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Description	

Detection of Surface Modification of Polyimide Containing Steroidal Structure as a Function of Storage Time Using Second-Order Nonlinear Optical Spectroscopy

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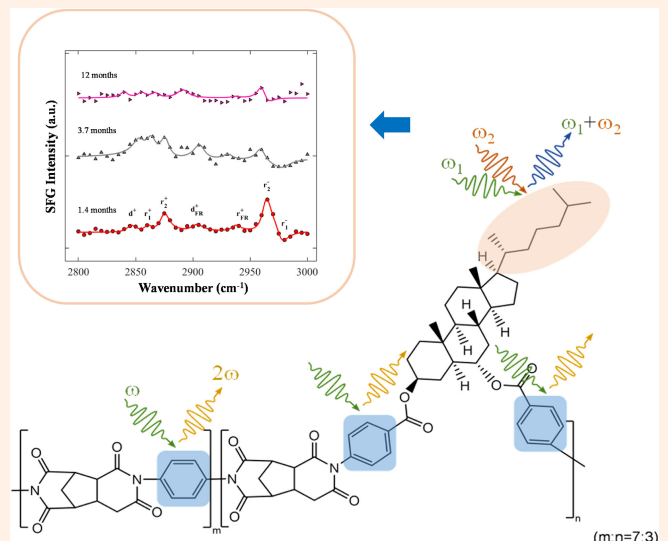
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The modification of a polyimide surface containing a 30% fraction of steroidal structure was studied as a function of storage time by vibrational sum frequency generation (SFG) spectroscopy and optical second-harmonic generation (SHG). The variation of the symmetric and anti-symmetric stretching modes of the CH₃ isopropyl group at the end of the side chain of the rubbed polyimide was detected in the SFG spectra after a 3-month storage time in a practical environment. It suggests that the isopropyl group might be reoriented. On the other hand, the SHG response of the same sample showed an insignificant storage-time dependence. As a result, the phenyl rings of the polyimide are judged to be unmodified after long-term storage time. The change is suggested to occur for two main reasons. One is the interaction between the polyimide polymers and the ambient water molecules. The other is the adsorption of unknown organic molecules on the polyimide surface.

Keywords Polyimide; Steroidal structure; Surface quality degradation; Vibrational sum frequency generation spectroscopy; Second harmonic generation



I. INTRODUCTION

Polyimide containing steroidal structure is known as a semi-aromatic polyimide. The microscopic structure of such a polyimide studied in this work is shown in [Figure 1](#). This polyimide possesses outstanding properties like the general polyimides, such as high thermal stability, excellent mechanical properties, and high chemical resistance [1–3]. Besides, the steroidal structure in this polyimide makes it possess unique properties. For example, it shows better electrical properties as the material for the alignment layers in the liquid crystal display (LCD) panel [4] than the ones with long alkyl chains or fluorine atoms. In addition, the pretilt angles of liquid crystal (LC) molecules for various LCD modes can be precisely controlled by changing the fraction of monomeric units of polyimide containing steroidal struc-

ture [4]. In principle the LC alignment on rubbed polyimide film surfaces is determined by the molecular interaction between polyimide film surface and LC molecules [5, 6]. Consequently, ensuring the high quality of the polyimide film surface is imperative for achieving optimal LCD performance. Regular monitoring and detection of any surface modifications of the film are essential in maintaining its quality.

Vibrational sum frequency generation (SFG) and second-harmonic generation (SHG) have been demonstrated as practical tools to probe polymer surfaces due to their sensitivity to asymmetric parts of materials unlike infrared or Raman spectroscopies which pick up the information from the both surface and bulk parts of the polymer film. While vibrational SFG spectroscopy can provide information about the surface vibrational resonances and the average orientation of the molecules at the surface [7–11], SHG can provide informa-

