

Sum-frequency generation (SFG) vibrational spectroscopy of side alkyl chain structures of polyimide surfaces

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Sum-frequency generation (SFG) vibrational spectroscopy was used to study how side alkyl chains of a polyimide are oriented at the air-polymer interface and how they are affected by mechanical rubbing and adsorption of a liquid crystal monolayer. The spectra of polyimides with various alkyl chain lengths all indicate that the chains protrude out of the polyimide surface with a very broad distribution. Longer alkyl chains appear to contain more gauche defects. While the polyimide backbones are aligned by rubbing, the side chain orientation is hardly affected. Adsorption of a liquid crystal monolayer on the surface significantly reduces the gauche defects in the alkyl chains.

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INTRODUCTION

Polymer surfaces and interfaces play an important role in many applications. Therefore, they have been extensively studied in the past. It is known that the surface structure and composition of a polymer generally govern the physical and chemical properties of the polymer surface. For advances of polymer surface science and technology, one must be able to characterize polymer surfaces at the molecular level. However, work in this respect has been fairly limited because few available techniques are effective.

In recent years, sum-frequency generation (SFG) vibrational spectroscopy has been developed into a powerful surface analytical probe.^{1,2} It is highly surface-specific and possesses a submonolayer sensitivity. The surface specificity arises because under the electric-dipole approximation, SFG is forbidden in media with inversion symmetry, but allowed at a surface or interface where such symmetry is broken.³ As has been demonstrated, the technique can be used to obtain vibrational spectra of surfaces and interfaces of bulk materials such as neat liquid-liquid,^{4,5} liquid-vapor,⁶⁻⁹ liquid-solid,¹⁰⁻¹⁴ and solid-vapor^{15,16} interfaces. In particular, it is ideally suited for probing polymer surfaces and interfaces. Indeed it has been applied successfully to the studies of surfaces of polyethylene, polypropylene,¹⁷ polyvinyl alcohol,¹⁸ polyimide¹⁹ and others. We report here our recent SFG spectroscopic study of the surface structure of a side-chain polyimide.

Polyimide materials are noted for their good high thermal stability, excellent insulating integrity, and superior electrical and mechanical properties.²⁰⁻²² and are widely adopted as substrates or insulating dielectric materials in modern electronics. Here, we focus on their application in liquid crystal (LC) display devices. Rubbed polyimide is commonly used to yield homogeneous LC bulk alignment in LC displays. The surface structure of rubbed polyimide determines the surface anchoring and pretilt angle of an LC film,

and thus influences the performance of an LC device. It is, therefore, important to know the surface structure of a polyimide and the interfacial interaction between polyimide and LC at the molecular level. For this purpose, a number of techniques have been employed, e.g., ellipsometry²³ and infrared (IR) spectroscopy,²⁴ atomic force microscopy,²⁵ and near-edge x-ray absorption fine structure spectroscopy.²⁶ They have found varying degrees of success. SFG vibrational spectroscopy has the surface monolayer specificity and sensitivity and allows probing of selected atomic groups appearing at the surface. It provides, for example, information on the alignment of polymer backbone at the surface induced by rubbing.

In this paper, we discuss the use of SFG spectroscopy to study the orientation and conformation of alkyl side chains at a side-chain polyimide surface. First, we make sure that SFG reflections from air-polyimide indeed are dominated by contribution from the polyimide surfaces at the interfaces. Second, we show how SFG spectra depend on the alkyl chain lengths, yielding information on change of the chain conformation and the orientation of the terminal methyl groups with the chain length. Finally, we discuss the effects of rubbing and adsorption of an LC monolayer on the polyimide surface.

THEORETICAL BACKGROUND

The basic theory of SFG for surface studies has already been described elsewhere.^{1-3,27,28} Here, we give a brief account for convenience of later discussion. Surface SFG is generated by a second-order nonlinear polarization $P^{(2)}(\omega_{\text{SF}} = \omega_{\text{vis}} + \omega_{\text{IR}})$ induced at an interface by an incoming laser field $E(\omega_{\text{vis}})$ and $E(\omega_{\text{IR}})$. The SFG output intensity in the reflected direction is given by

$$S(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2 |E(\omega_{\text{vis}})E(\omega_{\text{IR}})|^2, \quad (1)$$

with

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$$\chi_{\text{eff}}^{(2)} = [e_{\omega_{\text{SF}}} \cdot L(\omega_{\text{SF}})] \cdot \chi^{(2)} : [e_{\omega_{\text{vis}}} \cdot L(\omega_{\text{vis}})] [e_{\omega_{\text{IR}}} \cdot L(\omega_{\text{IR}})],$$

where $L(\Omega)$ is the transmission Fresnel factor at frequency Ω , and e_{Ω} is a unit vector specifying the polarization of the beam at Ω . The nonlinear susceptibility $\chi^{(2)}$ is related to the molecular polarizability by

$$\chi_{ijk}^{(2)} = N_s \sum_{\xi, \eta, \zeta} \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta}) \rangle \alpha_{\xi\eta\zeta}^{(2)}, \quad (2)$$

where N_s is the surface density of molecules i, j, k refer to the lab coordinates (x, y, z) , ξ, η, ζ refer to the molecular coordinates and the brackets denote an average over a molecular orientational distribution function. Near resonances, we assume that $\alpha^{(2)}$ can be written as

$$\tilde{\alpha}^{(2)} = \tilde{\alpha}_{\text{NR}} + \sum_q \frac{\tilde{a}_q}{(\omega_{\text{IR}} - \omega_q) + i\Gamma_q}, \quad (3)$$

where α_{NR} represents the nonresonant contribution, and a_q , ω_q , and Γ_q denote the strength, resonant frequency and the damping factor of the q th vibrational mode, respectively. We then have

$$S(\omega_{\text{SF}}) \propto \left| \tilde{\chi}_{\text{NR}} + \sum_q \frac{\tilde{A}_{q,\text{eff}}}{(\omega_{\text{IR}} - \omega_q) + i\Gamma_q} \right|^2. \quad (4)$$

