Optical Second Harmonic Generation Study of a Rubbed Polyimide Film Containing Steroidal Structure Side Chains

Muhammad Samir Ullah
School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Ishikawa 923-1292, Japan, and Department of Physics, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Shohei Asai, Yousuke Inomata, Khuat Thi Thu Hien, and Goro Mizutani
School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Ishikawa 923-1292, Japan

Yoshihata Murakami and Takashi Okada
LCD Materials 2nd Laboratory, Display Materials Research Laboratories, JSR Corporation, 100 Kawajiri-cho, Yokkaichi, Mie 510-8552, Japan

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We have studied the optical second harmonic generation (SHG) of a rubbed novel polyimide (PI) film having steroidal structure side chains prepared by spin coating on an indium tin oxide (ITO)-coated glass substrate. The second order nonlinear susceptibility \( \chi^{(2)} \) elements were obtained from the fitting of the SHG data. The symmetry of the polymer chains roughly belonged to Cs symmetry with the rubbing direction parallel to the mirror plane. The average polar (tilt) angle of the rubbed PI chains was determined to be around 16° by using the measured \( \chi^{(2)} \) elements. [DOI: 10.1380/ejssnt.2017.7]

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I. INTRODUCTION

Liquid crystal displays (LCDs) are quite widely used in home electric appliances, industry equipment and other devices having displays [1]. In LCDs, the orientation of liquid crystal molecules on the alignment polymer film substrates are regulated by the applied voltage in the devices. These alignment polymer films directly affect the orientation of the liquid crystal molecules on the alignment polymer film substrates. There are two important issues about polyimide films. One is the control of the pretilt angle and the other is the rubbing treatment. The pretilt angle is the orientation angle of the liquid crystal molecules at just the interface between the substrate and the liquid crystal layers. The chemical structure of the polyimide is composed of two parts: long chain polymer playing a major role for aligning LC molecules due to the rubbing effect, and chemically attached hydrocarbon branches producing a pretilt angle [5, 6]. In order to get high contrast LCD, it is necessary to control the pretilt angle precisely at the interface between the alignment film and the LC molecules [7]. In order to induce the pretilt angle, one generally introduces hydrophobic alkyl base of fluoroalkyl base in the polymer structures [8-10]. Nishikawa developed polyimide with steroidal structure side chains to induce high pretilt angles, rigid chemical structure, and good electrical properties [11]. The developed films show more stable pretilt angle and higher voltage holding ratio than a simple long alkyl chain structure. The resultant pretilt angle is controllable between 3° and 90°.

The mechanical rubbing treatment of the polyimide layer, as the second important issue, also plays an important role for controlling the unidirectional alignment of LC molecules in the display performance of LCD panels [12-14]. From that point of view, it is highly important to know the orientational distribution of rubbing induced PI alignment of the layer surface with the steroidal structures. In spite of the abundant accumulation of the experience on the devices fabricated by rubbing, the mechanism of the orientation of the LC molecules are not well known except that it could be affected by the interaction between the side chains and the LC molecules.

In this study, in order to make a step in understanding the mechanism of the rubbing effect, we fabricated polyimide polymer films having steroidal structures, rubbed them and observed their optical second harmonic response. We wish to investigate the effect of rubbing on the structure of the main long chains, so we prepared polyimide without mesogens for inducing the liquid crystal orientation.

Previously we tried X-ray near edge absorption fine structure (NEXAFS) spectroscopy, atomic force microscopy (AFM), dynamic viscoelastic measurement, and UV absorption to distinguish the rubbing effect of such long chain structures, but were not successful. On the other hand, second harmonic generation (SHG) is becoming a powerful method and recently is used for studying in the field of surface and interfaces science [15, 16]. There have been a lot of SHG measurements for determining the orientations of LC molecules or polymer chains [12-14, 17-20] so we use SHG in this study.