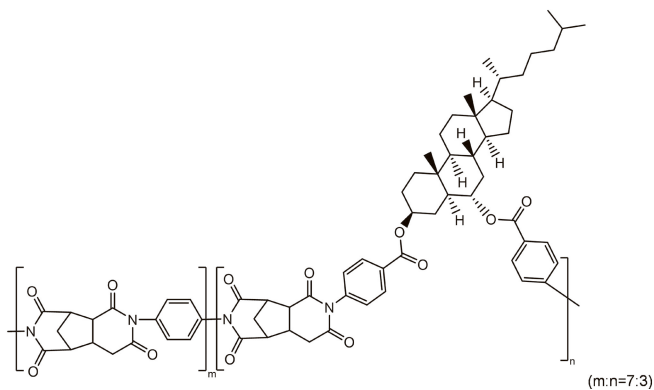


Figure 1: Chemical structure of polyimide containing steroidal structure used in this study.

tion about the electronic transitions of the surface molecules [12–16]. In fact, we found that the SFG response of the polyimide film originates mainly from the surface and the SFG contribution from the polyimide/glass interface and the bulk can be ignored [17]. The terminal isopropyl group in the side-chain of the polyimide containing steroidal structure as shown in Figure 1 is pointing toward the air side and the average tilt angle of the methyl group adjacent to the steroidal structure is $40^\circ \pm 10^\circ$ in the rubbing direction. Analyzing the SHG response of the polyimide containing steroidal structure, we also figured out that both the polyimide side chains and the main chains contribute to this response [18]. Considering the inherent properties of SFG and SHG, their combination holds great promise for effectively characterizing the surface condition of the LCD alignment layer.

In order to systematically detect surface modification behavior of polyimide films as a function of storage time, we used a combination of vibrational SFG spectroscopy to analyze the difference of vibrational modes in the CH stretching range and SHG to examine the variation of the SHG response of polyimide film surfaces, especially phenyl rings. The sample polyimide is that in Figure 1 because we have an ample experience of this specific polyimide [17]. The purpose of this study is to establish a method to detect the change of the surface condition of an LCD alignment layer in a practical environment.

II. MATERIALS AND METHODS

Figure 1 illustrates the chemical structure of a polyimide containing 30% fraction of steroidal structure used in this study. The sample preparation procedure can be found in our previous paper [17]. Briefly, the polyimide films with a layer thickness of ~ 80 nm were prepared by spin-coating on non-alkali glass substrates and then were rubbed once by a rubbing machine with a weak strength. After preparation, the polyimide films were put in plastic boxes and then stored in a dry box kept at humidity $25 \pm 3\%$ and temperature $21 \pm 2^\circ\text{C}$.

The SFG spectra of the polyimide film were recorded using a narrowband SFG system. The details of the exper-

imental setup for the SFG measurement have been published elsewhere [19]. In short, a visible beam (532 nm) and a tunable infrared beam were overlapped on the polyimide film surface at angles of incidence of 80° and 45° , respectively, to generate an SFG signal. The energies of the visible beam and infrared beam used were $\sim 80 \mu\text{J}$ and from 135 to 280 μJ , respectively. After appropriate optical filtering, the SFG output was collected in the reflection direction by a monochromator and a photomultiplier tube. In this experiment, the SFG spectra were recorded in the CH-stretching region (2800 to 3000 cm^{-1}) for a PPP (P-polarized SFG, P-polarized visible, P-polarized IR) polarization combination at a 5 cm^{-1} interval. For rubbed polyimide films, the SFG spectra were measured with the wave vectors of the incident beams parallel to the rubbing direction. The SFG signal was averaged over 600 pulses for each wavelength using a gated integrator to reduce noise. All the SFG spectra were fitted by the following equation [20];

$$I(\omega_{\text{SFG}}) \propto \left| A_{\text{NR}}^{(2)} e^{i\phi} + \sum_q \frac{A_q \Gamma_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \right|^2. \quad (1)$$

Here, $A_{\text{NR}}^{(2)}$ and ϕ denote the amplitude and phase of the non-resonant SFG signal, ω_{IR} is the infrared frequency. A_q , ω_q , and Γ_q denote the amplitude, the resonant frequency, and the line width of the q th vibrational mode, respectively.