Scanning of ω_{IR} over resonances yields a surface SFG spectrum. Note that $(A_q)_{ijk}$ and $(a_q)_{\xi\eta\zeta}$ are related by the same relation as $\chi_{ijk}^{(2)}$ and $\alpha_{\xi\eta\zeta}^{(2)}$ in Eq. (2).

The theory of SFG vibrational spectroscopy shows that the strength of each resonance a_q is described as

$$(a_q)_{\xi\eta\zeta} = -\frac{1}{2\varepsilon_0\omega_q} \frac{\partial\alpha_{\xi\eta}}{\partial Q} \frac{\partial\mu_{\zeta}}{\partial Q}, \quad (5)$$

where ε_0 is permittivity in vacuum, and $\partial\alpha_{\xi\eta}/\partial Q$ and $\partial\mu_{\zeta}/\partial Q$ are derivatives of Raman polarizability and IR dipole moment for the normal mode Q , respectively. In our SFG measurement on alkyl chains, the CH_3 stretch modes were probed. As a simple model for molecular polarizability, we assume that the terminal CH_3 group of alkyl chains has C_{3v} symmetry. We set the symmetry axis of the CH_3 group as $\hat{\zeta}$ and the plane containing $\hat{\zeta}$ and one of the C–H bonds as the $\hat{\xi}$ – $\hat{\zeta}$ plane with $\hat{\xi}$ perpendicular to $\hat{\zeta}$. The normal coordinate for the symmetric stretch mode is $Q = \sqrt{(m_{\text{H}}/3)}(r_1 + r_2 + r_3)$, where m_{H} is the atomic hydrogen mass and r_i is C–H bond stretch distance. Each C–H bond has $\partial\mu/\partial r$ component along the bond direction, and $\partial\mu/\partial Q = (\partial\mu/\partial r)/\sqrt{3/m_{\text{H}}}$. It also has Raman elements $\partial\alpha_{\parallel}/\partial r$ and $\partial\alpha_{\perp}/\partial r$ with α_{\parallel} and α_{\perp} referring to polarizabilities parallel and perpendicular to the bond. We can write $\partial\alpha_{\perp}/\partial r = R(\partial\alpha_{\parallel}/\partial r)$, where $R=0.14$ has been obtained theoretically for a C–H bond.²⁹ We can then find, using the C–H bond additivity model, $\partial\alpha/\partial Q$ and $\partial\mu/\partial Q$, and hence a_q in Eq. (5), in terms of $\partial\alpha_{\parallel}/\partial r$ and $\partial\mu/\partial r$ for the CH_3 stretch modes. We obtain for the symmetric stretch

$$(a_s)_{\xi\xi\zeta} = (a_s)_{\eta\eta\zeta} = \frac{4+5R}{1+8R} (a_s)_{\zeta\zeta\zeta} = \frac{4+5R}{9} a_0, \quad (6)$$

with

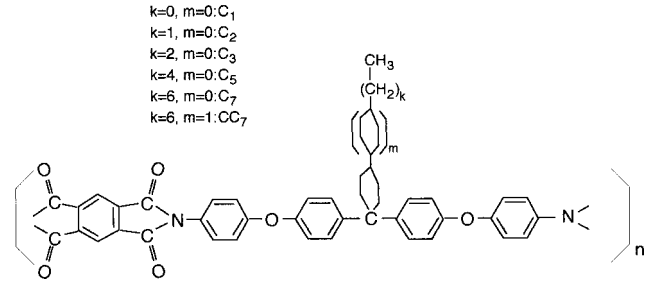


FIG. 1. Chemical structures of polyimide used in this study.

$$a_0 = -\frac{1}{2\varepsilon_0\omega_q m_{\text{H}}} \frac{\partial\mu}{\partial r} \frac{\partial\alpha_{\parallel}}{\partial r}. \quad (7)$$

In Refs. 29 and 30, $\partial\alpha_{\parallel}/\partial r$ and $\partial\mu/\partial r$ for CH have been determined to be $3.0 \times 10^{-30} \text{ mCV}^{-1}$ and $-2.9 \times 10^{-20} \text{ C}$,³⁰ respectively. We then have $a_0 \approx 5.4 \times 10^{-27} \text{ m}^4 \text{V}^{-1} \text{ s}^{-1}$.

