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Optical Second Harmonic Generation Analysis of Unrubbed Polyimide Surfaces as a Function of the Content of Steroidal Structure Side Chains

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Contribution of main chains and side chains of unrubbed polyimide films with steroidal structure side chains to second harmonic generation (SHG) response was studied by varying their molar fraction of side-chain diamine. The SHG intensity in $P_{in}/P_{out}$ polarization ($P$-polarization input and $P$-polarization output) configuration does not depend strongly on the molar fraction. This indicates that both the main chains and side chains at the surface contribute similarly to the SHG intensity. The SHG intensity in $S_{in}/P_{out}$ polarization configuration normalized by that of $P_{in}/P_{out}$ polarization configuration was the smallest for the molar fraction of side-chain diamine of 0%. This fact indicates that the microscopic nonlinear dipoles are standing nearly upright at the surface of the film consisting only of the main chains, while their orientational spread is wider when the side chains are involved.

Keywords Second harmonic generation; Polyimide; Polymer surface; Steroidal structure

I. INTRODUCTION

An alignment film is a thin film located on the indium-tin-oxide-coated glass substrate used in liquid crystal display (LCD) panels [1]. It is an essential component of the LCD, especially for large-screen LCD televisions because it controls the alignment of liquid crystal (LC) molecules. In recent years, polyimide (PI) is one of the most appropriate material for alignment films with its outstanding properties such as high thermal stability, superior electrical insulation and good chemical resistance [2, 3]. Nishikawa synthesized a novel polyimide containing steroidal structure side chains as shown in Figure 1 in 2011. In this polyimide the rigid side chain owing to the steroidal structure gives more stable pretilt angle of the LC molecules and better chemical properties than polyimide containing long alkyl side chain structure [4]. However, this polyimide has not been commercially spread so far because the orientation and conformation of polyimide main chains and steroidal structure side chains at the polyimide surface before and after rubbing has not fully been determined yet.

Optical second harmonic generation (SHG) is a useful tool for studying polymer surfaces and interfaces. This
The basic theory for SHG for surface studies has already been described in detail elsewhere [7]. In this section, we give only a brief description of relevant equations for later discussion. For molecules with a dominant hyperpolarizability element $\chi^{(2)}_{\xi\xi\xi}$ along the long molecular axis $\xi$, the macroscopic nonlinear susceptibility responsible for the SHG is given by

$$\chi^{(2)}_{ijk} = N_s((i \cdot \xi)(j \cdot \xi)(k \cdot \xi))\alpha^{(2)}_{\xi\xi\xi},$$

where $N_s$ is the surface molecular density, $i$, $j$, and $k$ refer to the laboratory coordinates $x$, $y$, or $z$, and the brackets mean an average over the molecular orientations. In unrubbed polymer films, the molecular distribution is polar with respect to the surface normal direction and is isotropic in the surface $x$-$y$ plane. Thus, there are only two independent nonvanishing elements of $\chi^{(2)}$ related to the molecular orientation as:

$$\chi^{(2)}_{zzz} = N_s(\cos^2\theta)\alpha^{(2)}_{\xi\xi\xi},$$

$$\chi^{(2)}_{xii} = \chi^{(2)}_{yij} = \chi^{(2)}_{zij} = \frac{1}{2} N_s(\sin^2\theta \cos \theta)\alpha^{(2)}_{\xi\xi\xi},$$

where $(i, j) = (x, y)$ and $\theta$ is the angle between $\hat{\xi}$ and $\hat{z}$. Here, $\hat{z}$ is along the normal to the film surface.

If we further assume that we have two kinds of polar molecules on the surface, then the expression will become,

$$\chi^{(2)}_{zzz} = N_M(\cos^3\theta)\alpha^{(2)}_{M\xi\xi},$$

$$\chi^{(2)}_{xii} = \chi^{(2)}_{yij} = \frac{1}{2} N_M(\cos \theta - \cos^3\theta)\alpha^{(2)}_{M\xi\xi} + \frac{1}{2} N_X(\cos \theta - \cos^3\theta)\alpha^{(2)}_{X\xi\xi}. $$

The hyperpolarizabilities $\alpha^{(2)}_{M\xi\xi}$ and $\alpha^{(2)}_{X\xi\xi}$ are those of units without and with the steroidal structure side chains in Figure 1, respectively.