The details of the experimental setup for the SHG measurement can be found elsewhere [21]. In short, a fundamental beam (532 nm) with energy at $\sim 20 \mu\text{J}$ irradiated the polyimide film at an angle of 45° to generate an SHG signal (266 nm). The SHG output was collected in the same way as the SFG output. In the SHG experiment, we mounted the polyimide film on a 360° rotational stage. Then its SHG response at sample rotation angle intervals of 10° for a Pin/Pout (P-polarized fundamental beam and P-polarized SHG) polarization combination was recorded. The SHG signals of 1000 pulses were accumulated for each data point.

III. RESULTS

A. SFG spectra of polyimide films as a function of storage time

The polyimide films were carefully kept in a dry box to reduce the impact of the environment unless they were under SFG observation. Still, the polyimide surface was modified after long-term storage. To check the quality of the polyimide film surfaces at different storage times, we collected the SFG spectra of the polyimide films in the CO/CH stretching regions and above 3000 cm^{-1} . Herein we just show the SFG spectra obtained in the CH stretching region because the spectra obtained in the CO stretching region and above 3000 cm^{-1} were ambiguous.

Figure 2 shows SFG spectra of rubbed polyimide films for the PPP polarization combination as a function of the storage time. The detailed assignments of the vibrational modes at the bottom are based on those for fresh polyimide in our

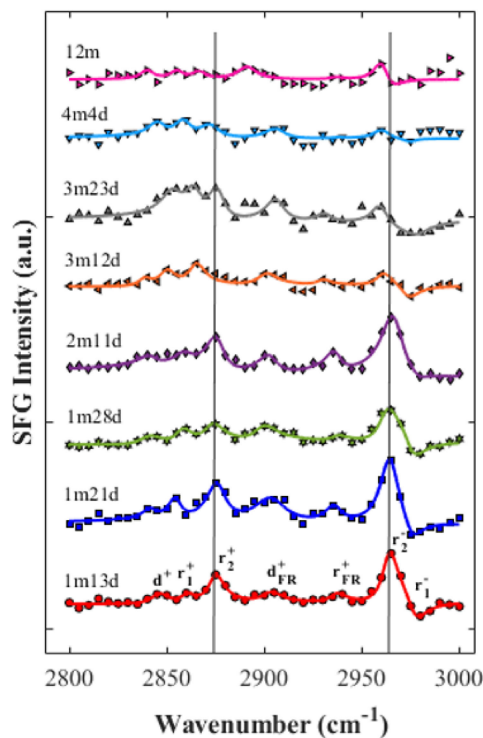


Figure 2: SFG spectra of the rubbed polyimides for the PPP polarization combination as a function of the storage time. The solid lines are the fitting curves obtained using Eq. (1).

previous paper [17]. The fitting parameters used for the theoretical curves can be found in [Supplementary Material](#). While the polyimide spectra observed at and before the storage time of 2 months and 11 days show only a slight change from the bottom spectrum, those after longer storage time show significant changes. As shown in Figure S1 ([Supplementary Material](#)), the amplitude ratios of the r_2^+ peak (CH₃ symmetric stretching mode of the isopropyl group) and the r_2^- peak (CH₃ anti-symmetric stretching mode of the isopropyl group) within the storage time of 2 months and 11 days are similar whereas those ratios of the r_2^+ peak and the r_2^- peak significantly change after longer storage time. Moreover, a considerable variation of the shape of the r_2^- peak is observed as a function of the storage time. Vibrational SFG is extremely sensitive to order and conformation of molecules at surfaces, the variations of the r_2^+ and r_2^- peaks therefore suggest that the structures of the isopropyl groups on the polyimide surface changed somehow after a long-term storage time. These changes result in a loss of uniformity on the polyimide surface, and a decrease in SFG intensity of the CH₃ stretching modes.

In a similar way we investigated SFG response of *un-rubbed* polyimide film surfaces after different storage times (Figure S2, [Supplementary Material](#)). We found that the modification of polyimide surface occurs in the un-rubbed polyimide film as well as in the rubbed polyimide film. To check the impact of ambient environment factors such as moisture and oxygen on the polyimide surface, we recorded SFG spectra of the rubbed polyimide film kept in a quartz

cell filled with dry N₂ gas as a function of storage time (Figure S3, [Supplementary Material](#)). Although the number of observed peaks in the SFG spectrum of the sample after the 10-month storage time are like those at 7 days, the relative peak intensities and the peak positions are quite different. The results indicate that the polyimide surface in dry N₂ gas also might be modified after the 10-month storage time.