If $(A_s)_{ijk}$ for the CH_3 symmetric stretch can be deduced from fitting the corresponding resonance feature in the SFG spectra, we can determine the average orientation of the CH_3 group using Eq. (2) with A_s and a_s replacing $\chi^{(2)}$ and $\alpha^{(2)}$, respectively. We have explicitly for an isotropic surface

$$\begin{aligned} (A_s)_{xxz} &= (A_s)_{yyz} = \frac{1}{2} N_s (a_s)_{\zeta\zeta\zeta} \\ &\quad \times [(1+u)\langle \cos \theta \rangle \\ &\quad - (1-u)\langle \cos^3 \theta \rangle], \\ (A_s)_{xzx} &= (A_s)_{yzy} \\ &= (A_s)_{zxx} \\ &= (A_s)_{zyy} = \frac{1}{2} N_s (a_s)_{\zeta\zeta\zeta} [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] (1-u), \end{aligned} \quad (8)$$

where $u = (4+5R)/(1+8R)$, and θ is the angle between the symmetric axis of CH_3 and the surface normal.

EXPERIMENT

Figure 1 illustrates the chemical structures of side-chain polyimides used in this study. The alkyl side chain is connected to the backbone through cyclohexane and its length can be varied. The different side chains are symbolized by $C_m C_k$ shown in Fig. 1. We have studied samples with $(m=0, k=1, 2, 3, 5, \text{ and } 7)$ labeled as $C_1, C_2, C_3, C_5,$ and C_7 and $(m=1, k=7)$ labeled as CC_7 . In our experiment, the polyimide samples with a layer thickness of $\sim 40 \text{ nm}$ were prepared by spin-coating on fused quartz. To obtain uniform layers, polyamic acid solutions were first filtered with membrane filters. It was then spin-coated on a substrate at 3500 rpm for 60 s. For the imidization reaction, the samples were baked at 250°C for 20 min. Rubbing to align the polyimide surface structure to the saturation level was carried out by a rubbing machine with a velvet cloth. Deuterated 4'-n-pentyl-4-cyanobiphenyl (5CB) was used in our experiment of LC monolayers deposited on polyimide. The deposition was done by evaporation of 5CB at 70°C and moni-

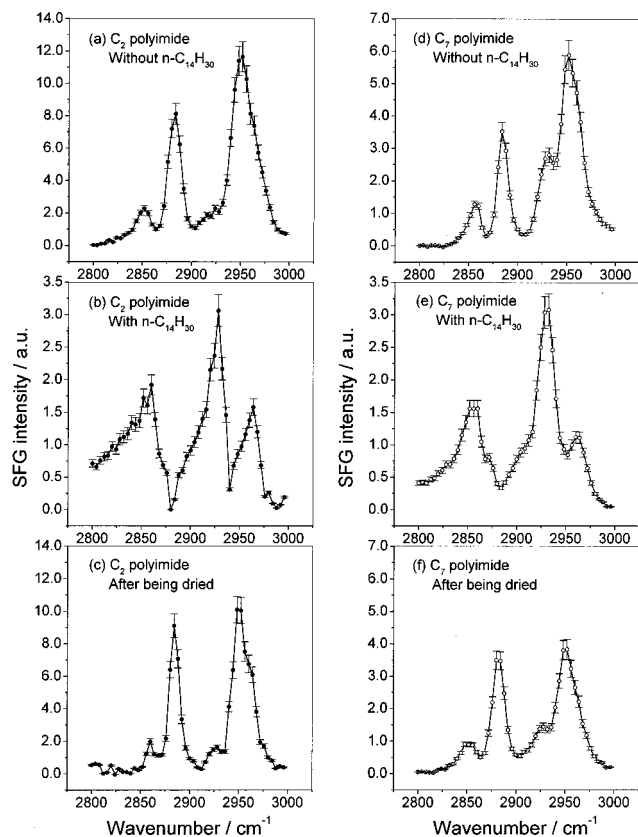


FIG. 2. SFG spectra for C_2 and C_7 polyimides. (a)–(c) describe spectra for C_2 polyimide in air, immersed in n -tetradecane, and removed from n -tetradecane and dried, respectively. (d)–(f) describe spectra for C_7 polyimide similarly prepared.

toring the second harmonic generation (SHG) signal *in situ*. The SHG output appeared saturated when the surface coverage of 5CB reached a monolayer.

The experimental setup for the surface SFG measurement has also been described elsewhere.^{1,2,5,15,31} Briefly, a picosecond Nd:YAG laser (Continuum, PY61) operating at 20 Hz was used to pump an optical parametric system and generate a tunable near-IR output. Difference frequency mixing of the latter and the laser beam in a LiNbO_3 crystal yielded an IR output tunable from 2.6 to 3.7 μm , with a pulse energy of $\sim 100 \mu\text{J}$, a pulsewidth of ~ 15 ps, and a linewidth of $\sim 6 \text{ cm}^{-1}$. For the SFG experiment, the laser beam at 1.06 μm (used as the “visible” input) and the tunable IR beam were overlapped at the sample surface with incidence angles of 45° and 57° , and approximate spot sizes of 1.2 and 0.5 mm, respectively. The SFG signal in the reflected direction was recorded by a CCD camera after appropriate filtering.

