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Study of the molecular orientation of steroidal side chains at polyimide surfaces using sum frequency generation vibrational spectroscopy

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ABSTRACT

The molecular orientation of steroidal side chains at rubbed polyimide (PI) surfaces is studied by sum frequency generation (SFG) vibrational spectroscopy. The main objective is to find a correlation between the molecular structure of the PI film and the liquid crystal alignment on the polymer. Analysis of the SFG spectra shows that rubbing of the polymer film appears to cause conformational changes in the methyl group of the polymer side chain near the steroidal structure. However, rubbing does not significantly influence the orientation of the isopropyl group at the end of the polymer side chain. This shows that the liquid crystal alignment is not correlated with the orientation of the isopropyl group.

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I. INTRODUCTION

Owing to extensive research and development, the liquid crystal display (LCD) has become an essential component of electronic devices, such as smartphones, flat-screen televisions, and laptop personal computers (PCs). In a conventional LCD device, the liquid crystal (LC) molecules are sandwiched between two alignment layers. The angle between the plane of the alignment layer and the axis of the LC molecule is called the pretilt angle. This angle plays an important role in determining the optical and electrical performance of LCD devices. If the pretilt angle is not constant throughout the LCD panel, the orientation of the LC molecule is not uniform and a distorted image is produced.¹ In addition, each LCD mode requires a specific pretilt angle;^{2,3} for example, 3°–6° for twisted nematic mode, 55° for no-bend-bias optically compensated bend mode, and nearly 90° for vertical alignment mode. Hence, the precise control of the pretilt angle for each LCD mode is essential to achieve a high-quality LCD. One method of achieving this is to use a polyimide (PI) containing steroidal side chains.³ By changing the fraction of units on the PI chain that have a steroidal side chain, any required pretilt angle from 3° to 90° can be achieved. The side chain

of this PI has a chemical structure like that of a typical LC molecule, as shown in Fig. 1, consisting of two benzoate groups, a rigid steroidal structure, and a flexible alkyl chain. The steroidal structure and alkyl chain are also the main parts of a cholesterol molecule, and their sum frequency generation (SFG) response was studied by Kett *et al.*⁴

To produce a uniform alignment of the LC molecules, the PI surface is commonly treated by a mechanical rubbing process. In general, experimental results indicate that the orientations of PI main chain molecules at the surface become uniformly aligned after the rubbing process.^{5–8} After the rubbing process, the molecular orientation of the PI side chain sometimes changes, and sometimes does not. This change depends on the length, components, and configuration of the PI side chain.^{7–10} Oh-e *et al.*⁸ investigated PIs with short alkyl side chains (1–7 carbon atoms) and reported that their orientation is hardly affected by the rubbing process. In contrast, Jayathilake *et al.*¹⁰ observed significant azimuthal anisotropy in PIs with long alkyl side chains (18 carbon atoms) induced by the rubbing process.

Pis containing steroidal side chains possess unique properties,³ and they hold great potential as excellent alignment layers for

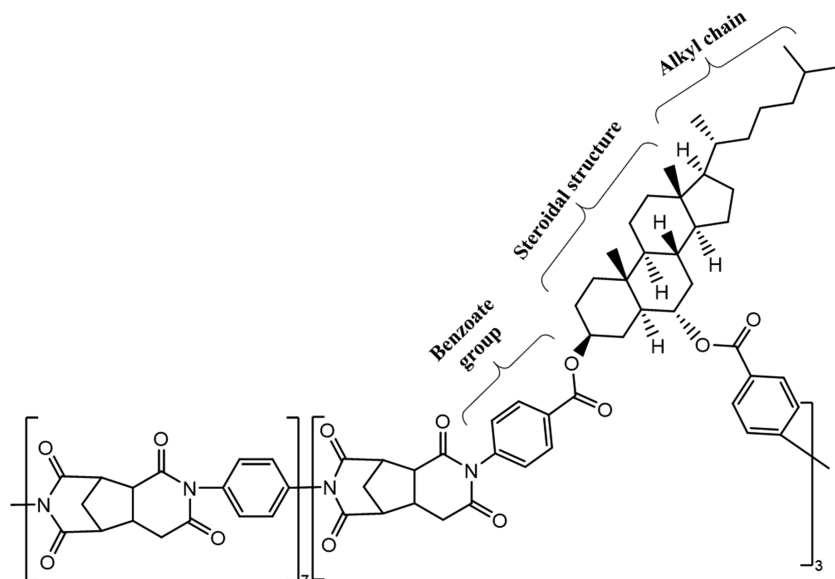


FIG. 1. Chemical structure of PI containing steroidal side chains used in this study.

various LCD applications. Previously, the orientation of phenyl rings in the PI side chain has been probed using optical second harmonic generation (SHG).^{11,12} However, the molecular orientation and conformation of the steroidal structure and the alkyl chain of PI at the surface are not yet fully known. Several analytical techniques are available to study polymer films, including infrared (IR) spectroscopy,¹³ atomic force microscopy (AFM),¹⁴ and near-edge x-ray absorption fine structure spectroscopy (NEXAFS).^{7,15} Unfortunately, these techniques are not appropriate for analyzing the steroidal structure and the alkyl chains, as it is difficult to distinguish the contribution of the bulk and the surface signals of polymer films in IR spectra. The PI sample is not rigid enough for a good image to be captured by AFM. NEXAFS is surface-sensitive, but the signal is dominated by resonances arising from transitions from the 1s core level to unoccupied molecular orbitals with π^* and σ^* symmetries, such as the carbon double bond and the nitrogen triple bond.^{7,15}

SFG is a well-known second-order nonlinear optical process.^{16–20} SFG occurs when visible light of a fixed wavelength and IR light of a varying (tunable) wavelength simultaneously illuminate the same location on a sample. SFG is commonly applied to determine the vibrational resonances of molecules adsorbed on surfaces and at interfaces because it is sensitive to non-centrosymmetric parts of materials. Using vibrational SFG spectra as a function of IR frequency and molecular symmetry, quantitative information on molecular orientation on surfaces or at interfaces can be determined.