B. SHG intensity patterns of polyimide films as a function of time

As previously mentioned, we cannot extract molecular information of the polyimide main chain, namely the imide group and phenyl ring, from the SFG spectra. This information is crucial to determine the origin causing the polyimide surface modification after long-term storage. The optical SHG technique is widely known for its capability to primarily probe surface species and are sensitive to π -bonds, such as phenyl rings or imide rings. These particular species exhibit a high degree of electron cloud delocalization and lead to a significant optical nonlinearity [12–16]. When the side chain tilts by rubbing, these phenyl rings and the ester bonds also tilt because the CN bonds attached to the phenyl rings are expected to be flexible. The electrons in the phenyl rings in the polyimide in [Figure 1](#) feel an asymmetric potential field from the ester bonds. Then a new asymmetry emerges in the rubbing direction in the surface layer. Hence, we use optical SHG as a supplementary method to check the orientation of the phenyl rings and imide rings in the surface molecular layer of the polyimide.

[Figure 3](#) shows SHG intensity patterns of rubbed polyimide films possessing a 30% fraction of steroidal structure as a function of the storage time. Due to the rubbing process, an anisotropy of SHG intensity, namely a larger SHG response around 0° or in the rubbing direction, is observed for the fresh sample [[Figure 3\(a\)](#)]. The SHG anisotropy was also obtained for the rubbed samples at the storage times of 5 months and even at 13 months [[Figure 3\(b, c\)](#)]. The results indicate that the SHG response is independent of the storage time. Similarly, we recorded SHG responses of un-rubbed polyimide films, as shown in [Figure 4](#). As it is natural, no essential anisotropy is seen in the SHG response of the samples measured at the storage times of either 28 days [[Figure 4\(a\)](#)], 8 months [[Figure 4\(b\)](#)], or 13 months [[Figure 4\(c\)](#)]. The SHG response of both rubbed and un-rubbed samples show negligible dependence on the storage time. Interestingly, these SHG results look inconsistent with the SFG ones of the same samples.

IV. DISCUSSION

In the previous section, we reported that the storage-time dependence of the anisotropy of the SHG response in the rubbed polyimide containing steroidal structures was not found to be remarkable. However, upon further analysis, we have discovered significant variations in the vibrational modes within the CH region of the vibrational SFG spectrum

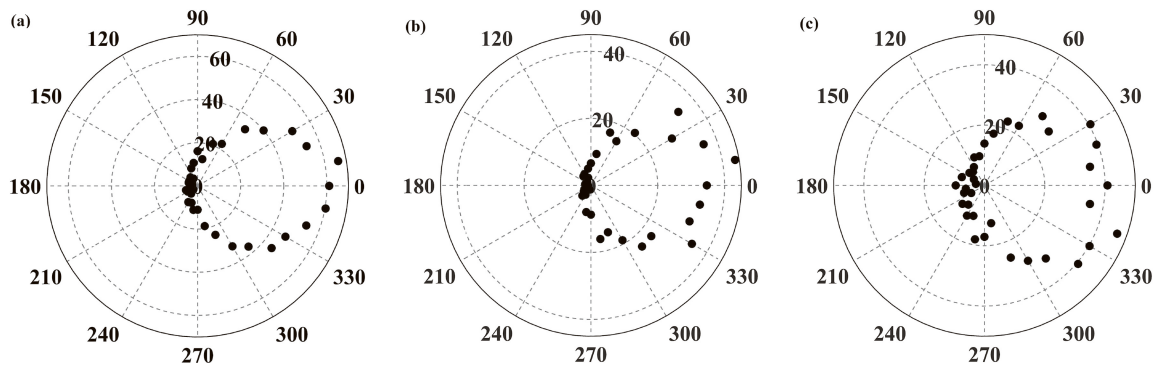


Figure 3: SHG intensity pattern of the rubbed polyimide film as a function of sample rotation angle for Pin/Pout polarization combination measured at the storage times of (a) 20 days, (b) 5 months, and (c) 13 months. 0 degrees means that the beam propagation direction is in the rubbing direction.