RESULTS AND DISCUSSION

We first present in Figs. 2(a) and 2(d) as examples SFG reflection spectra from C_2 and C_7 air–polyimide interfaces. The spectra were taken with the SSP (SF output, visible input, and IR input are s -, s -, and p -polarized, respectively) polarization combination at room temperature. They cover the CH stretch region from 2800 to 3000 cm^{-1} for the side chain. The CH stretch modes associated with the polyimide

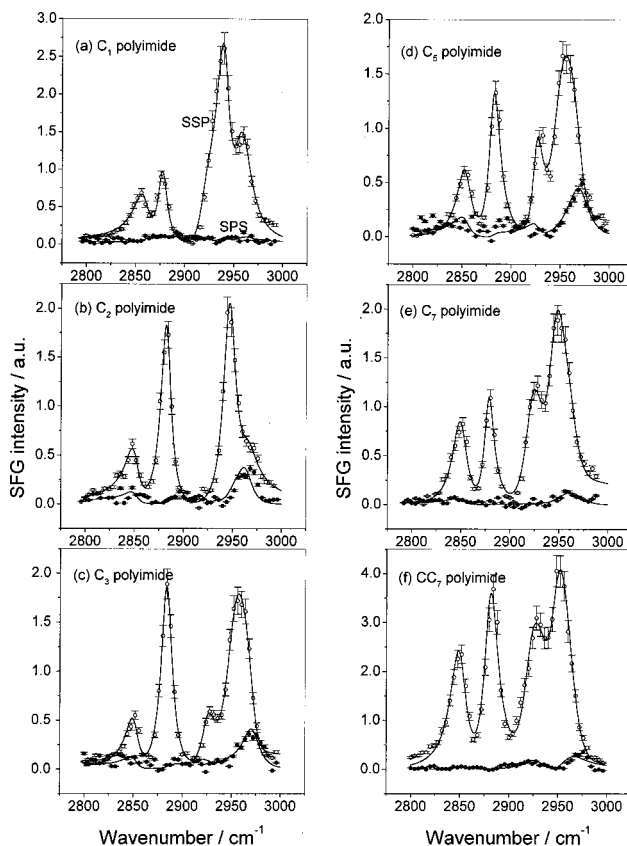


FIG. 3. SFG spectra for polyimides with different side alkyl chain lengths. Open and solid circles refer to data taken with SSP and SPS polarization combinations. Solid lines are fit with Eq. (4).

backbone appear above 3000 cm^{-1} , which we have confirmed using poly[4,4'-oxydiphenilene-pyromellitimide], a polyimide without side chains. Before interpreting the spectra, however, it is important to be sure that the spectra do originate from the air–polyimide interface. As is well known, electric-quadrupole contribution from the bulk may also contribute to SFG although in many cases it appears negligible. In our case of thin polymer films, we must also worry about possibly significant SFG from the polyimide/fused quartz interface. To check these points, an effective way is to perturb the interface under investigation and see how the SFG spectrum changes. In our experiment, we immersed the polyimide sample in n -tetradecane liquid and carried out the reflection SFG measurement from the fused quartz side. The observed spectra are shown in Figs. 2(b) and 2(e). It is seen that the CH_3 symmetric stretch mode at 2875 cm^{-1} associated with the polyimide side chains disappear completely. This is because the contribution from CH_3 of tetradecane at the interface cancels that from the polyimide side chains. In addition, the other peaks in the spectra also change drastically. When the samples were removed from the tetradecane liquid and dried, the spectra completely recovered, as displayed in Figs. 2(c) and 2(f). The results indicate that the SFG spectra we obtained from the air–polyimide side were indeed dominated by contribution from that interface.

We now present in Fig. 3 the SFG spectra of air–polyimide interfaces for side-chain polyimides with different

TABLE I. Parameters of a z -cut quartz crystal that was used to normalize SFG spectra.

	ω_{SF}	ω_{vis}	ω_{IR}
Wavelength $\lambda/\mu\text{m}$	0.814	1.06	3.47
Refractive index $n=n_0$	1.539	1.534	1.490
Beam angle β/deg	20.1	45.0	57.0
Fresnel factor L_{xx}	0.806	0.900	1.009
L_{yy}	0.770	0.684	0.613

alkyl chain lengths and with the SSP and SPS polarization combinations. As typical for alkyl chains, five vibrational modes can be identified in the spectra: CH_2 symmetric stretch (d^+) at $\sim 2850\text{ cm}^{-1}$, CH_3 symmetric stretch (r^+) at $\sim 2875\text{ cm}^{-1}$, CH_2 antisymmetric stretch (d^-) at $\sim 2920\text{ cm}^{-1}$, Fermi resonance of CH_3 symmetric stretch with bending overtone (r_{FR}^+) at $\sim 2950\text{ cm}^{-1}$ and CH_3 antisymmetric stretch (r^-) at $\sim 2970\text{ cm}^{-1}$. The spectra for polyimides with different chain lengths are different, mainly due to changes in chain conformation. All spectra can be fit by the expression in Eq. (4) as described by the solid lines in Fig. 3.