In this study, we use SFG vibrational spectroscopy to investigate the molecular orientation and conformation of the steroidal structure and the alkyl chain at the surface of rubbed PI containing steroidal side chains. In addition, SHG is used to study the orientation and conformation of the PI main chain. From these results, we discuss the correlation between PI-surface molecular orientation and the alignment of LC molecules on the PI substrate.

II. THEORETICAL BACKGROUND

Basic SFG theory has been presented extensively elsewhere.^{20–22} The azimuthal angle γ is defined as the angle between the rubbing direction and the plane of incidence, as shown in Fig. 2. Analysis of the SFG spectra, which depend on the azimuthal angle, gives information on molecular orientation on the surface or at the interface.¹⁰ The SFG intensity in the reflection direction is given by

$$I(\omega_{SFG}) \propto |\chi_{eff}^{(2)}|^2 I(\omega_{vis})I(\omega_{IR}), \quad (1)$$

where $I(\omega_{vis})$ and $I(\omega_{IR})$ are the intensities of the visible and IR beams, respectively. $\chi_{eff}^{(2)}$ is the effective second-order nonlinear susceptibility tensor. For the PPP (P-polarized SFG, P-polarized visible, and P-polarized IR) polarization combination, there are eight elements of second-order nonlinear susceptibility, $\chi_{ijk}^{(2)}$, contributing to the SFG signal,

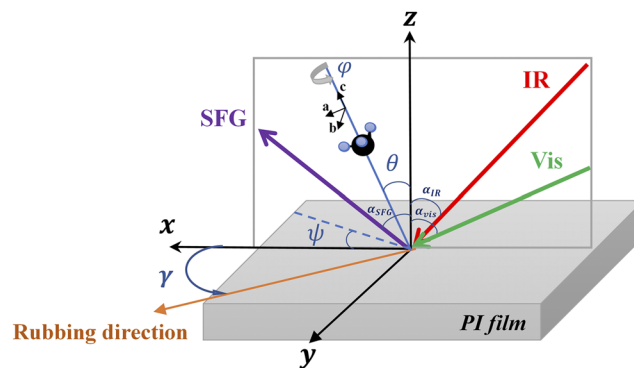


FIG. 2. Experimental geometry and coordinate systems on the PI surface.

$$\begin{aligned} \chi_{\text{eff,PPP}}^{(2)}(\gamma) = & -L_x(\omega_{\text{SFG}})L_x(\omega_{\text{vis}})L_x(\omega_{\text{IR}})\cos\alpha_{\text{SFG}}\cos\alpha_{\text{vis}}\cos\alpha_{\text{IR}}\chi_{\text{xxx}}^{(2)} - L_x(\omega_{\text{SFG}})L_x(\omega_{\text{vis}})L_z(\omega_{\text{IR}})\cos\alpha_{\text{SFG}}\cos\alpha_{\text{vis}}\sin\alpha_{\text{IR}}\chi_{\text{xzz}}^{(2)} \\ & - L_x(\omega_{\text{SFG}})L_z(\omega_{\text{vis}})L_z(\omega_{\text{IR}})\cos\alpha_{\text{SFG}}\sin\alpha_{\text{vis}}\sin\alpha_{\text{IR}}\chi_{\text{zzz}}^{(2)} - L_x(\omega_{\text{SFG}})L_z(\omega_{\text{vis}})L_x(\omega_{\text{IR}})\cos\alpha_{\text{SFG}}\sin\alpha_{\text{vis}}\cos\alpha_{\text{IR}}\chi_{\text{zxx}}^{(2)} \\ & + L_z(\omega_{\text{SFG}})L_x(\omega_{\text{vis}})L_x(\omega_{\text{IR}})\sin\alpha_{\text{SFG}}\cos\alpha_{\text{vis}}\cos\alpha_{\text{IR}}\chi_{\text{zxx}}^{(2)} + L_z(\omega_{\text{SFG}})L_z(\omega_{\text{vis}})L_x(\omega_{\text{IR}})\sin\alpha_{\text{SFG}}\sin\alpha_{\text{vis}}\cos\alpha_{\text{IR}}\chi_{\text{zxx}}^{(2)} \\ & + L_z(\omega_{\text{SFG}})L_x(\omega_{\text{vis}})L_z(\omega_{\text{IR}})\sin\alpha_{\text{SFG}}\cos\alpha_{\text{vis}}\sin\alpha_{\text{IR}}\chi_{\text{zxx}}^{(2)} + L_z(\omega_{\text{SFG}})L_z(\omega_{\text{vis}})L_z(\omega_{\text{IR}})\sin\alpha_{\text{SFG}}\sin\alpha_{\text{vis}}\sin\alpha_{\text{IR}}\chi_{\text{zxx}}^{(2)}, \end{aligned} \quad (2)$$

where the coordinates x , y , and z are defined in Fig. 2. $L_i(\omega)$ ($i = x, y, z$) is the Fresnel factor, representing the local field of incident and output radiations at the surface at frequency $\omega = \omega_{\text{SFG}}$, ω_{vis} , or ω_{IR} . To calculate the Fresnel factors, a four-layer model was used.^{10,23} α_{SFG} , α_{vis} , and α_{IR} are the angles of incidence of the SFG, visible, and IR beams relative to the surface normal, respectively.