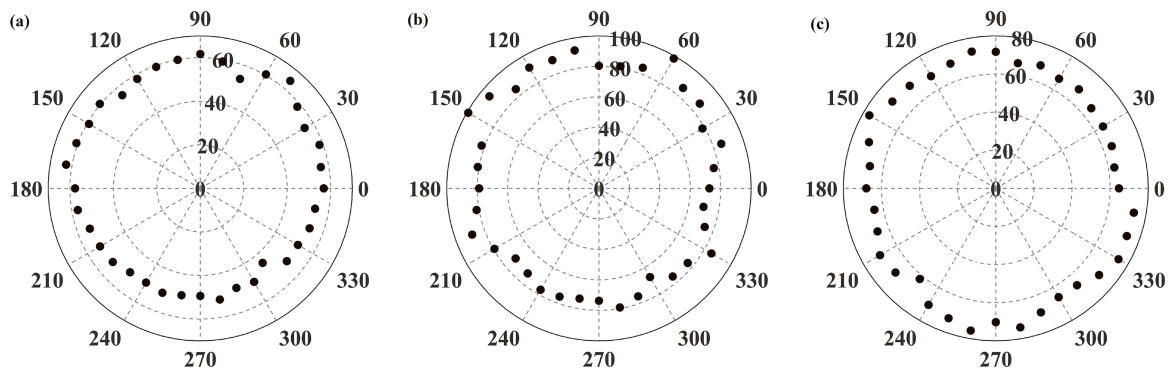


Figure 4: SHG intensity pattern of the unrubbed polyimide film as a function of sample rotation angle for Pin/Pout polarization combination measured at the storage times of (a) 28 days, (b) 8 months, and (c) 13 months.

of the same sample after a storage period of three months. Practically, these observations are not necessarily inconsistent because SFG and SHG can generally originate from different parts of the polyimide film surface [12, 22]. Namely, the SFG signal in Figure 2 is assigned as molecular vibrations of the CH_2 groups or the CH_3 groups in the surface side chains, while the SHG signal in Figures 3 and 4 are suggested to come from the aromatic rings and imide rings. As we already stated above the phenyl rings and the ester bonds tilt by rubbing and the electrons in the phenyl rings feel an asymmetric potential field from the ester bonds. From the result of Figure 3, we suggest that the tilt angle of the phenyl rings and the ester bonds do not change until 13 months. That is the reason why the SHG patterns in Figure 3 are the same for all the elapsed time. The change observed in the SFG spectra in Figure 2 at the 3-months storage time could be attributed to the fact that only a specific portion of the side chain undergoes modifications over time. Next, we focus on interpreting the variations of the symmetric and anti-symmetric stretching modes of the CH_3 isopropyl group (r_2^+ , r_2^-) in the polyimide SFG spectra as a function of storage time because these variations were systematically observed in Figure 2.

The variation of the r_2^+ and r_2^- peaks of the isopropyl group after the 3-month storage time as reported in Section

III.A can be due to six candidate origins as:

- (1) Change of Fresnel factors.
- (2) Breaking down or oxidation in air of the isopropyl group.
- (3) Breaking down of the main chain.
- (4) Breaking down of the steroidal structure.
- (5) Effect of the environmental moisture on the polyimide film and a resultant modification of the isopropyl group's orientation.
- (6) Polyimide surface contamination.

Fresnel factor is used to correct the SFG intensity for its modification by linear optical effect of input and output radiations at surfaces or interfaces [23]. In order to compare the Fresnel factors for the polyimide/air interface for the fresh rubbed polyimide film and the one after the 10-month storage time, the refractive indices of these samples were measured using spectroscopic ellipsometry (Supplementary Material). We found no significant variation between the refractive indices of the fresh sample and those of the sample after the 10-month storage time. Hence, the change of the peak intensity as a function of the storage time in Figure 2 is judged to be not due to the modification of the Fresnel factors, and we can exclude candidate (1).

