG can be used as a qualitative gauge of the conformational order of the alkane chain. Compared to the unrubbed and weakly rubbed samples, CH$_2$ vibrational modes are more pronounced in the SFG spectra of the strongly rubbed sample. This suggests that stronger rubbing may, in addition to alignment, cause conformational changes of the polymer side chains.

**DISCUSSION**

Analysis of the obtained azimuthal dependence of the SFG spectra was performed in order to deduce the molecular orientation at the rubbed polyimide surface. For a given vibrational mode ($r^+$ or $d^+$), we begin by assuming a symmetry-dictated relationship between the elements of the second order nonlinear hyperpolarizability tensor $\beta^{(2)}_{lmm}$, defined in the molecular frame $(a,b,c)$. We approximate the CH$_3$ terminal methyl group
as having $C_{3v}$ symmetry, with $c$ being the $C_3$ symmetry axis. For the totally symmetric $r^+$ vibrational mode, there are only three non-zero components of the $\rho^{(2)}_{lmn}$ tensor,

\begin{equation}
\rho^{(2)}_{auc} = \rho^{(2)}_{bhc}, \quad \rho^{(2)}_{ccc}
\end{equation}

Different values have been reported in the literature for the ratio of the two independent tensor elements $R = \rho^{(2)}_{auc} / \rho^{(2)}_{ccc}$, most in the range from 1.66 to 4.0.\cite{37,45-47} We assume, in accordance with the majority of the reports, the value $R=3.4$ for the terminal methyl of a long-alkyl chain.\cite{40} However, we investigated the sensitivity of the results to this parameter (see below) to ensure that our conclusions are not affected by the uncertainty in the value of $R$.

For the CH$_2$ groups of the chain, we assume approximate $C_{2v}$ symmetry with $c$ being the $C_2$ symmetry axis, $a$ in-plane axis, and $b$ axis perpendicular to CH$_2$ plane. Then the following nonzero tensor elements exist for the totally symmetric $d^+$ vibrational mode:\cite{45}

\begin{equation}
\rho^{(2)}_{auc}, \quad \rho^{(2)}_{ccc}
\end{equation}

The bond additivity model\cite{29,45} suggests the ratio of these elements $\rho^{(2)}_{auc} \approx 2\rho^{(2)}_{ccc}$.

Next, we transform from the molecular frame ($a,b,c$) (represented by indices $l,m,n$) to the surface frame ($x,y,z$) (represented by indices $i,j,k$) to calculate the molecular surface susceptibility tensor

\begin{equation}
\chi^{(2)}_{ijk}(\theta,\psi,\phi) = \sum_{lmn} U_{ijk,lmn}(\theta,\psi,\phi)\rho^{(2)}_{lmn},
\end{equation}
i.e., the susceptibility of a single molecular group (e.g., CH$_3$ or CH$_2$) whose orientation is given by the Euler angles $(\theta, \psi, \phi)$ (Figure 1). The 6$^{th}$ rank transformation tensor $U_{ijklmn}(\theta, \psi, \phi)$ is a product of three Euler matrices. The surface-fixed coordinate system is depicted in Figure 1, with $z$-axis defined as the surface normal, and $xz$-plane being the plane of incidence of the laser beams. (Note: for clarity, Figure 1 shows Euler angles for the whole alkyl chain, whereas these, in fact, determine orientation of the CH$_3$ or CH$_2$ groups). In order to calculate the macroscopic surface susceptibility tensor, we average over the orientational distribution $f(\theta, \psi, \phi)$:

$$X^{(2)}_{ijk}(\Psi) = N \iiint d\theta d\psi d\phi f(\theta, \psi, \phi) \chi^{(2)}_{ijk}(\theta, \psi, \phi)$$  \hspace{1cm} (7)