The C_1 polyimide has the shortest side chain composed of only a CH_3 group and cyclohexane link. Its SSP spectrum in Fig. 3(a) is dominated by the three peaks associated with CH_3 , but two CH_2 modes at ~ 2850 and $\sim 2925\text{ cm}^{-1}$ also show up. The latter must come from the CH_2 groups on the cyclohexane link. That the CH_3 modes are prominent in the SSP spectrum but not discernible in SPS indicates that CH_3 has a very broad orientational distribution with its average along the surface normal, similar to the case of methanol.⁶ Compared to those of C_1 polyimide, the spectra of C_2 and C_3 polyimides [Figs. 3(b) and 3(c)] exhibit significant changes. The r^+ mode for CH_3 becomes more pronounced in the SSP spectrum while the r^- mode appears weaker. The d^+ CH_2 mode barely changes, indicating that it comes mainly from the cyclohexane link. In the SPS spectrum, the r^- mode is now clearly visible. These observed spectra can be understood if we assume that the cyclohexane links of the C_1 – C_3 polyimides are similarly oriented at the surfaces. For the C_1 polyimide, the CH_3 spectral features in the spectra are qualitatively the same as those of the air–methanol interface. Then as in the methanol case, we can conclude that the CH_3 groups protruding out at the C_1 polyimide surface are oriented on average along the surface normal with a broad distribution. The spectra of C_2 and C_3 are qualitatively similar to those of a surface monolayer of all-trans alkyl chains oriented more or less along the surface normal (although the less intense r^- peak in SPS suggests that the former has a much broader distribution). In this case, the average orientation of then CH_3 groups has a 35° tilt from the surface normal. We can therefore conclude that for the C_1 – C_3 polyimides, the orientations of the alkyl chains at the surface are similar to those of the C_1 – C_3 alcohols, with probably broader orientational distributions. This implies that the cyclohexane links for the C_1 – C_3 polyimides, have similar orientations at the surfaces. The same appears to be for polyimides with longer alkyl chains [C_5 , C_7 , CC_7 in Figs. 3(d)–3(f)]. However, gauche defects set in with the longer chain lengths to enhance the CH_2 modes in the SSP spectra, but the

TABLE II. Parameters used in the calculation of $(A_q)_{yyz}$ and $(A_q)_{yzy}$.

	ω_{SF}	ω_{vis}	ω_{IR}
Wavelength $\lambda/\mu\text{m}$	0.814	1.06	3.47
Refractive index n	1.453	1.450	1.410
Beam angle β/deg	20.1	45.0	57.0
Fresnel factor L_{xx}	0.832	0.920	1.023
L_{yy}	0.799	0.717	0.649
L_{zz}	1.168	1.080	0.977

amount of defects seems small as judged from their relatively weak spectral peaks.

As seen from Eq. (8), we can find $\langle \cos \theta \rangle$ and $\langle \cos^3 \theta \rangle$ if $(A_{r^+})_{yyz}$ and $(A_{r^+})_{yzy}$ for the r^+ mode as well as N_s and $(a_{r^+})_{\zeta\zeta\zeta}$ are known. We can then in principle determine the average tilt angle θ_0 and the width of the distribution $\Delta\theta$ assuming a Gaussian distribution for θ . From the SFG spectra of SSP and SPS polarization combinations, we can deduce $(A_{r^+})_{yyz}$ and $(A_{r^+})_{yzy}$ from

$$(A_{r^+})_{\text{eff,SSP}} = L_{yy}(\omega_{\text{SF}})L_{yy}(\omega_{\text{vis}})L_{zz}(\omega_{\text{IR}})\sin\beta_{ir}(A_{r^+})_{yyz},$$

$$(A_{r^+})_{\text{eff,SPS}} = L_{yy}(\omega_{\text{SF}})L_{zz}(\omega_{\text{vis}})L_{yy}(\omega_{\text{IR}})\sin\beta_{\text{vis}}(A_{r^+})_{yzy}, \quad (9)$$

where L_{ii} 's are the Fresnel factors, the calculated values of which for our systems are listed in Tables I and II. The SFG spectral intensities were normalized against SFG from a reference z -cut quartz crystal. We obtained from Fig. 3 $(A_{r^+})_{\text{eff,SSP}} = (6.6 \pm 2.4) \times 10^{-10}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$ and $(A_{r^+})_{\text{eff,SPS}} = (0 \pm 0.1) \times 10^{-10}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$ for the C_1 polyimide. We also have $N_s \approx 1.2 \times 10^{14}/\text{cm}^2$ and from Eq. (6), $(a_{r^+})_{\zeta\zeta\zeta} = 0.24a_0 = 1.3 \times 10^{-27}\text{ m}^4\text{ V}^{-1}\text{ s}^{-1}$. We then find $(A_{r^+})_{yyz} = (1.4 \pm 0.6) \times 10^{-9}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$, $(A_{r^+})_{yzy} = (0 \pm 0.2) \times 10^{-10}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$, $\langle \cos \theta \rangle = 0.40$, and $\langle \cos^3 \theta \rangle = 0.40$.

Unfortunately, the very weak SPS spectrum of the C_1 polyimide prevents us from deducing meaningful quantitative information (namely, θ_0 and $\Delta\theta$ with not too large an uncertainty) about the orientation of the side chains. This is also true for the other polyimides. However, the results do indicate that for all polyimides studied here the side chains at

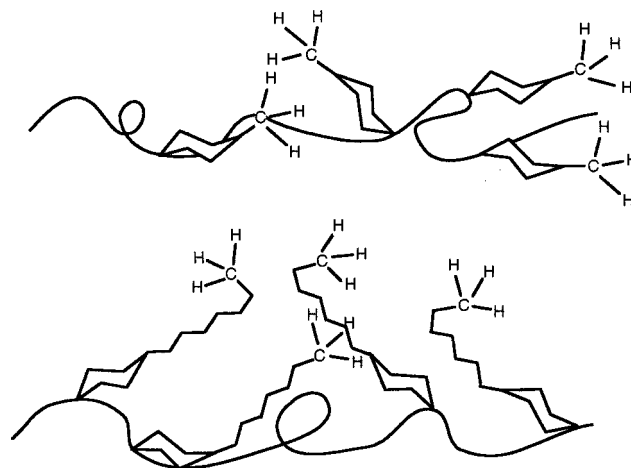


FIG. 4. A schematic model of side alkyl chain structure at the air–polyimide interface.