Now we look at candidate (2), namely breaking down or oxidation by oxygen in air of the isopropyl group. The

isopropyl group is the simplest structure group containing a tertiary carbon - a carbon atom directly bound to three other carbon atoms. Generally, this group is extremely stable in normal room temperature conditions [24, 25]. Since the storage of our samples was carried out in a very mild condition, we can exclude this candidate (2).

Next, we consider candidate (3), namely breaking down of the main chain. In general, chemical bonds between C and N atoms in the imide group or C and C atoms are the two most easily broken bonds in polyimide [26–29]. Since the strength of the C–N bond is lower than that of the C–C bond [28], the C–N breakage might most likely occur after the 3-month storage time in this polyimide. On the other hand, the SHG intensity patterns of the polyimide films show slight difference as a function of storage time. One can see in Figure 1 that if the C–N breakage occurred, it would affect the configuration of the aromatic rings. The SHG results indicate that it is not the case. Hence, candidate (3) may not have caused the variations of the r_2^+ and r_2^- peaks in the SFG spectra as a function of storage time.

We can clearly exclude candidate (4), namely breaking down of the steroidal structure. Due to the ‘trans’ configuration at all three fusions, the steroidal structure is commonly rigid and remains semi-flat [30]. That is why cholesterol, the most abundant steroid in animals, is so stable in animal’s body [31]. Hence, this structure is not easily broken in normal environmental conditions.

Here, we discuss candidate (5), namely the effect of moisture on the polyimide and a resultant modification of the surface isopropyl group’s orientation. In our previous study [17], we suggested that the isopropyl group points toward the air side from the rubbed polyimide surface when the film is fresh. Water molecules can affect the isopropyl group in two ways: Firstly, moisture in the air may drive the hydrophobic isopropyl group into the bulk. Secondly, water molecules in the polyimide bulk may drive the isopropyl group already in the bulk back toward the air side. Then, to minimize the total energy of the film surface, the hydrophobic isopropyl group may most likely take more disordered configuration due to its interaction with water molecules after a long-term storage time than when the film is fresh [32, 33]. This view also explains the fact that the SFG spectra of unrubbed polyimide film changes as a function of time as seen in Figure S2 (Supplementary Material).

Lastly, we discuss candidate (6), namely polyimide surface contamination. The surface contamination might occur due to the adsorption of unknown organic components on the polyimide surfaces. Then, the interaction between hydrophobic side chains of polyimide and hydrophobic organic contaminants might affect the orientation of the isopropyl group. As expected, the modification of the polyimide surface was also observed in the polyimide kept in the quartz cell filled dry N₂ gas (Figure S3, Supplementary Material). Candidates (5) and (6) have opposite behaviors, and one or both of them may be the reason for the variations of the r_2^+ and r_2^- peaks in the SFG spectra as a function of storage time. Further study is necessary for determining which one is intense.

V. CONCLUSIONS

Vibrational SFG spectroscopy and SHG were used to detect the modification of polyimide film surfaces containing a 30% fraction of steroidal structure as a function of storage time. The r_2^+ and r_2^- peaks in the SFG spectra of the rubbed polyimide film showed systematic storage time dependence whereas the SHG response of the same sample just showed slight variation. Disorder of the orientation of the isopropyl groups in the polyimide side chain due to the interaction with moisture or surface contamination might be the main reason for these observed facts. The phenyl rings of the polyimide were found not to be reoriented because the SHG response of the same samples showed an insignificant storage-time dependence. The experimental results prove that the combination of vibrational SFG spectroscopy and optical SHG can be a useful method to detect the change of the polymer film surface in a practical environment.

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Appendix

The fitting parameters used for the theoretical curves in Figure 2, the SFG spectra of the unrubbed polyimide and the rubbed polyimide film kept in a quartz cell filled with dry N₂ gas are found in Supplementary Material at <https://doi.org/10.1380/ejsnt.2023-065>.

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