($N$ is the number of CH$_3$ or CH$_2$ groups at the surface). The orientational distribution is assumed to be Gaussian along $\theta$ (tilt angle) and $\psi$ (azimuthal angle). We assume flat $(1/2\pi)$ distribution along $\phi$ (torsional angle), corresponding to random rotation of each alkyl side group around its chain axis,

$$f(\theta, \psi, \phi) = \frac{1}{4\pi^2 \sigma_\theta \sigma_\psi} \exp \left( -\frac{(\theta - \theta_0)^2}{2 \sigma_\theta^2} - \frac{(\psi - \Psi)^2}{2 \sigma_\psi^2} \right)$$  \hspace{1cm} (8)

where $\theta_0$ is the average tilt angle and $\sigma_\theta$ is the tilt angle distribution width. The azimuthal distribution is assumed to be centered along the rubbing direction, i.e. $\Psi$ is the azimuthal rotation angle of the sample as a whole with respect to the laser beam incidence plane (Figure 1), and $\sigma_\psi$ is the width of azimuthal distribution.

Finally, we calculate the effective susceptibility $X^{(2)}_{ppp}(\Psi)$ for the experimental geometry and beam polarizations,
Here, $\hat{i}, \hat{j}, \hat{k}$ are unit vectors along the axes $x, y, z$ and $\hat{p}$ are unit vectors along the P-polarization of the fields; the scalar products represent projections of the fields onto the surface frame. $L_j(\omega)$ ($j=x, y, z$) are the Fresnel factors representing local fields at the surface for the SFG, visible, and IR beams.\textsuperscript{37,49} For the PPP polarization combination, in general eight components of second-order nonlinear susceptibility contribute to the SFG signal,

$$X_{ppp}^{(2)}(\Psi) = \sum_{ijkl} L_i(\omega_{SFG})L_j(\omega_{vis})L_k(\omega_{IR}) (\hat{i} \cdot \hat{p}_{SFG}) (\hat{j} \cdot \hat{p}_{vis}) (\hat{k} \cdot \hat{p}_{IR}) X_{ijkl}^{(2)}(\Psi)$$

(9)

where $\alpha_{SFG}$, $\alpha_{vis}$, $\alpha_{IR}$ are the angles of incidence with respect to the surface normal for visible, IR and outgoing SFG beams.

For the thin polymer films used in the present study (film thickness $h$ on the order of 100 nm), a few points should be noted regarding the Fresnel factors $L_j(\omega)$. First, interference with the light waves reflected from the bottom surface of the polymer film must be taken into account. The 4-layer model (Figure 8) that includes (1) air ($n_1=1$), (2) air/polymer interfacial layer ($n'$), (3) bulk polymer ($n_2$), and (4) substrate ($n_3$, in our case
CaF$_2$), was considered by Feller, Chen, and Shen, who derived the complex Fresnel factors in the form

\[
L_x(\omega) = 1 - \frac{R_{p12} + R_{p23}e^{2i\beta}}{1 + R_{p12}R_{p23}e^{2i\beta}}
\]

\[
L_y(\omega) = 1 + \frac{R_{s12} + R_{s23}e^{2i\beta}}{1 + R_{s12}R_{s23}e^{2i\beta}}
\]

\[
L_z(\omega) = \left(1 + \frac{R_{p12} + R_{p23}e^{2i\beta}}{1 + R_{p12}R_{p23}e^{2i\beta}}\right)\left(\frac{n_1}{n'}\right)^2
\]

Here $R_{s,p12}$ and $R_{s,p23}$ are the usual reflection Fresnel factors for s or p polarized beams at air/polymer (1-2) and polymer/CaF$_2$ (2-3) interfaces, e.g.