The second-order nonlinear hyperpolarizability $\beta_{lmn}^{(2)}$ of a molecule is normally defined in molecular coordinates (a , b , and c), as shown in Fig. 2. $\beta_{lmn}^{(2)}$ has 27 elements in total, but there are fewer non-zero elements owing to molecular symmetry. We assume that the CH_3 group has C_{3v} symmetry. In this case, there are only three nonvanishing independent elements, β_{ccc} and $\beta_{aac} = \beta_{bbc} = r\beta_{ccc}$. The value of r ranges from 1.66 to 3.5.^{24–26} However, in Sec. IV, we show that this variation in the parameter r does not significantly affect our discussion. The orientation of a methyl group is given by the Euler angles (θ, ψ, φ) , as described in Fig. 2. The transformation of $\beta_{lmn}^{(2)}$ to the molecular surface susceptibility of the methyl group $\beta_{ijk}^{(2)}$ is expressed as

$$\beta_{ijk}^{(2)}(\theta, \psi, \varphi) = \sum_{lmn} U_{ijk,lmn}(\theta, \psi, \varphi) \beta_{lmn}^{(2)}, \quad (3)$$

where $U_{ijk,lmn}(\theta, \psi, \varphi)$ is a product of three Euler matrices.²⁷ To determine the macroscopic surface susceptibility tensor of the methyl group, we average over the orientational distribution $f(\theta, \psi, \varphi)$,

$$\chi_{ijk}^{(2)}(\gamma) = N \iiint d\theta d\psi d\varphi f(\theta, \psi, \varphi) \beta_{ijk}^{(2)}(\theta, \psi, \varphi). \quad (4)$$

Equations (3) and (4) indicate that the second-order nonlinear susceptibility of the surface depends on the molecular number density N , molecular orientation, and the hyperpolarizability of the methyl group. If the hyperpolarizability is known, the orientation of methyl group can be determined by measuring the SFG spectra of the corresponding CH_3 vibration at different azimuthal angles. We assume that each methyl group can freely rotate around the c -axis, so the rotation angle φ can be integrated from 0 to 2π to average over all possible orientations measured in the experiment.^{10,28} Consequently, $f(\theta, \psi, \varphi)$ becomes a function of the tilt angle θ and the azimuthal angle ψ of the methyl group,

$$f(\theta, \psi, \varphi) = \frac{1}{4\pi^2\sigma_\theta\sigma_\psi} \exp\left(-\frac{(\theta - \theta_0)^2}{2\sigma_\theta^2} - \frac{(\psi - \gamma)^2}{2\sigma_\psi^2}\right). \quad (5)$$

Here, θ_0 is the average tilt angle, σ_θ is the tilt angle distribution width, and σ_ψ is the azimuthal-angle distribution width.

III. EXPERIMENTAL SECTION

We used a PI with units possessing a 30% fraction of steroidal side chains (PI-30). As shown in Fig. 1, the side chains have a rigid steroidal structure with a flexible 6-methylheptan-2-yl group at the end. The PI films were prepared using the following procedure: First, (polyamic) acid (PAA) solution was synthesized from 2,3,5-tricarboxy-cyclopentyl acetic dianhydride (TCA-AH), 1,4-phenylenediamine, and a side-chain diamine. The molar ratio of TCA-AH: phenylenediamine: side-chain diamine was fixed at 10:7:3. The PAA films were then prepared by spin-coating on non-alkali glass plates. The coated films were baked for 2 min at 80 °C to evaporate the solvent and 30 min at 230 °C under a nitrogen atmosphere to induce imidization. The thickness of the PI film was ~80 nm. The PI films were rubbed once by using a rubbing machine with a roller covered with nylon cloth: the rotational speed of the roller was 400 rpm, the translational speed of the sample was 30 mm/s, and the pile impression depth, indicating the rubbing strength, was 0.4 mm. The rubbing strength was weak enough to produce reorientation of the PI side chain only, and not reorientation of the main chain. After the rubbing process, the glass plates were cut into 20 × 15 mm² pieces for SFG measurements. As a reference sample, rubbed PI without steroidal side chains (PI-0) was used. The sample preparation procedure for the rubbed PI-0 film was similar to that of the rubbed PI-30 film, except that the molar fraction of TCA-AH: phenylenediamine: the side-chain diamine for the rubbed PI-0 film was fixed at 10:10:0.

The experimental configuration for the SFG measurement has been published elsewhere.^{29,30} Briefly, to generate an SFG signal, a visible beam of 532 nm from a harmonic unit (HMPL/SH/TH/FH, EKSPLA) and a tunable IR beam (from 300 to 600 nm) from a parametric generator (PG401/DFG2-18P, EKSPLA) driven by a mode-locked Nd³⁺:YAG laser (PL2143B, EKSPLA) at 1064 nm were spatially and temporally overlapped on the PI surface with incidence angles of 80° and 45°, respectively. The two beams had a pulse duration of 30 ps and a repetition rate of 10 Hz. The laser power was ~250 μJ/pulse for the IR beam and ~80 μJ/pulse for the visible beam, and the spot area was ~2 mm². The SFG output was detected in the reflection direction using a monochromator (SG-100, Nihon Koken Kogyo) and a photomultiplier tube (R-585, Hamamatsu), and was recovered using a Boxcar integrator (SR250, Stanford Research Systems). The PI-30 film was mounted on a 360° rotational stage, and the SFG spectra were measured using different azimuthal angles. Signals of 600 pulses were accumulated for each wavelength for the SFG spectrum. To ensure reproducibility, all SFG spectra were recorded at least twice. The uniformity of the rubbed PI-30 sample was checked (Fig. S1, supplementary material).

The experimental configuration for SHG measurement was published in our previous paper.¹² A frequency-doubled light of

2.33 eV (532 nm) with a 30 ps pulse duration and a 10 Hz repetition rate from a mode-locked Nd³⁺:YAG laser (PL2143B, EKSPLA) was used as the incident light source. Incident light was directed to a rubbed PI-0 film at a 45° angle. The PI-0 film was mounted on a 360° rotational stage, and the SHG response was observed as a function of the sample rotation angle. The SHG electrical signal was recorded in the same way as the SFG signal. The polarization combination was Pin/Pout (P-polarized fundamental beam and P-polarized SHG). Signals of 1500 pulses were recorded for each data point to construct an SFG intensity pattern.