In this study, an attempt has been taken to determine the nonlinear susceptibility elements of rubbed PI long
chains with steroidal structures and evaluate the polar (tilt) angle of the polymer chain orientation from the rotational dependence of the SHG signal. The polymer has steroidal structures in the side chains and flexible main long chain structures with a zigzag shape illustrated later. The content of this steroidal structure is around 30% and the film has a low pretilt angle ($10^\circ$). We did rubbing treatment for the film and measured their SHG response. From the obtained susceptibility elements we determined the average tilt angle of the rubbed polymer. So far as we know there has been no SHG measurement of polyimide polymers with steroidal structures. We will discuss the structure of the long chain polymers of our samples.

II. EXPERIMENTAL

A. General procedure of Synthesis of polyamic acid (PAA) solution

All source materials were used as received without further purification. A 500 ml round flask was charged with 1, 4-Phenylenediamine (10.30 g, 95.2 mmol), side-chain diamine (40.8 mmol) and 240 g of NMP (N-methylpyrrolidone) under nitrogen atmosphere. After 1 hour stirring, 2, 3, 5-tricarboxycyclopentyl acetic dianhydride (23.36 g, 126.5 mmol) was added to the solution and stirred at 25$^\circ$C for 3 hours. The solution was diluted to 3.5 wt% with NMP and ethylene glycol monobutyl ether and filtered through a 0.20 $\mu$m Teflon filter. Figure 1 shows the chemical structures of the related compounds. Figure 2 is the chemical structure of the synthesized polyimide. Seeing the chemical structure of Fig. 2, the strongest response of SHG should come from the aromatic rings in the chains. Therefore, the SHG response in our experiment should reflect the orientation of the main chain of the polymers.

B. Preparation of a rubbed polyimide (PI) film

The polyamic acid (PAA) solution was spin-coated on an ITO-coated glass substrate, and then the coated substrate was dried at 80$^\circ$C for 2 min to remove the solvent. The thickness was controlled by the spinning rate. The pre-dried film was annealed in an oven at 230$^\circ$C for 30 minutes under nitrogen atmosphere to obtain the PI film of 100 nm thickness.

C. Mechanical rubbing condition

The PI film was rubbed by a rubbing machine using nylon cloth. In the mechanical rubbing process the rotational speed of the roller was 400 rpm, the translational speed was 30 mm/sec, and the pile impression depth indicating the rubbing strength was 0.4 mm. The film was rubbed only one time.

D. Optical second harmonic generation experiment

The optical setup of SHG measurement is shown in Fig. 3. As excitation we used the SHG output with photon energy of 2.33 eV from a harmonic unit driven by a
Nd:YAG laser with a pulse duration of 30 ps and a repetition rate of 10 Hz. The photon energy of 2.33 eV was chosen according to literature [12–14, 17]. The incident laser beam was directed onto the rubbed and unrubbed polyimide samples at 45° from the surface normal. The sample was rotated from 0° to 350° with 10° steps on the rotational stage. The incident beam was focused by a lens of focal length of 350 mm. The beam was kept slightly off focus at the sample surface to avoid the sample damage. The second harmonic field was detected from the sample at the photon energy of 4.66 eV. The SHG signal from the sample was separated from the fundamental light with ω-cut filter in the output path beam. Then it was detected by a monochromator and photomultiplier, and the electrical signal was amplified with a boxcar integrator and finally accumulated in a computer. We measured the SHG from the sample with four combinations of input/output polarization denoted as $P_{\text{in}}/P_{\text{out}}$, $P_{\text{in}}/S_{\text{out}}$, $S_{\text{in}}/P_{\text{out}}$, and $S_{\text{in}}/S_{\text{out}}$. Here, for example, the notation $S_{\text{in}}/P_{\text{out}}$ means that the fundamental light is s-polarized and p-polarized SHG light is detected.