\[
R_{p12} = \frac{n_2 \cos \alpha_1 - n_1 \cos \alpha_2}{n_2 \cos \alpha_1 + n_1 \cos \alpha_2}
\]

\[
R_{s12} = \frac{n_1 \cos \alpha_1 - n_2 \cos \alpha_2}{n_1 \cos \alpha_1 + n_2 \cos \alpha_2}
\]

where $\alpha_1 = \alpha$ is the incidence angle in medium 1, $\alpha_2$ is the refracted angle in medium 2, and $\alpha_3$ is the refracted angle in medium 3, $n_1(\omega)\sin \alpha_1 = n_2(\omega)\sin \alpha_2 = n_3(\omega)\sin \alpha_3$ (Figure 8). Note that all four refractive indices $n_1$, $n_2$, $n_3$, and $n'$ are wavelength-dependent and thus the Fresnel factors have to be evaluated for each frequency, $\omega = \omega_{SFG}$, $\omega_{vis}$, $\omega_{IR}$. The factor

\[
\beta = 2\pi \frac{n_2 h \cos \alpha_2}{\lambda_0}
\]

is the phase for the interference at the air/polymer interface 1-2 between the incident beam and reflection from 2-3 interface, where $h$ is the polymer layer thickness and $\lambda_0$...
wavelength in vacuum. It is easily seen that in the limit \(h/\lambda_0 \to 0\), Eqs. (11-13) yield the Fresnel factors for the 3-layer model \((n_1, n_2, n')\) usually used in the SFG analysis.\(^{37}\)

The second point is that while all media are transparent at the visible (800 nm) and SFG (650 nm) wavelengths, the polymer layer is absorbing at the IR wavelength (in fact it is close to the absorption peak). Thus \(n_2(\omega_{IR})\) is complex and its real part may be well outside the usual range for non-resonant values. We measured the IR absorption spectrum \(A(\omega_{IR})\) of the polyimide film to calculate the imaginary part of the refractive index,

\[
\text{Im}[n_z(\omega_{IR})] = \frac{2.303}{8\pi^2h\omega_{IR}^2} A(\omega_{IR})
\]

and calculated the real part using the Kramers-Kronig relationship (Figure 9).

\[
\text{Re}[n_z(\omega_{IR})] = 1 + 2 \pi \int_0^\infty \frac{\omega \text{Im}[n_z(\omega)]}{\omega^2 - \omega_{IR}^2} d\omega
\]

The refractive index of the interfacial layer \(n'(\omega)\) is the subject of the usual uncertainty in the SFG analysis.\(^{37}\) It can be estimated using the slab model with a hemispherical cavity\(^{28}\)

\[
\left(\frac{1}{n'}\right)^2 = \frac{4n_z^2 + 2}{n_z^2 \left(\frac{n_z^2 + 5}{n_z^2 + 5}\right)}
\]

We find, however, that this model underestimates \(n'\) (giving \(n\) values in the 1.2 – 1.25 range, approximately average between bulk polymer and air) and does not allow us to
reproduce the experimental \( \Psi \)-dependences. The data in Figures 5-7 indicate that \( n' \) is closer to the bulk polymer value (in the 1.3-1.35 range for the nonresonant beams), i.e., that the laser fields at the air/polymer interface are attenuated by the polymer layer. The optical parameters used for the analysis are collected in Table 2.

The calculated \( X_{\mu \nu}^{(2)}(\Psi) \) dependencies are compared with experimental results in Figures 5, 6, and 7 in order to extract information on the orientation of the alkyl side chains, i.e. average tilt angle \( \theta_0 \), width of the tilt distribution \( \sigma_{\theta_0} \), and width of azimuthal distribution around the rubbing direction \( \sigma_{\psi} \) for the methyl and methylene groups. The results of the SFG orientational analysis are summarized in Table 3.