IV. RESULTS AND DISCUSSION

Figure 3 shows a typical SFG spectrum of the rubbed PI-30 film for the CH stretching region, from 2800 to 3000 cm⁻¹ at an azimuthal angle of $\gamma = 0^\circ$ and a PPP polarization combination. It took 41 min to perform this measurement. Before discussing the details of this SFG spectrum, we first examine whether or not the SFG response originates from the PI-30 film surface. We measured the SFG spectra of the rubbed PI-30 films with and without a poly (methyl methacrylate) (PMMA) layer for the PPP and SSP (S-polarized SFG, S-polarized visible, P-polarized IR) polarization combinations (Fig. S2, [supplementary material](#)). The thickness of the PMMA layer was ~5 nm. For the PPP polarization combination, the SFG intensity decreased dramatically after the sample was covered with the thin PMMA layer. For the SSP polarization combination, the peaks in the spectra changed drastically after PMMA deposition. The peak at 2860 cm⁻¹ disappeared for both the SSP and PPP polarization combinations, and a new peak at 2955 cm⁻¹ appeared in the SSP spectrum of the sample with the PMMA layer. These results indicate that the SFG of the rubbed PI-30 originates mainly from the PI surface; and the SFG contribution from the PI/glass substrate interface and the bulk PI can be ignored.

As mentioned in Sec. I, the steroidal structure and the alkyl chain present in the PI-30 film in Fig. 1 also constitute the main parts of the molecule cholesterol. Kett *et al.*⁴ investigated the SFG spectrum of a cholesterol monolayer film and assigned its vibrational modes. We mainly followed their assignments for the vibrational modes in the PI-30 spectrum in Fig. 3 (see Table I).^{4,8,10,26} The red solid line in Fig. 3 was obtained by fitting the data points to the following equation:¹⁰

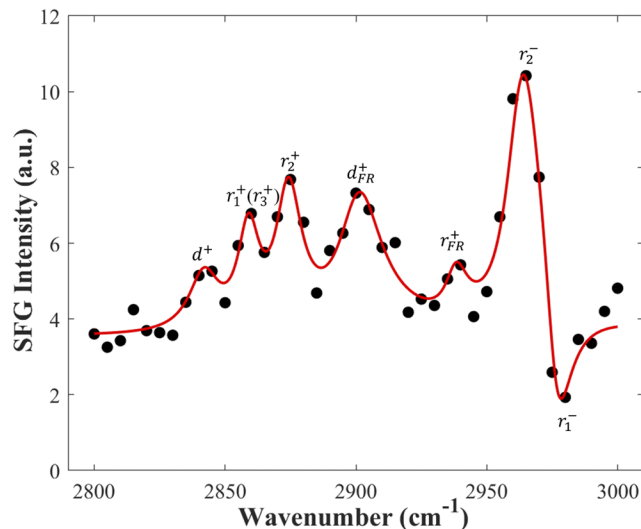


FIG. 3. SFG spectrum of a rubbed PI-30 film for a PPP polarization combination at $\gamma = 0^\circ$. The red solid line is the fitting curve obtained using Eq. (6).

$$I(\omega_{SFG}) \propto \left| A_{NR}^{(2)} e^{i\phi} + \sum_q \frac{A_q \Gamma_q}{\omega_{IR} - \omega_q + i\Gamma_q} \right|^2, \quad (6)$$

where $A_{NR}^{(2)}$ and ϕ are the amplitude and phase of the non-resonant part of the SFG response, ω_{IR} is the frequency of the IR light, and A_q , ω_q , and Γ_q are the amplitude, resonant frequency, and line width of the q th vibrational mode, respectively. The fitting parameters are listed in Table S4 ([supplementary material](#)).

The P-polarized light field has x and z components on the surface. Hence, in the PPP polarization combination, eight non-zero $\chi_{ijk}^{(2)}$ elements, i.e., $\chi_{xxx}^{(2)}$, $\chi_{xxz}^{(2)}$, $\chi_{zzz}^{(2)}$, $\chi_{xzx}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zxx}^{(2)}$, and $\chi_{zzz}^{(2)}$ contribute to the SFG response.^{17,18} These elements involve vibrational transition moments perpendicular to the surface. As a result, the PPP-SFG spectrum of CH resonances is generally sensitive to the polar orientation of CH groups at the surface.

TABLE I. Vibrational assignments of the rubbed PI-30 film in the CH stretching region. (Subscript 1 denotes the CH₃ groups on the steroidal structure of the PI side chain and the adjacent CH₃ group; subscript 2 denotes the isopropyl group.)

| Vibrational mode | Wavenumber (cm ⁻¹) | Description |
|---------------------|--------------------------------|---|
| d^+ | 2842 | CH ₂ symmetric stretch |
| r_1^+ (r_3^+) | 2859 | Symmetric stretch of the CH ₃ groups on the steroidal structure of the PI side chain and the adjacent CH ₃ group |
| r_2^+ | 2874 | CH ₃ symmetric stretch of the isopropyl group |
| d_{FR}^+ | 2901 | Fermi resonance of the CH ₂ symmetric stretch |
| r_{FR}^+ | 2938 | Fermi resonance of the CH ₃ symmetric stretch |
| r_2^- | 2963 | CH ₃ anti-symmetric stretch of the isopropyl group |
| r_1^- | 2976 | Anti-symmetric stretch of the CH ₃ groups on the steroidal structure of the PI side chain and the adjacent CH ₃ group |

The SFG intensity of the CH_2 symmetric stretching mode (d^+) at 2842 cm^{-1} is weaker than those of the methyl groups (r_1^+ , r_2^+) at 2859 and 2874 cm^{-1} although in one side chain, the number of methylene groups is 11 and the number of methyl groups is 5. This means that the methylene groups in the steroidal structure and the alkyl chain have a small net polar orientation. The reason for this small net polar orientation is that the steroidal structure has a nearly flat shape, and the dipoles of the methylene groups in the structure almost completely cancel one another out. The net polar orientation of the methylene groups in the alkyl chains is not large even if there are gauche defects, as the number of methylene groups is small.