### III. THEORETICAL BACKGROUND

The SHG intensity at frequency $2\omega$ generated from nonlinear polarization induced at a surface is given by [21]

$$I_{2\omega} \propto \left| \vec{E}_{2\omega} \right|^2$$

(1)

and

$$\vec{E}_{2\omega} = \epsilon_0 \chi^{(2)}_{\text{s, eff}} : \vec{E}(\omega) \vec{E}(\omega).$$

(2)

Here $\vec{E}(\omega)$ is the incident field at frequency $\omega$ and $\chi^{(2)}_{\text{s, eff}}$ is the effective second order surface nonlinear susceptibility tensor of the illuminated medium [22]. The susceptibility tensor $\chi^{(2)}_{\text{s, eff}}$ is defined as [23]

$$\chi^{(2)}_{\text{s, eff}} = \left[ \hat{e}(2\omega) \cdot L(2\omega) \right] \chi^{(2)}_{\text{s}} : \left[ L(\omega) \cdot \hat{e}(\omega) \right] \left[ L(\omega) \cdot \hat{e}(\omega) \right].$$

(3)

Here $\hat{e}(2\omega)$ and $\hat{e}(\omega)$ are the unit polarization vectors for the second harmonic beam at frequency $2\omega$ and fundamental beam at $\omega$, respectively. $L(2\omega)$ and $L(\omega)$ are the local field factor or Fresnel factor tensors for SHG field and fundamental beam, respectively. We calculated the amplitude of the SHG wave in a three-layered dielectric structure using Maxwell’s equations with a nonlinear source term [24]. The three layers are the air, surface, and bulk layers. The surface layer has second-order optical nonlinearity. In the simulation the thickness of the surface layer was assumed to be 1 nm. The dielectric constants of the film measured by ellipsometry are listed in Table I and they were used in the electromagnetic calculation. The linear dielectric function of the rubbed polyimide is isotropic. There are 10 independent second order nonlinear susceptibility elements (i.e., $xxx, xzx, xzy, xzz, yxy, yyz, zxx, zxz, zyy, zzz$ elements) for the face of Cs symmetry like in our case of the rubbed polyimide film. Here $x$ is in the rubbing direction, and $z$ is in the direction normal to the film surface. We minimized the sum of the squares of the deviations of the experimental data from the simulation curves by varying the nonlinear susceptibility elements in the complex plane [24]. Using the SHG data with different input and output polarization combination, we evaluated the independent $\chi^{(2)}_{ijkl}$ elements of the surface layer.

### IV. RESULTS AND DISCUSSION

The SHG intensity as a function of the rotational angle $\psi$ of the rubbed and unrubbed PI thin films with steroidal structure side chains with input/output polarization combinations are shown as black dots in Figs. 4 and 5. Here $\psi$ is defined as zero when the wave vector component of the incident light wave parallel to the substrate is in the rubbing direction.

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Not stable separately. The $\chi^{(2)}_{ijk}$ values are normalized so that $\chi^{(2)}_{zzz}$ becomes unity in the complex plane.

In order to find the molecular orientational distribution of the rubber polymer chain we need to convert the information given by the macroscopic nonlinear susceptibility elements $\chi^{(2)}_{ijk}$ to a microscopic polymer chain polar angle. For this purpose we assumed simply that polymer units have one dominant component $\beta^{(2)}_{\xi\xi}$ along the axis $\xi$ as shown in Fig. 2. This is an approximation adopted by other papers [25], although it is a crude assumption and should be revised in a more sophisticated analysis in the future. The relation between the nonlinear susceptibility and molecular nonlinear polarizability is given as [25]

$$
\chi^{(2)}_{ijk} = N_s \langle \hat{i} \cdot \hat{\xi} \rangle \langle \hat{j} \cdot \hat{\xi} \rangle \langle \hat{k} \cdot \hat{\xi} \rangle \beta^{(2)}_{\xi\xi}.
$$

Here $N_s$ is the molecular density of the surface, $i$, $j$ and $k$ denote the sample coordinate $x$, $y$, or $z$, and the bracket sign indicates the average over molecular orientational distribution function. The individual elements of the nonlinear susceptibility $\chi^{(2)}_{ijk}$ gives the information about the orientation and arrangement of the molecules of the rubbed polyimide layer. Nonvanishing elements of $\chi^{(2)}_{ijk}$ due to a molecule with a hyperpolarizability $\beta^{(2)}_{\xi\xi}$ directed at the polar angle $(\theta, \phi)$ are [26]

$$
\chi^{(2)}_{xxz} = N_s \langle \cos^3 \theta \rangle \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{yyx} = N_s \langle \sin^3 \theta \cos^3 \phi \rangle \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{yyz} = N_s \langle \sin^3 \theta \cos^3 \phi \rangle \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{zzz} = N_s \langle \cos^2 \theta - \cos^3 \theta \rangle (1 - \cos^2 \phi) \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{xyy} = N_s \langle \sin \theta \sin \phi \rangle \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{yyz} = N_s \langle \sin \theta \sin \phi \rangle \beta^{(2)}_{\xi\xi},
$$

$$
\chi^{(2)}_{zzz} = N_s \langle \sin^3 \theta \rangle (\cos \phi - \cos^3 \phi) \beta^{(2)}_{\xi\xi}.
$$