Due to the existing uncertainty in the local field correction factors, we did not perform a global optimization for all three orientational parameters \((\theta_0, \sigma_{\theta_0}, \sigma_{\psi})\). Nevertheless, several trends are clear from this analysis. For the terminal methyl groups of the alkyl side chains, the shape of the \( \Psi \)-dependence can only be reproduced for the average tilt angle \( \theta_0 \) in the range between 25° and 35°. To demonstrate this, \( \Psi \)-dependences of the \( r^+ \) mode for other values of \( \theta_0 \) are plotted in Figures 5 and 6 for comparison. Accordingly, the distribution width \( \sigma_{\theta_0} \) cannot be very broad, \( \sigma_{\theta_0} < 10^\circ \) for the strongly rubbed sample and \( < 15^\circ \) for the weakly rubbed sample. The modulation depth of the \( \Psi \)-dependence of the \( r^+ \) mode corresponds to the distribution width \( \sigma_{\psi} \) of the azimuthal angle for the methyl groups: narrower distribution results in a deeper minimum at \( \Psi = 180^\circ \) (compare the calculated \( \Psi \)-dependencies shown in Figures 5 and 6). For the weakly rubbed surface, we find \( \sigma_{\psi} = 80^\circ \), whereas for the strongly rubbed polyimide, good agreement with the experimental data is achieved for \( \sigma_{\psi} = 30^\circ \). Based on the model
calculations, we estimate ±10° uncertainty in these parameters due to the uncertainty in the local field correction factors. Therefore it can be concluded that stronger rubbing causes a narrower azimuthal distribution of the alkyl side chains, but does not significantly change the tilt angle.

We should emphasize that the polar tilt angle $\theta_0$ corresponds to the symmetry axis of the terminal CH$_3$ group, not to the polar orientation of the alkyl side chain as a whole. For an all-trans alkyl chain, the angle of the terminal C-C bond with respect to the chain axis is ~35°. Our finding of $\theta_0 \approx 30^\circ$ average tilt of the terminal methyl group therefore indicates that the polymer side chains are only slightly tilted from the normal direction. Depending upon the strength of the rubbing, the temperature, the nature of the liquid crystal, such as alkylcyanobiphenyls (nCB), and the number of methylene units in the tail (n), the polar orientation of the LC symmetry axis can vary from a polar pretilt angle of 0° up to ~50°. For the range of rubbing strengths reported in this paper, homeotropic LC alignment with small pretilt angles (<10°) is usually observed, which is consistent with the small tilt angle of the polymer side chain measured by SFG in this work.

For the d$^+$ (CH$_2$ symmetric stretch) vibrational mode, observed in the stronger rubbed sample, we find good agreement with the experimental data for tilt angle of the C$_{2v}$ axis of $\theta_0 = 50^\circ$ from normal, with a somewhat broader distribution than the CH$_3$ groups, $\sigma_\theta = 20^\circ$ (Figure 7). The azimuthal distribution width is the same as for the CH$_3$ group. The more pronounced appearance of the d$^+$ mode of long alkyl chains in surface SFG spectra is usually interpreted as increase in the number of gauche-defects.$^{32,47,51-54}$
Therefore, our results may suggest that stronger rubbing induces some additional gauche-defects in the side chains. It is possible that the azimuthal alignment of the side chains occurs partially by introducing gauche-defects in some of the chains to make their top segments align along the rubbing direction.

The peaks at frequencies above 2900 cm\(^{-1}\) do not show systematic azimuthal dependence. A possible reason for this behavior is that several transitions are overlapped in this frequency range, including the asymmetric stretches and the CH\(_3\) Fermi resonance band (r\(^+\)FR), which is a combination of the symmetric stretch and CH\(_3\) bend overtone. According to a Raman spectroscopic study,\(^55\) the intensity of this band is extremely sensitive to the chain-chain coupling (intermolecular interactions). Azimuthal rotation of the sample results in probing different surface spots, and our laser beam spot size (150\(\mu\)m diameter) may be comparable to the size of the domains with different chain-chain coupling, which can explain the irregular patterns observed for the r\(^+\)FR band. In contrast, the symmetric stretch modes r\(^+\) and d\(^+\) are better decoupled and thus less sensitive to the intra-chain interactions, which was one of the reasons for choosing these modes for orientational analysis.

We note that the length of the alkyl side chain may be a critical parameter in determining whether temporally robust molecular organization (in the present case, azimuthal anisotropy) may be created at the surface. For alkane chain length m > 16, the bulk melting temperature exceeds room temperature, and the surface crystallization has been found to occur within 3°C above the bulk melting transition.\(^56,57\) Qualitatively similar trends have been observed in Langmuir monolayers,\(^53\) Langmuir-Blodgett films,\(^58\)
and comb polymer surfaces.\textsuperscript{59,60} Longer alkane chains tend to exhibit better molecular organization and order at interfaces. Despite many principal differences between these types of surfaces, better molecular order, including two-dimensional crystallization, in the top monolayer of alkyl chains, arises for longer chains (typically, \( m > 10 \)). Such universal behavior presumably is due to the competition between the relatively weak van der Waals interactions between alkyl chains and the entropic advantage of having orientationally and conformationally disordered chains.