As shown in Table I, the frequencies of the symmetric and anti-symmetric stretching modes of the CH_3 isopropyl group (r_2^+ , r_2^-) are different from those of the two methyl groups of the steroidal structure and the adjacent methyl group (r_1^+ , r_1^-).⁴ The CH_3 isopropyl group contributes two positive peaks at 2874 cm^{-1} (r_2^+) and 2963 cm^{-1} (r_2^-) to the SFG spectrum, indicating that the methyl groups are pointing away from the PI surface, in line with the discussion of Kett *et al.*⁴ In contrast, r_1^+ and r_1^- modes were observed as positive and negative peaks, respectively. As shown in Table S4 (supplementary material), the amplitudes of r_1^+ and r_1^- modes have opposite signs. A similar phenomenon was observed by Kett *et al.*⁴ for a cholesterol monolayer film. They reported that the r^+ and r^- resonances were out of phase in the PPP-SFG spectrum because of the two different orientations of the CH_3 groups in the film.³¹ We would expect the same situation here for the CH_3 groups on the steroidal structure of the PI side chain and the adjacent CH_3 group. The methyl groups on the steroidal structure point toward the surface, and the methyl group adjacent to the steroidal structure points away from the surface. The r_1^+ mode is observed as a positive peak because the symmetric stretching mode of the adjacent methyl group is strong enough to cancel out the negative signals from the methyl groups on the steroidal structure. However, the anti-symmetric stretching mode of the adjacent methyl group is not strong enough to cancel out the negative signals from the two methyl groups on the steroidal structure, and the r_1^- mode is observed as a negative peak. Here, we adopt the interpretation of Kett *et al.*⁴ to explain the positive r_1^+ , r_2^+ , and r_2^- peaks and the negative r_1^- peak in the SFG spectrum of a PI-30 film in Fig. 3.

McGall *et al.*³² discussed film thickness interference effects in the SFG spectra of polymer films. They reported that interference can occur between SFG sources at the rear and front interfaces of films and can cause a phase difference between different CH_3 stretching modes. However, such interference can be excluded for our sample (supplementary material) because the SFG response in this study was shown to originate mainly from the rubbed PI-30 film surface, as described at the beginning of this section.

To consider the effect of the rubbing process on the molecular orientation of the PI side chains, we measured SFG spectra at different azimuthal angles γ before and after rubbing. Figure 4 shows the SFG spectra of unrubbed and rubbed PI-30 films for the PPP polarization combination, at azimuthal angles of $\gamma = 0^\circ$, 90° , and 180° . As expected, the spectral shapes of the unrubbed PI-30 in Fig. 4(a) do not show significant variation as a function of the azimuthal angle. As shown in Fig. 4(b), rubbed PI-30 also does not appear to show a clear dependence on azimuthal angle. As we measured the spectra of rubbed PI-30 under these conditions, the differences cannot be easily seen.

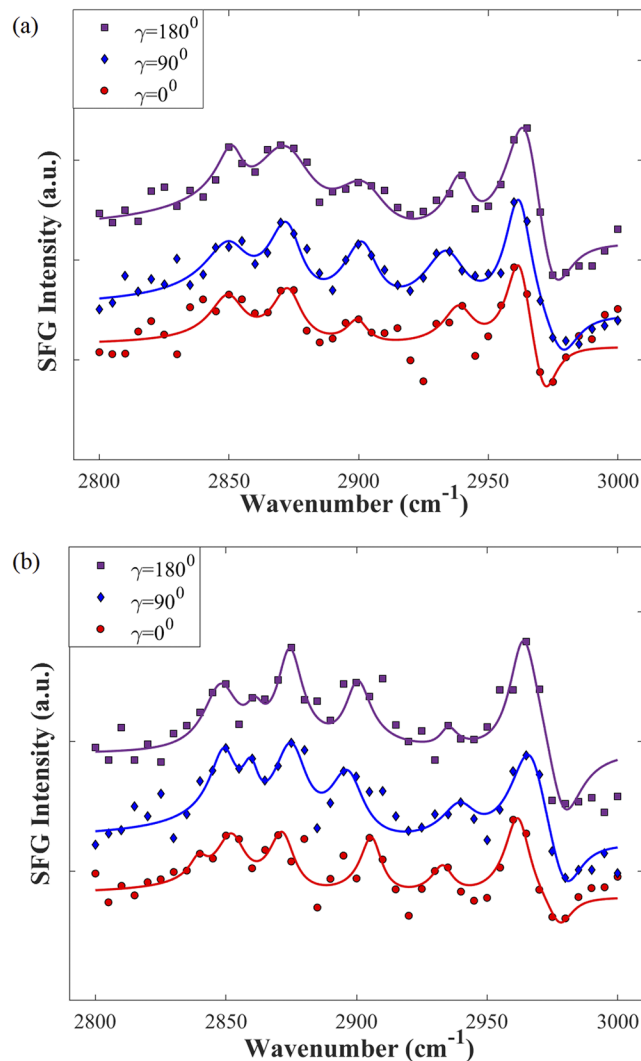


FIG. 4. SFG spectra of the (a) unrubbed PI-30 film and (b) rubbed PI-30 film for the PPP polarization combination at azimuthal angles of $\gamma = 0^\circ$, 90° , and 180° . The solid lines are the fitting curves obtained using Eq. (6).

For a detailed analysis of the rubbed PI-30 film, we focus on the CH_3 symmetric stretching modes in the $2850\text{--}2890\text{ cm}^{-1}$ region for the following reasons: (i) The molecular hyperpolarizability tensor elements for these modes are well-known,^{10,18,26} (ii) the main polyimide chain in the PI-30 film does not have CH_3 groups, so all CH_3 signals likely come from the side chains, and (iii) symmetric stretching modes are normally less sensitive to intermolecular interactions.¹⁰

We obtained SFG spectra for a rubbed PI-30 film at azimuthal-angle intervals of 45° with a PPP polarization combination to further investigate the effect of the rubbing process on the orientation of the methyl groups. The results are presented in Fig. 5. As previously discussed, the symmetric stretching mode of the methyl