If we assume that the polymer molecules are tilted in $x$ direction, $\phi$ is zero. If we assume that the polar angle $\theta$ is

Table II. Second order nonlinear susceptibility elements $\chi^{(2)}_{ijk}$ of the rubbed polyimide sample. The values of $\chi^{(2)}_{ijk}$ are normalized by that of $\chi^{(2)}_{zzz}$.

<table>
<thead>
<tr>
<th>$ijk$</th>
<th>$\chi^{(2)}_{ijk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$xxx$</td>
<td>(0.09803, 0.044661)</td>
</tr>
<tr>
<td>$zzz$</td>
<td>(0.4107, −0.0240)</td>
</tr>
<tr>
<td>$yyy$</td>
<td>(1.0000, 0.0000)</td>
</tr>
<tr>
<td>$xyy$</td>
<td>(0.0, 0.0)</td>
</tr>
<tr>
<td>$xxy$</td>
<td>(−−, −−)</td>
</tr>
<tr>
<td>$yyx$</td>
<td>(−−, −−)</td>
</tr>
<tr>
<td>$yyz$</td>
<td>(−−, −−)</td>
</tr>
<tr>
<td>$xzz$</td>
<td>(−−, −−)</td>
</tr>
</tbody>
</table>

Figure 6 shows the contribution of each nonlinear susceptibility element to the theoretical SHG data in Fig. 4. Here we assumed $\chi^{(2)}_{xyy}$ and $\chi^{(2)}_{yxy}$ as zero due to the later discussion in eq. (13). Several elements of the nonlinear susceptibility have negative interference with each other during the numerical minimization of the summed squared deviations, and the fitting result was stabilized when we took the contribution from $\chi^{(2)}_{xzz}$, $\chi^{(2)}_{xz}$, $\chi^{(2)}_{yy}$, and $\chi^{(2)}_{xzy}$ elements in one group. Table II shows the nonlinear susceptibility elements obtained by this fitting for the rubbed polyimide. The values of $\chi^{(2)}_{xzz}$, $\chi^{(2)}_{xyy}$, $\chi^{(2)}_{xzy}$, and $\chi^{(2)}_{yxy}$ elements are not shown because they are not stable separately. The $\chi^{(2)}_{ijk}$ values are normalized so that $\chi^{(2)}_{zzz}$ becomes unity in the complex plane.
FIG. 7. Schematic model of the rubbing effect of the polyimide with steroid side chain.

distributed around $\theta_{ave}$ then eqs. (5) to (10) are approximated as

$$\chi_{xzx}^{(2)} \approx N_s \cos^3 \theta_{ave} \beta_{xzx}^{(2)}$$  \hspace{1cm}(11)

$$\chi_{xxx}^{(2)} \approx N_s \sin^3 \theta_{ave} \beta_{xxx}^{(2)}$$ \hspace{1cm}(12)

$$\chi_{zxx}^{(2)} = \chi_{yzy}^{(2)} = \chi_{yyz}^{(2)} \approx 0$$ \hspace{1cm}(13)

$$\chi_{zzz}^{(2)} \approx N_s \sin^2 \theta_{ave} \cos \theta_{ave} \beta_{zzz}^{(2)}$$ \hspace{1cm}(14)

$$\chi_{zzz}^{(2)} = \chi_{zxx}^{(2)} = \chi_{xxx}^{(2)} \approx N_s \sin \theta_{ave} \cos^2 \theta_{ave} \beta_{zzz}^{(2)}$$ \hspace{1cm}(15)

$$\chi_{zzy}^{(2)} = \chi_{yzy}^{(2)} = \chi_{zyy}^{(2)} \approx 0.$$ \hspace{1cm}(16)