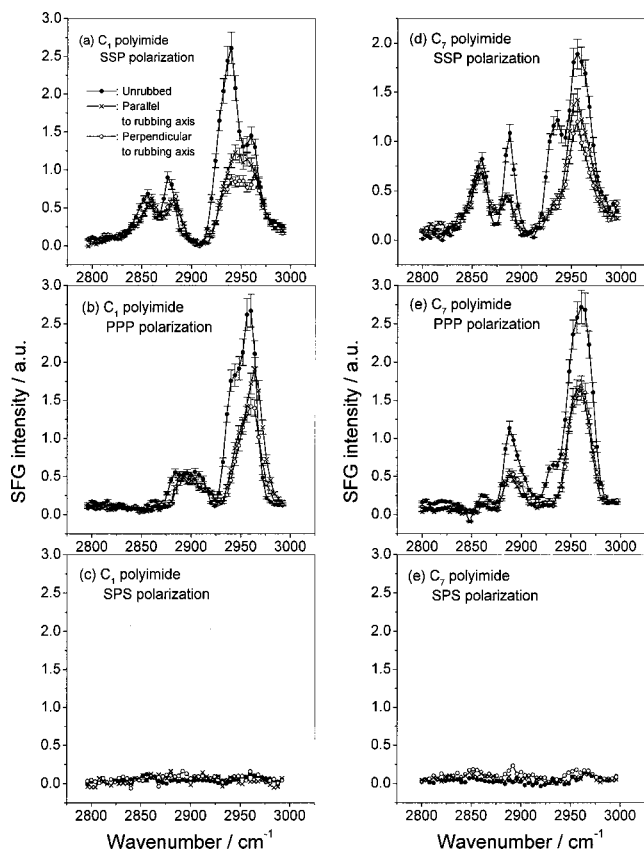


FIG. 5. SFG spectra for C_1 [(a)–(c)] and C_7 [(d)–(f)] polyimides before and after rubbing, with SSP [(a) and (d)], PPP [(b) and (e)], and SPS [(c) and (f)] polarization combinations. Solid circles, open circles, and crosses refer to data taken from unrubbed surfaces and rubbed surfaces with incident plane perpendicular and parallel to the rubbing direction, respectively.

the surface are pointing outward along the surface normal with a very broad orientational distribution. Figure 4 shows a schematic model of the side-chain arrangement at a polyimide surface. The cyclohexane link protruding out of the surface is stable in the chair-shaped conformation. For the C_1 polyimide, the CH_3 group sits at the top of the chair. The surface CH_3 groups are then expected to have the same broad orientational distribution of cyclohexane at the surface with an average along the surface normal. For other side-chain polyimides, the surface structures are similar, except that CH_3 on C_1 polyimide is replaced by an alkyl chain (or another cyclohexane ring with an alkyl chain in the case of CC_7). For longer chain lengths, gauche defects are likely to appear near the terminal end.

To see how mechanical rubbing changes the alkyl side chain structures of polyimide at a surface, we measured SFG spectra of C_1 and C_7 polyimide thin films before and after rubbing as shown in Fig. 5. The spectra were taken with and without rubbing, and the rubbed films were measured so that the incoming beam was parallel and perpendicular to the rubbing direction with the polarization combinations of SSP, PPP, and SPS, respectively. Comparing the spectra between rubbed and unrubbed films, the intensity of the r^+ and r_{FR}^+ modes in the rubbed films was decreased, and especially in the case of C_7 polyimide, the intensity of d^- mode was also reduced in comparison to the unrubbed polyimide film. If the side chains were reoriented towards the rubbing direction, an