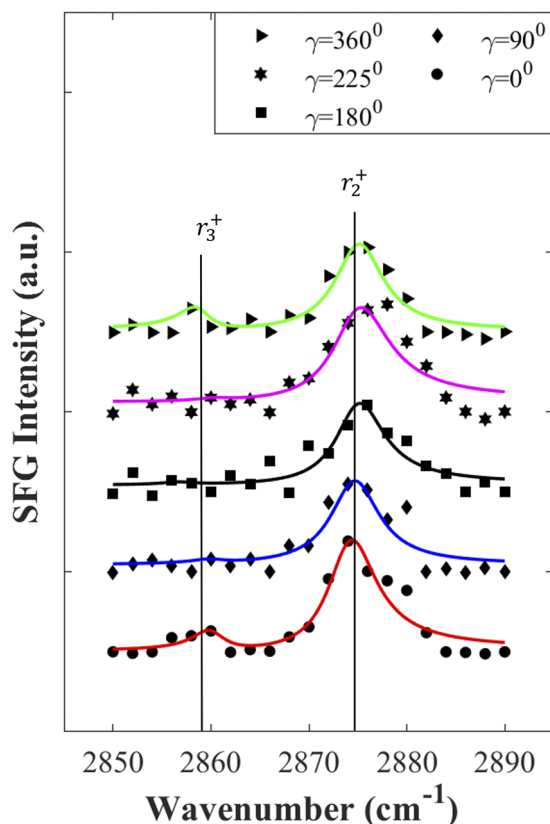


FIG. 5. SFG spectra of the rubbed PI-30 film for the PPP polarization combination at azimuthal angles of $\gamma = 0^\circ, 90^\circ, 180^\circ, 225^\circ,$ and 360° in the $2850\text{--}2890\text{ cm}^{-1}$ region. The solid lines are the fitting curves obtained using Eq. (6).

group adjacent to the steroidal structure overwhelms the negative signals from the methyl groups on the steroidal structure; so, the main SFG signal in the positive peak (r_1^+) at $\sim 2860\text{ cm}^{-1}$ is assumed to be from the methyl group adjacent to the steroidal

structure. The “ r_1^+ mode” is, therefore, renamed to the “ r_3^+ mode.” The subscript 3 denotes the CH_3 group adjacent to the steroidal structure. The best-fit parameters for the CH_3 symmetric stretching modes (r_3^+ and r_2^+) are summarized in Table II. Please note here that the values of ω_1 inside the parentheses are tentative values; they cannot be precisely determined when the amplitude of the r_3^+ mode is too small. The r_3^+ mode appears to show a slight anisotropy in the SFG spectra; that is, the intensity of this mode appears to be stronger in the rubbing direction at $\gamma = 0^\circ$ and 360° and weaker at $\gamma = 180^\circ$. The results suggest that the methyl group adjacent to the steroidal structure is reoriented in the rubbing direction. However, the rubbing process does not significantly affect the r_2^+ peaks of the CH_3 isopropyl group. As shown in Table II, the amplitudes and positions of the r_2^+ mode at different azimuthal angles are generally similar to each other within the bounds of statistical error.

To analyze the dependence of the peak intensity of the CH_3 symmetric stretching mode r_3^+ from the CH_3 group adjacent to the steroidal structure on the azimuthal angle we show $|\chi_{PPP,r_3^+}^{(2)}(\gamma)|^2$ values in Fig. 6 obtained using the relationship¹⁰

$$|\chi_{PPP,r_3^+}^{(2)}|^2 \equiv |A_1|^2. \quad (7)$$

The vertical axis in Fig. 6 is normalized to unity at $\gamma = 0^\circ$. Using these measured values, we obtain an approximate orientational distribution function $f(\theta, \psi, \varphi)$ for the CH_3 group adjacent to the steroidal structure using Eqs. (2) and (4) like in Ref. 10. The measured and calculated $|\chi_{PPP,r_3^+}^{(2)}(\gamma)|^2$ dependencies are shown in Fig. 6. As mentioned in Sec. II, the value of $r = \beta_{aac}/\beta_{ccc}$ and the IR refractive index are not well-known, but we found that the shape of the curve in Fig. 6 is not sensitive to the values of these parameters when r is between 1.7 and 4.0, and the refractive index is between 1.4 and 1.8. However, the shape of the curve is sensitive to the value of the average tilt angle θ_0 . The effects of the tilt angle distribution width σ_θ and the azimuthal distribution width σ_ψ on the curve are investigated (Fig. S4, supplementary material). For the best estimation, we found that

TABLE II. Fitting results for CH_3 symmetric stretching modes of the rubbed PI-30 film. The error bars in this table come from the fitting procedure.

| γ (deg) | Symmetric stretch of the CH_3 group adjacent to the steroidal structure (r_3^+) | | Symmetric stretch of the CH_3 isopropyl group (r_2^+) | |
|----------------|--|------------------|--|------------------|
| | ω_1 (cm^{-1}) | A_1 (a.u.) | ω_2 (cm^{-1}) | A_2 (a.u.) |
| 0 | 2860 | 0.74 ± 0.074 | 2874 | 2.32 ± 0.232 |
| 45 | 2859 | 0.54 ± 0.162 | 2875 | 1.38 ± 0.414 |
| 90 | (2860) | 0.13 ± 0.023 | 2875 | 1.72 ± 0.310 |
| 135 | (2859) | 0.15 ± 0.008 | 2874 | 2.30 ± 0.127 |
| 180 | (2857) | 0.10 ± 0.020 | 2875 | 1.68 ± 0.336 |
| 225 | (2860) | 0.08 ± 0.015 | 2875 | 1.75 ± 0.333 |
| 270 | 2862 | 0.30 ± 0.057 | 2875 | 2.06 ± 0.391 |
| 315 | 2860 | 0.85 ± 0.298 | 2874 | 2.00 ± 0.700 |
| 360 | 2859 | 0.80 ± 0.096 | 2875 | 2.04 ± 0.245 |