In the following, the suffixes ‘M’ and ‘X2’ attached to several physical parameters represent main and side chains, respectively, like the ones in Figure 1, adopting the naming in Ref. 4. The above nonvanishing elements of $\chi^{(2)}$ can be measured by SHG. The SHG intensity is given by [8]

$$I(2\omega) \propto |\chi^{(2)}_{\text{eff}}|^2 I^2(\omega).$$

Here $I(\omega)$ is the intensity of the incident laser beam and $\chi^{(2)}_{\text{eff}}$ is the effective nonlinear susceptibility. $\chi^{(2)}_{\text{eff}}$ is defined by [7]

$$\chi^{(2)}_{\text{eff}} = [\hat{\theta}(2\omega) \cdot L(2\omega)]\chi^{(2)}: [L(\omega) \cdot \hat{\theta}(\omega)][L(\omega) \cdot \hat{\theta}(\omega)].$$
Here, $\hat{e}$ are unit polarization vectors for input beam at $\omega$ and output beam at $2\omega$, and $\mathbf{L}$’s are the local-field factor or Fresnel factor tensors for SHG field and fundamental beam, respectively. Using $\chi^{(2)}$ determined by SHG measurements and $\mathbf{L}$, the independent $\chi^{(2)}$ elements can be deduced.

III. EXPERIMENT

We have studied polyimide samples with five different in polyimide named PI-0, PI-30, PI-60, PI-90, and PI-100 molar fractions of side-chain diamine. Here the molar fraction in mol% is represented by the number after “PI-”. Figure 1 illustrates the chemical structure of the polyimide used in this study. The polyimide has the steroidal structure in the side chains and flexible main chains.

The samples for the experiment were prepared in the following process. First, the (polyamic) acid was obtained by reacting 2,3,5-tricarboxy-cyclopentyl acetic dianhydride with 1,4-phenylenediamine and side-chain diamine. We have changed the ratio of 1,4-phenylenediamine and side-chain diamine to obtain different kinds of polyimide samples. Then the (polyamic) acid solution was spin coated on indium tin oxide-coated glass substrate. The samples were then baked for 2 min at 80 °C for evaporation of solvents and 30 min at 230°C under nitrogen atmosphere for the indium tin oxide-coated glass substrate. The samples were then baked for 2 min at 80°C for evaporation of solvents and 30 min at 230°C under nitrogen atmosphere for an imidization reaction. The thickness of the polyimide layer was controlled by the spinning rate. We used polyimide an imidization reaction. The thickness of the polyimide layer elsewhere [6]. Briefly, a picosecond Nd$^3+$:YAG laser was used in this study. The polyimide has the steroidal structure in the side chains and flexible main chains.

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IV. RESULTS AND DISCUSSION

Figure 3 shows a dependence of the SHG intensity from the unrubbed polyimide film in the $P_{in}/P_{out}$ configuration on the molar fraction of side-chain diamine in polyimide. As it is shown in Figure 2, the SHG intensity from the unrubbed polyimide film is isotropic as a function of the rotation angle of the sample around its surface normal. $S_{in}/P_{out}$ SHG is below the noise level, as it is seen in Figure 2(b, d) and it is expected from symmetry consideration. Thus, we measured SHG intensities for $P_{in}/P_{out}$ and $S_{in}/P_{out}$ polarization combinations at one fixed azimuthal angles of the samples.

The SHG intensity in the $P_{in}/P_{out}$ configuration of all the polyimide films are presented in Figure 3(a). The SHG intensity from the film only with the main chains (PI-0) is non-zero, i.e., $I_{pp}(PI-0) \neq 0$. We can say that the nonlinear hyperpolarizability of the main chain without the side chains is non-zero, i.e., $\alpha_X^{(2)} \neq 0$. We note that $\alpha_X^{(2)}$ was found to contribute remarkably to the anisotropy of the SHG intensity for the rubbed films of the same polyimide film at the molar fraction of 30% [6].

Figure 3(b) shows the SFG intensity in $S_{in}/P_{out}$ configuration of all the unrubbed polyimide films as a function of the molar fraction of side-chain diamine. The SHG intensity for the PI-0 is the smallest among the samples. In Figure 3(c), we show the $S_{in}/P_{out}$ SHG intensity divided by $P_{in}/P_{out}$ SHG intensity for all the films. In Figure 3(c), the SHG intensity ratio is the smallest for the PI-0 sample, $I_{S/S}(PI-x)/I_{P/P}(PI-x)$ is more than 5% for $x \geq 30$, while it is around 4% for $x = 30$. The corresponding ratio of the nonlinear susceptibility elements $\chi^{(2)}_{zzz}/\chi^{(2)}_{xxz}$ (PI-0) should be the

Figure 3: SHG intensity of unrubbed polyimide films of the structure shown in Figure 1 as a function of the molar fraction of side-chain diamine for (a) $P_{in}/P_{out}$ configuration, (b) $S_{in}/P_{out}$ configuration, and (c) $S_{in}/P_{out}$ configuration normalized by that for $P_{in}/P_{out}$ configuration.
Table 1: $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ of unrubbed polyimide films with different molar fraction of side-chain diamine in polyimide.

| Molar fraction of side-chain diamine in polyimide (mol%) | $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ |
|----------------------------------------------------------|----------------------------------|
| 0                                                       | 0.0487 ± 0.0062                  |
| 30                                                      | 0.0804 ± 0.0071                  |
| 60                                                      | 0.0829 ± 0.0145                  |
| 90                                                      | 0.0665 ± 0.0065                  |
| 100                                                     | 0.0775 ± 0.0168                  |

Table 1 shows the refractive indices of five unrubbed polyimide films measured by spectroscopic ellipsometry.