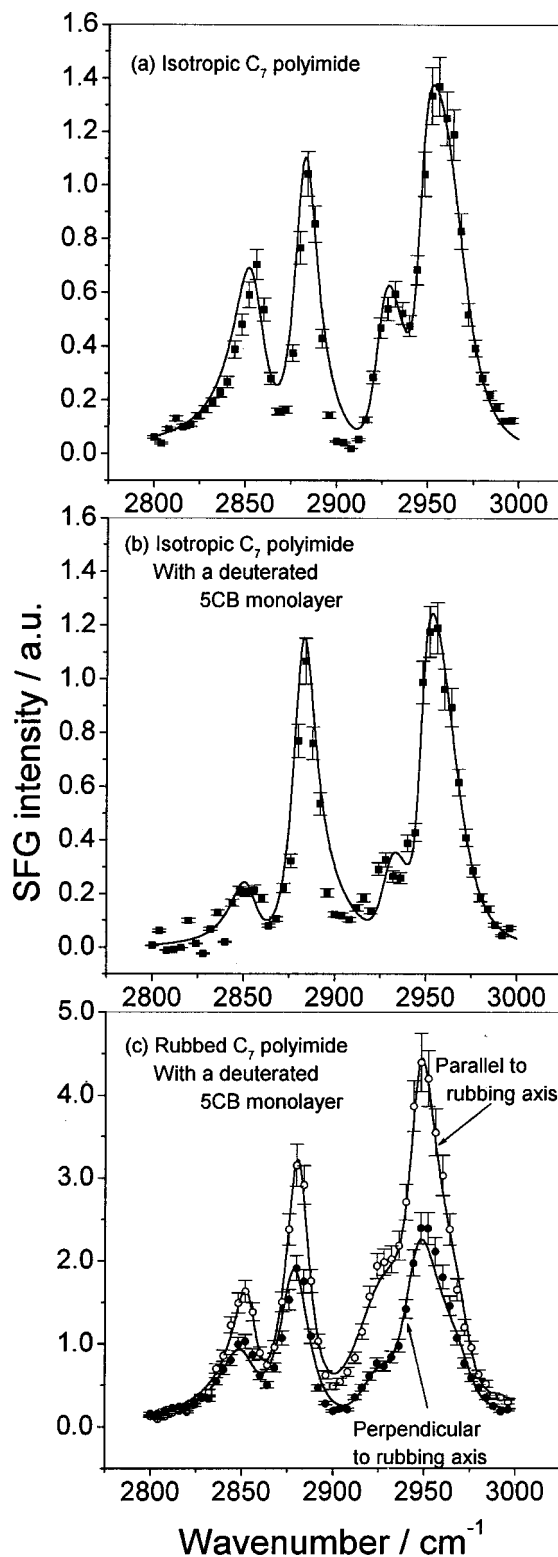


FIG. 6. SFG spectra for an unrubbed C_7 polyimide film (a) without and (b) with a deuterated 5CB monolayer, and (c) SFG spectra of a deuterated 5CB monolayer on a rubbed C_7 polyimide.

anisotropy in the SFG spectra would be expected, e.g., the $\text{CH}_3 r^+$ mode would be stronger along the rubbing direction. However, the anisotropy exhibited in Fig. 5 is very weak. In the SPS spectra, the spectral features are still hardly detectable. The results suggest that the side alkyl chains on polyimides are not appreciably reoriented by rubbing, although

second harmonic generation measurements on these polyimides do indicate alignment of the polymer backbones by rubbing. The lower spectral intensities in the SSP spectra of the rubbed polyimides compared to the unrubbed ones can be understood as the result of a broader orientational distribution of the side chains after rubbing.

Figure 6 presents the SFG spectra (SSP) of a C_7 polyimide film with and without an LC monolayer on it. The significantly reduced CH_2 peaks in the spectrum with an LC monolayer indicates a significant reduction of gauche defects in the C_7 alkyl side chain. In the literature, the ratio of the peak strength of the d^+ mode to that of the r^+ mode ($G = A_{d^+}/A_{r^+}$) in the SSP spectrum is used as a measure to describe the relative conformational order of alkyl chains. From Figs. 6(a) and 6(b), we obtain for the unrubbed C_7 polyimide surface without and with the $5CB$ monolayer, $G = 0.76$ and 0.39 , respectively. The difference of these ratios would be considerably larger were it not for the fact that the cyclohexane links always contribute appreciably to the observed CH_2 peaks. We originally had intended to use completely deuterated $5CB$ to remove the SFG signal from the alkyl chains of $5CB$. Unfortunately, IR absorption spectroscopy shows that deuteration achieved on $5CB$ was only about 70%. Thus the spectra in Fig. 6 are the sum of the signal from polyimide and $5CB$. Even so, the observed spectra still allow us to conclude that the gauche defects of the alkyl side chains of a polyimide are greatly reduced upon adsorption of an LC monolayer. For a rubbed C_7 polyimide surface without and with a $5CB$ monolayer, the observed SFG spectra yielded $G = 1.17$ and 0.55 , respectively. In addition, as shown in Fig. 6(c), we did observe an appreciable anisotropy in the spectra for the rubbed C_7 polyimide surface with a $5CB$ monolayer. Presumably this is because the $5CB$ monolayer is aligned with the rubbed surface and its interaction with the long alkyl chains of the C_7 polyimide aligns the alkyl chains at the surface. The reduction of gauche defects in the alkyl chains at a polyimide surface by adsorption of an LC monolayer is possibly due to an exclusive volume effect.^{32,33}

CONCLUSION

We have used SFG vibrational spectroscopy to study surfaces of polyimides with alkyl side chains, rubbed and unrubbed, with and without an adsorbed deuterated $5CB$ monolayer in the CH stretch region. The drastic difference between the SFG spectra with the polyimide samples in air and in *n*-tetradecane assures that the spectra come from the air-polyimide interfaces. Analysis of the spectra indicates that the cyclohexane-linked alkyl side chains protrude out of the surface with a very broad orientational distribution. Different spectra for polyimides with different alkyl chain lengths reflects mainly the increased disordering of chain conformation with increased chain length at the surface. Rubbing causes alignment of the polyimide, but does not significantly affect the orientation of the alkyl side chains. The broadly distributed alkyl chains, however, become more ordered at the surface in both orientation and conformation with adsorption of an LC monolayer on the surface.