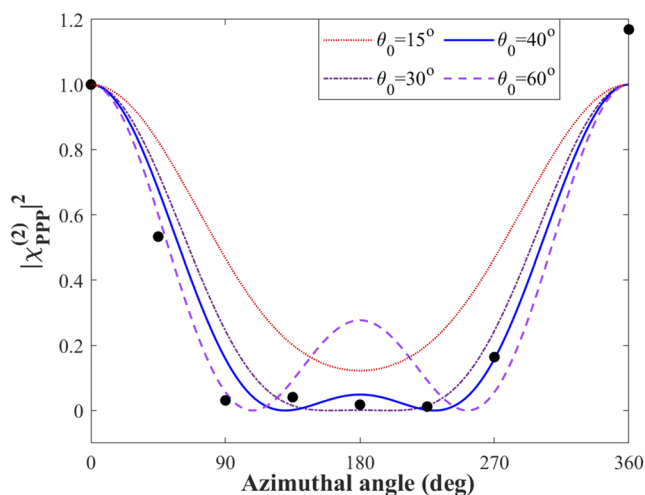


FIG. 6. Intensity of the CH_3 symmetric stretching mode from the CH_3 group adjacent to the steroidal structure as a function of the azimuthal angle. The dots are the experimental data, and the curves are the calculated data. The orientational parameters used in the model calculation are $\sigma_\theta = 15^\circ$ and $\sigma_\psi = 10^\circ$.

$$\theta_0 = 40^\circ \pm 10^\circ,$$

$$\sigma_\theta = 15^\circ \pm 10^\circ,$$

$$\sigma_\psi \leq 20^\circ.$$

The value of the angle θ_0 indicates that the methyl group adjacent to the steroidal structure is aligned with the rubbing direction on the surface, with an average 40° upward tilt, as illustrated in Fig. 7. The tilt angle distribution width σ_θ and the azimuthal distribution width σ_ψ are not very broad. The terminal CH_3 groups are randomly oriented because the length of the alkyl chain in the PI-30 film is short. Similar results have been observed in PIs with short alkyl side chains (1–7 carbon atoms).⁸ It is known that the length of an alkyl side chain is a crucial parameter for determining the molecular organization and order of the terminal CH_3 group on surfaces or at interfaces.¹⁰ More specifically, long alkyl chains with more than ten carbon atoms have better

molecular organization and order on surfaces than shorter alkyl chains.

The molecular interaction between an alignment layer and LC molecules is the most important factor in LC alignment.^{33,34} Therefore, the ultimate goal of our study was to establish which structural factor of rubbed PI films with steroidal side chains is most strongly correlated with LC alignment. Practically, LC molecules become aligned in the rubbing direction when they are placed on rubbed PI-30 films.³ To establish which structural factor has the strongest correlation, the possible candidate structures were considered:

- (1) the phenyl rings in the PI side chain,
- (2) the phenyl rings in the PI main chain,
- (3) the steroidal structure and the CH_3 group adjacent to the steroidal structure,
- (4) the isopropyl group and the neighboring methylene group in the PI side chain.

First, we discuss factor (1), namely, the orientation and conformation of phenyl rings in the PI side chain. Ullah *et al.*¹² reported that the SHG intensity of the rubbed PI-30 film shows anisotropic SHG intensity patterns as a function of the sample rotation angle. The anisotropy of the SHG intensity is explained by the reorientation of the side chains of the PI-30 film. Moreover, SHG is sensitive to the anisotropy of the orientation of phenyl rings.⁶ Combining this information, we suggest that rubbing may cause reorientation of the phenyl rings in the side chains of the PI-30 film. Thus, the correlation between factor (1) and the LC alignment is possible.

Next, we discuss factor (2), namely, the orientation and conformation of the PI main chain. Figure 8 is an SHG intensity pattern of the rubbed PI film without steroidal side chains (PI-0), which is a function of the sample rotation angle around the surface normal of the film. There is very small anisotropy in this pattern, even if the PI film is rubbed. In contrast, in a similarly measured SHG pattern of a rubbed PI-30 film, remarkable anisotropy has been reported, as mentioned in the previous paragraph.¹² Thus, rubbing does not induce anisotropy of the phenyl rings of the PI main chain, unlike the case of Sakai *et al.*⁷ Hence, the correlation between factor (2) and the LC alignment is excluded.

Now, we discuss factor (3), namely, the orientation and conformation of the steroidal structure and the adjacent CH_3 group. In our

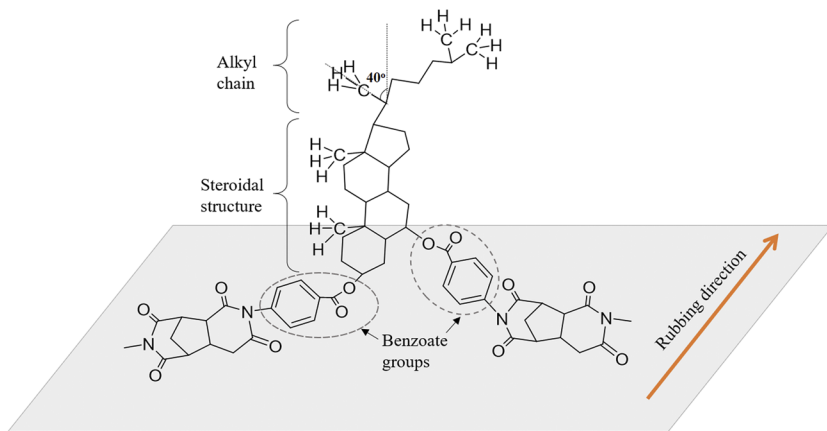


FIG. 7. Schematic representation of the conformation of the steroidal side chain.