CONCLUSIONS

Our results indicate temporally robust azimuthal anisotropy of the long alkyl side chains at polyimide surfaces induced by mechanical rubbing. The chains are found to tilt preferentially along the rubbing direction, and the distribution width decreases as the rubbing strength increases. We also find qualitative evidence that rubbing produces additional \textit{gauche}-defects in the alkyl chains.

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Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for partial support of this research under the ACS-PRF grant #40868-G6. The Liquid Crystal Group at Case Western Reserve (MHZ and CR) is supported by the Department of Energy under grant DE-FG02-01ER45934, and by the NSF under grant DMR-0345109.
References


Table 1. Fitting results for the $r^+$ vibrational mode of weakly rubbed polymer, $r^+$ and $d^+$ vibrational modes of the strongly rubbed polymer. Amplitudes of $r^+$ and $d^+$ modes are normalized to the $r^+$ and $d^+$ amplitudes of the spectra recorded at $\Psi = 0^\circ$ azimuthal angle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Psi$ (deg)</th>
<th>Vibrational mode$^a$</th>
<th>$\omega_j$ (cm$^{-1}$)</th>
<th>$B_j$ (a.u.)$^b$</th>
<th>$I_j$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>strongly rubbed</td>
<td>0</td>
<td>$d^+$</td>
<td>2850</td>
<td>1.00</td>
<td>10.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r^+$</td>
<td>2880</td>
<td>1.00</td>
<td>12.64</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>$d^+$</td>
<td>2848</td>
<td>0.86</td>
<td>8.94</td>
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<tr>
<td></td>
<td></td>
<td>$r^+$</td>
<td>2878</td>
<td>0.70</td>
<td>10.62</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>$d^+$</td>
<td>2849</td>
<td>0.44</td>
<td>16.25</td>
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<td></td>
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<td>$r^+$</td>
<td>2878</td>
<td>0.29</td>
<td>10.58</td>
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<tr>
<td></td>
<td>225</td>
<td>$d^+$</td>
<td>2854</td>
<td>0.60</td>
<td>18.42</td>
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<tr>
<td></td>
<td></td>
<td>$r^+$</td>
<td>2876</td>
<td>0.48</td>
<td>11.03</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>$d^+$</td>
<td>2850</td>
<td>1.00</td>
<td>10.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r^+$</td>
<td>2880</td>
<td>1.00</td>
<td>12.64</td>
</tr>
<tr>
<td>weakly rubbed</td>
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<td>$r^+$</td>
<td>2880</td>
<td>1.00</td>
<td>22.74</td>
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<tr>
<td></td>
<td>90</td>
<td>$r^+$</td>
<td>2881</td>
<td>0.82</td>
<td>19.99</td>
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<tr>
<td></td>
<td>180</td>
<td>$r^+$</td>
<td>2885</td>
<td>0.63</td>
<td>20.91</td>
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<tr>
<td></td>
<td>240</td>
<td>$r^+$</td>
<td>2880</td>
<td>0.73</td>
<td>30.66</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>$r^+$</td>
<td>2880</td>
<td>1.00</td>
<td>14.85</td>
</tr>
</tbody>
</table>

$^a$Vibrational mode assignments: $r^+$ - CH$_3$ symmetric stretch, $d^+$ - CH$_2$ symmetric stretch

Table 2. Optical parameters used in the SFG orientational analysis.