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- ¹Y. R. Shen, in *Proceedings of the International School of Physics "Enrico Fermi," Course CXX, Frontier in Laser Spectroscopy*, edited by T. W. Hansch and M. Inguscio (North Holland, Amsterdam, 1994), p. 139.
- ²Y. R. Shen, *Surf. Sci.* **299/300**, 551 (1994).
- ³Y. R. Shen, *The Principle of Nonlinear Optics* (Wiley, New York, 1984).
- ⁴Q. Du, E. Freysz, and Y. R. Shen, *Science* **264**, 826 (1994).
- ⁵D. E. Gragson and G. L. Richmond, *Langmuir* **13**, 4804 (1997).
- ⁶R. Superfine, J. Y. Huang, and Y. R. Shen, *Phys. Rev. Lett.* **66**, 1066 (1991).
- ⁷Q. Du, R. Superfine, E. Freysz, and Y. R. Shen, *Phys. Rev. Lett.* **70**, 2313 (1993).
- ⁸C. D. Stanners, Q. Du, R. P. Chin, P. Cremer, G. A. Somorjai, and Y. R. Shen, *Chem. Phys. Lett.* **232**, 407 (1995).
- ⁹G. A. Sefler, Q. Du, P. B. Miranda, and Y. R. Shen, *Chem. Phys. Lett.* **235**, 347 (1995).
- ¹⁰S. R. Hatch, R. S. Polizzotti, S. Dougal, and P. Rabinowitz, *Chem. Phys. Lett.* **196**, 97 (1992).
- ¹¹S. R. Hatch, R. S. Polizzotti, S. Dougal, and P. Rabinowitz, *J. Vac. Sci. Technol. A* **11**, 2232 (1993).
- ¹²Q. Du, E. Freysz, and Y. R. Shen, *Phys. Rev. Lett.* **72**, 238 (1994).
- ¹³D. Zhang, R. S. Ward, Y. R. Shen, and G. A. Somorjai, *J. Phys. Chem. B* **101**, 9060 (1997).
- ¹⁴D. Zhang, R. S. Ward, Y. R. Shen, and G. A. Somorjai, *Polym. Reprints (Am. Chem. Soc. Div. Polym. Chem.)* **38**, 674 (1997).
- ¹⁵R. P. Chin, J. Y. Huang, T. J. Chuang, H. Seki, and Y. R. Shen, *Phys. Rev. B* **54**, 8243 (1996).
- ¹⁶Z. Chen, D. H. Gracias, and G. A. Somorjai, *Appl. Phys. B: Lasers Opt.* **68**, 549 (1999).
- ¹⁷D. Zhang, Y. R. Shen, and G. A. Somorjai, *Chem. Phys. Lett.* **281**, 394 (1997).
- ¹⁸X. Wei, X. Zhuang, S. Hong, T. Goto, and Y. R. Shen, *Phys. Rev. Lett.* **82**, 4256 (1999).
- ¹⁹D. Kim and Y. R. Shen, *Appl. Phys. Lett.* **74**, 3314 (1999).
- ²⁰E. D. Feit and C. W. Wilkins, *Polymer Materials for Electronic Applications, APS Symp. Ser. Vol. 184* (American Chemical Society, Washington, D.C., 1982).
- ²¹*Polyimides Synthesis, Characterization and Applications*, edited by K. L. Mittal (Plenum, New York, 1984).
- ²²*Recent Advances in Polyimide Science and Technology*, edited by W. D. Weber and M. R. Gupta (Society of Plastics Engineers, Mid-Hudson Section, 1987).
- ²³I. Hirose, *Jpn. J. Appl. Phys.* **35**, 5873 (1996).
- ²⁴R. Hasegawa, Y. Mori, H. Sasaki, and M. Ishibashi, *Jpn. J. Appl. Phys.* **35**, 3492 (1996).
- ²⁵Y. M. Zhu, L. Wang, Z. H. Lu, Y. Wei, X. X. Chen, and J. H. Tang, *Appl. Phys. Lett.* **65**, 49 (1994).
- ²⁶Y. Ouchi, I. Mori, M. Sei, E. Ito, T. Araki, H. Ishii, K. Seki, and K. Kondo, *Physica B* **208&209**, 407 (1995).
- ²⁷Y. R. Shen, *Annu. Rev. Phys. Chem.* **40**, 327 (1989).
- ²⁸Y. R. Shen, in *Nonlinear Spectroscopy for Molecular Structure Determination*, edited by R. W. Field, E. Hirota, J. P. Maier, and S. Tsuchiya, IUPAC Chemical Data Series (Blackwell Science, Oxford, UK, 1998), Chap. 10.
- ²⁹K. M. Gough, *J. Phys. Chem.* **91**, 2424 (1989).
- ³⁰K. B. Wiberg and J. J. Wendolosky, *J. Phys. Chem.* **88**, 586 (1984).
- ³¹J. Y. Zhang, J. Y. Huang, Y. R. Shen, and C. Chen, *J. Opt. Soc. Am. B* **10**, 1758 (1993).
- ³²T. Sugiyama, S. Kuniyasu, D.-S. Seo, H. Fukuro, and S. Kobayashi, *Jpn. J. Appl. Phys.* **29**, 2045 (1990).
- ³³D.-S. Seo, K. Araya, N. Yoshida, M. Nishikawa, Y. Yabe, and S. Kobayashi, *Jpn. J. Appl. Phys.* **34**, L503 (1995).