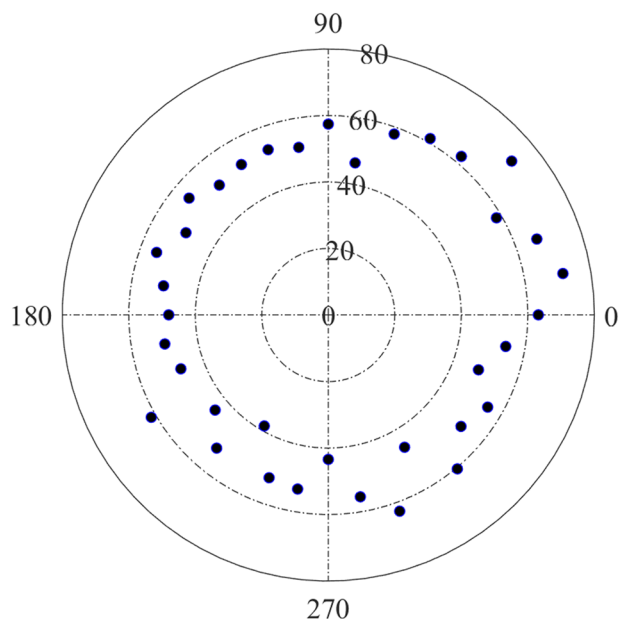


FIG. 8. SHG intensity pattern of the rubbed PI-0 film as a function of sample rotation angle in a Pin/Pout polarization combination. “0°” means that the beam propagation direction is in the rubbing direction.

case, the SFG response of the CH_2 and CH_3 groups of the steroidal structure is weak because the steroidal structure has a roughly flat shape; so, little can be said about the orientation of the steroidal structure using these CH_2 and CH_3 groups. However, Fig. 5 shows that the CH_3 group adjacent to the steroidal structure is oriented. This means that not only the CH_3 group adjacent to the steroidal structure but also the steroidal structure itself are oriented because the orientation of the CH_3 group restricts the structural boundary condition of the steroidal structure. Thus, a correlation between the steroidal structure, the CH_3 adjacent to the steroidal structure, and the LC alignment is possible.

Finally, we look at factor (4), namely, the orientation and conformation of the isopropyl group and the neighboring methylene group in the PI side chain. In the SFG spectra of the rubbed PI-30 films in Fig. 5, the intensity of the symmetric stretching mode of the terminal CH_3 groups does not change as a function of the azimuthal angle; hence, the terminal CH_3 groups are not oriented in the rubbing direction. As discussed earlier, when the length of an alkyl chain in the PI-30 film is short, the terminal CH_3 groups do not become significantly oriented by rubbing. Hence, the result in Fig. 5 is unsurprising. The observation that the isopropyl group is not oriented and LC alignment occurs on the PI surface means that the LC alignment is not correlated with the orientation of the isopropyl group. Consequently, the correlation between factor (4) and the LC alignment is denied.

Thus, factors (1) and (3), namely, the orientation of the phenyl rings, the steroidal structure, and the adjacent CH_3 group, are possibly correlated with the LC alignment. Unfortunately, we have no further evidence to determine which of these two factors is the most likely cause of LC alignment. However, the results of our study clearly show no correlation between the orientation of the phenyl

rings of the PI main chain [factor (2)] and LC alignment, and no correlation between the isopropyl group and the neighboring methylene group in the PI side chain [factor (4)] and LC alignment. To the best of our knowledge, there has not yet been an analysis of the orientation of an isopropyl group on a rubbed PI surface, like the one in this paper.

Generally, chemical structures located near the main chain within the side chain of a PI tend to have weaker interactions with LC molecules. In one example reported by Liu *et al.*,³⁵ rigid biphenyl rings in the side chain were nearly perpendicular to the PI main chain layer and carried alkoxy side-end groups such that they protrude from the PI bulk vertically; however, LC alignment behavior depended only on the length of the alkoxy side-end group. We, therefore, suggest that the phenyl rings in the side chain [factor (1)] may not be the main factor in LC alignment. In this case, the steroidal structure and the CH_3 group adjacent to the steroidal structure [factor (3)] are the main factor causing LC alignment. However, further study is necessary for the precise judgment of the correlation between factor (3) and LC alignment.

V. CONCLUSION

SFG vibrational spectroscopy is utilized to analyze the molecular orientation and conformation of the steroidal structure and the flexible alkyl (6-methylheptan-2-yl) group of rubbed polyimide films containing a 30% fraction of steroidal side chains. The experimental results show that the isopropyl group points toward the air side from the PI surface, but its average orientation is not affected by rubbing. Hence, the orientation of the isopropyl group is not a factor correlated with LC alignment. This result is in clear contrast with many past examples in which the CH_3 end group of alkyl chains affects the alignment of LCs. In the SFG spectra, slight anisotropy in the symmetric stretching mode of the CH_3 group adjacent to the steroidal structure is observed after rubbing, and the average tilt angle of the CH_3 group adjacent to the steroidal structure is estimated to be $\theta_0 = 40^\circ \pm 10^\circ$ in the rubbing direction. In our previous publication, we reported that the phenyl rings of the side chains may be oriented by rubbing. From this work, we are unable to determine which of the steroidal structure, the CH_3 group adjacent to the steroidal structure, or the phenyl ring in the PI side chain mainly influence the LC alignment.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for information about the uniformity of the rubbed PI-30 sample, proof of the SFG spectra from the PI-30/air interface, the fitting parameters of the PPP-SFG spectrum of the rubbed PI-30 film, and the effect of σ_θ and σ_ψ parameters on the curve in Fig. 6.

APPENDIX: REFRACTIVE INDICES OF THE RUBBED PI-30 FILMS

Here, we show the refractive indices of the rubbed PI-30 film used to calculate the Fresnel factors in the SFG orientational analysis. The refractive index of the rubbed PI-30 film was measured using spectroscopic ellipsometry (Table III). A slab model of the polyimide/air interface for the calculation of the local-field

TABLE III. Refractive indices of the rubbed PI-30 films.

| Beam | Refractive index | | |
|------------------|------------------|-----------------|---------------|
| | Polyimide | Glass substrate | Polyimide/air |
| IR (2149 nm) | 1.546 | 1.436 | 1.236 |
| Visible (532 nm) | 1.590 | 1.461 | 1.254 |
| SFG (462 nm) | 1.606 | 1.465 | 1.260 |

correction at the interface was used.²⁶ We adopted the refractive index of glass measured by Filmetrics, Inc. (KLA Corp.).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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