From eqs. (11) and (12) we obtain

$$\tan^3 \theta_{ave} = \frac{\chi_{xxx}^{(2)}}{\chi_{zxx}^{(2)}}$$ \hspace{1cm}(17)

and from eqs. (12) and (14) we have

$$\tan \theta_{ave} = \frac{\chi_{xxx}^{(2)}}{\chi_{zxx}^{(2)}}.$$ \hspace{1cm}(18)

Since we know the values of $\chi_{zxx}^{(2)}$ and $\chi_{xxx}^{(2)}$ from the fitting results of the SHG data as in Table II, the tilt angle of the polymer chains diamine can be determined. It is $\theta_{ave} = 15.7^\circ \pm 1.8^\circ$ from eq. (18). The error was calculated from the data of four independent measurements in the same condition. The obtained angle means that the polymer chain tilts by about 16$^\circ$ from the surface normal at $\phi = 0^\circ$. This result is illustrated schematically in Fig. 7. Here we disregard the small phase shift between the $\chi_{zxx}^{(2)}$ elements in Table II and simply took the ratio of their absolute value as an approximation in evaluating $\theta_{ave}$ from eq. (18). We did not use eq. (17) because $\chi_{zxx}^{(2)}$ may have a bigger error than $\chi_{xxx}^{(2)}$ and $\chi_{zxx}^{(2)}$. Namely, since Fig. 6 shows that the SHG intensity patterns for $P_{in}/P_{out}$ combination have contributions from many $\chi_{ijk}^{(2)}$ elements, the fitting can have more ambiguity of the values of the susceptibility elements including $\chi_{zxx}^{(2)}$. On the other hand, $\chi_{zxx}^{(2)}$ is the only element having contribution at 90$^\circ$ for $S_{in}/S_{out}$ configuration, and so is $\chi_{zxx}^{(2)}$ at 90$^\circ$ for $S_{in}/P_{out}$ configuration. So they are considered quite reliable.

The real chain of polyimide takes a zigzag structure as shown in Fig. 7 or Fig. 2. Before the rubbing treatment the chains are oriented in random directions. The side chains are exposed on the film surface because of their hydrophobicity. By the rubbing treatment, the side chains are thought to be pulled on the surface by the nylon cloth and the main zigzag chains lying perpendicular to the rubbing direction are pulled and in average tilt in the rubbing direction as schematically shown in Fig. 7. The flexibility of the zigzag chains permits the change of the structure by the rubbing. On the other hand, there was no anisotropy in the SHG patterns of Fig. 5(a) to (d) of the unrubbed sample. The patterns can be reproduced only by $\chi_{zxx}^{(2)}$, $\chi_{yzy}^{(2)}$, and $\chi_{zxx}^{(2)}$ elements. This is because the polymers are completely randomly oriented.

The SHG study of the dependence of the $\theta_{ave}$ on the rotational speed of the rubbing roller and rubbing strength is our future topic. We anticipate that $\theta_{ave}$ will not strongly depend on these parameters because the steroidal structure is very stable, and from our experience [11] the pretilt angle of the liquid crystal molecules depend rather on the content of the steroidal structure side chains than the rubbing strength or the rotational speed of the rubbing roller.

The reason for the deviation of the SHG intensity pattern from the simulation for $P_{in}/S_{out}$ configuration in Fig. 4(b) is not known. We fabricated 6 samples in the same condition in this study, and such deviation of the signal pattern from that of the Cs symmetry was observed for all the samples. It seems to indicate that the symmetry of the sample was slightly deviated from Cs. Our AFM observation of the films showed scratches created by the rubbing on all over the sample surface, so the symmetry of the surface might not be perfectly Cs. In our analysis above we disregarded this deviation as an approximation.

V. CONCLUSION

By using an optical second harmonic generation measurement, we have observed the molecular orientation of the rubbed polyimide having steroidal structure side chain diamine. We determined the average tilt angle of the polymer main chain toward the rubbing direction as $\theta_{ave} = 15.7^\circ \pm 1.8^\circ$.


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