<table>
<thead>
<tr>
<th>Beam</th>
<th>Angle of incidence</th>
<th>Refractive index</th>
<th>n$_2$ (polyimide)</th>
<th>n$_3$ (CaF$_2$)</th>
<th>n' (polymer/air interface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR, 2850 cm$^{-1}$ (d$^+$)</td>
<td>65°</td>
<td></td>
<td>1.7±0.4i</td>
<td>1.41</td>
<td>1.47±0.1i</td>
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<tr>
<td>IR, 2880 cm$^{-1}$ (r$^+$)</td>
<td></td>
<td></td>
<td>1.6±0.2i</td>
<td>1.43</td>
<td>1.45</td>
</tr>
<tr>
<td>Visible (800 nm)</td>
<td>65°</td>
<td></td>
<td>1.53</td>
<td>1.43</td>
<td>1.33</td>
</tr>
<tr>
<td>SFG (650 nm)</td>
<td>65° (outgoing)</td>
<td></td>
<td>1.54</td>
<td>1.44</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 3. Orientational parameters for CH$_3$ and CH$_2$ groups obtained for strongly rubbed and weakly rubbed polymer surfaces.

<table>
<thead>
<tr>
<th>Molecular group</th>
<th>Parameter</th>
<th>Strongly rubbed polymer</th>
<th>Weakly rubbed polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>$\theta_0$</td>
<td>$30^\circ±10^\circ$</td>
<td>$30^\circ±10^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_\theta$</td>
<td>$&lt;10^\circ$</td>
<td>$&lt;15^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_\psi$</td>
<td>$30^\circ±10^\circ$</td>
<td>$80^\circ±10^\circ$</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>$\theta_0$</td>
<td>$50^\circ±15^\circ$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_\theta$</td>
<td>$20^\circ$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_\psi$</td>
<td>$30^\circ±10^\circ$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Experimental geometry and surface coordinate system.
Figure 2. SFG spectra of unrubbed polymer for PPP polarization combination recorded at (a) 0°, (b) 90°, and (c) 180° azimuthal angles.
Figure 3. SFG spectra of weakly rubbed polymer for PPP polarization combination recorded at (a) 360°, (b) 240°, (c) 180°, (d) 90°, and (e) 0° azimuthal angles.
Figure 4. SFG spectra of strongly rubbed polymer for PPP polarization combination recorded at (a) 360°, (b) 225°, (c) 180°, (d) 90°, and (e) 0° azimuthal angles.
Figure 5. Experimentally measured (squares) and calculated (lines) azimuthal angle $\Psi$-dependence of CH$_3$ symmetric mode SFG intensity for weakly rubbed polyimide surface. Parameters used in model calculation: (a) $\theta_0=15^\circ$, $\sigma_\psi = 80^\circ$, (b) $\theta_0=50^\circ$, $\sigma_\psi = 80^\circ$, (c) $\theta_0=30^\circ$, $\sigma_\psi = 80^\circ$. 
Figure 6. Experimentally measured (squares) and calculated (lines) azimuthal angle $\Psi$-dependence of CH$_3$ symmetric mode SFG intensity for strongly rubbed polyimide surface. Parameters used in model calculation: (a) $\theta_0=45^\circ$, $\sigma_\psi=30^\circ$, (b) $\theta_0=30^\circ$, $\sigma_\psi=30^\circ$, (c) $\theta_0=15^\circ$, $\sigma_\psi=30^\circ$. 
Figure 7. Experimentally measured (squares) and calculated (lines) azimuthal angle $\Psi$-dependence of CH$_2$ symmetric mode SFG intensity for strongly rubbed polyimide surface. Parameters used in model calculation: (a) $\theta_0=15^\circ$, $\sigma_\psi=30^\circ$, (b) $\theta_0=65^\circ$, $\sigma_\psi=30^\circ$, (c) $\theta_0=50^\circ$, $\sigma_\psi=30^\circ$. 
Figure 8. The 4-layer model used to calculate the Fresnel coefficients for the SFG orientational analysis.
Figure 9. (a) Real (calculated, dashed blue line, right axis) and (b) Imaginary (measured, solid red line, left axis) parts of the refractive index of polyimide SE-1211 at the IR frequencies used in SFG spectroscopy measurements.