V. CONCLUSIONS

The molar fraction of side-chain diamine of unrubbed polyimide films with steroidal structure side chains were tuned and their SHG response was studied systematically. We found that not only the side chains but also the main chains contribute to the SHG intensity. The SHG intensity in $S_{sw}/P_{out}$ polarization configuration normalized by that of $P_{sw}/P_{out}$ configuration is smaller for the molar fraction 0% of side chain diamine in polyimide than that for the others. This fact indicates that the nonlinear polarization is standing in more perpendicular direction for the film of 0 mol% than for larger molar fractions of side-chain diamine.

Appendix

For the following reason. Since the imaginary part of the refractive indices of the polyimide films are not big as we can see it in Table A1, we can expect that the imaginary part of the hyperpolarizabilities $\alpha_{M}^{(2)}$ and $\alpha_{X2}^{(2)}$ are not big, either, according to Miller [9]. From Figure 3(a), we can see very roughly that $I_{PP}(PI-0) = I_{PP}(PI-100)$ and, from this relation, we can say that the absolute values of $\alpha_{M}^{(2)}$ and $\alpha_{X2}^{(2)}$ are similar. If $\alpha_{M}^{(2)}$ and $\alpha_{X2}^{(2)}$ have different signs, the SHG intensity of samples with molar fractions of side-chain diamine near 50% should be nearly zero by the negative interference between the nonlinear susceptibilities of $\alpha_{M}^{(2)}$ and $\alpha_{X2}^{(2)}$ of the two components. However, the experimental data of the PI-60 show that this value is far from zero. Hence, $\alpha_{M}^{(2)}$ and $\alpha_{X2}^{(2)}$ have the same sign and the relation can be assumed [Eq. (7)].

From Eqs. (7), (3), and (4), we can deduce straightforwardly a relation;

$$\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz} = \frac{1}{2} \frac{(\cos \theta_M - \cos^3 \theta_M) + N_X2 (\cos \theta_X2 - \cos^3 \theta_X2)}{N_M \cos^3 \theta_M + N_X2 \cos^3 \theta_X2}.$$  

Because of $0^\circ \leq \theta_M, \theta_X2 \leq 90^\circ$, the value of Eq. (8) takes a real positive value. Hence, the real part of $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ has real positive values.

Based on the result of SHG measurements, we calculated the Fresnel factors and the $\chi^{(2)}$ element ratio $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ of each film. The calculation was done using the Fortran software reported in Ref. 10. The result is shown in Table 1. The refractive indices of the polyimide films to be used in the calculation of the Fresnel factors were measured by a spectroscopic ellipsometer [11] and are shown in Appendix. Here we assumed that $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ has real positive value from the discussion of the previous paragraph.

Putting $N_X2 = 0$ in Eq. (8), we have

$$\frac{\chi^{(2)}_{xxx}}{\chi^{(2)}_{zzz}} = \frac{1}{2} \frac{(\cos \theta_M - \cos^3 \theta_M)}{(\cos^3 \theta_M)}.$$  

Here, let us roughly assume that the statistical average of $(\cos^3 \theta)$ with respect to the orientation angle $\theta$ of effective molecules is approximately unity because the effective molecules are standing almost upright. The statistical average of $(\cos \theta - \cos^3 \theta)$ should be zero when all the molecules are standing exactly upright or $\cos \theta = 0$. The experimental result that the $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ is not zero but the smallest among the different molar fractions of side-chain diamine in polyimide then means that $(\cos \theta_M - \cos^3 \theta_M)$ of the main chain is non-zero but small for the PI-0 films. This means that each nonlinear polarization induced in the main chains are indeed standing almost upright on the surface of the film.

More discussion on $\chi^{(2)}_{xxx}/\chi^{(2)}_{zzz}$ for the molar fraction of side-chain diamine in polyimide larger than 30 mol% using Eqs. (3) and (4) is not easy because an exact ratio of...
Table A1: Indices of refraction of five unrubbed polyimide films at different wavelengths.

| Molar fraction of side-chain diamine in polyimide (mol%) | Refractive index (n) | \( n \) (532 nm) | \( n \) (266 nm) |
|--------------------------------------------------------|----------------------|-----------------|-----------------|
| 0                                                      | 1.6258               | 1.7523 ± 0.2733i| 1.8323 ± 0.2939i|
| 30                                                     | 1.5919 + 0.0002i     | 1.6479 ± 0.2239i| 1.7279 ± 0.2439i|
| 60                                                     | 1.5755               | 1.6100 ± 0.2103i| 1.7000 ± 0.2303i|
| 90                                                     | 1.5673               | 1.5506 ± 0.2027i| 1.6706 ± 0.2227i|
| 100                                                    | 1.5602 ± 0.0063i     | 1.6328 ± 0.0975i| 1.7128 ± 0.1175i|

Note
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