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Author(s)	Nguyen, Trinh Thi; Yu, Sheng; Asakura, Shinya; Khuat, Thi Thu Hien; Mizutani, Goro; Murakami, Yoshitaka; Okada, Takashi
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Description	

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

Nguyen Thi Trinh,[a] Yu Sheng,[a] Shinya Asakura,[a] Khuat Thi Thu Hien,[a] Goro Mizutani,[a, †] Yoshitaka Murakami,[b] Takashi Okada[b]

[a] *School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan*
[b] *LCD Materials 2nd Laboratory, Display Materials Research Laboratories, JSR Corporation, 100 Kawajiri-cho, Yokkaichi, Mie 510-8552, Japan*
[†] *Corresponding author: mizutani@jaist.ac.jp*

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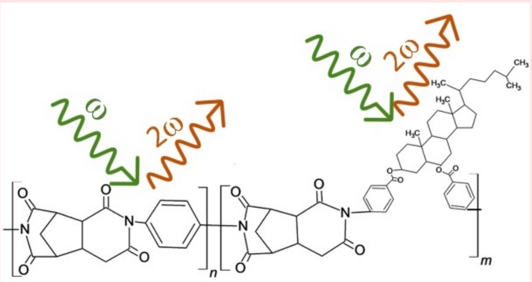
Contribution of main chains and side chains of unrubbed polyimide films with steroidal structure side chains to second harmonic generation (SHG) response was studied by varying their molar fraction of side-chain diamine. The SHG intensity in P_{in}/P_{out} polarization (P-polarization input and P-polarization 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

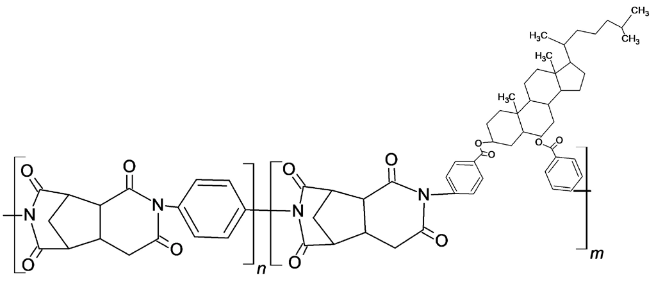


Figure 1: Chemical structure of the polyimide.

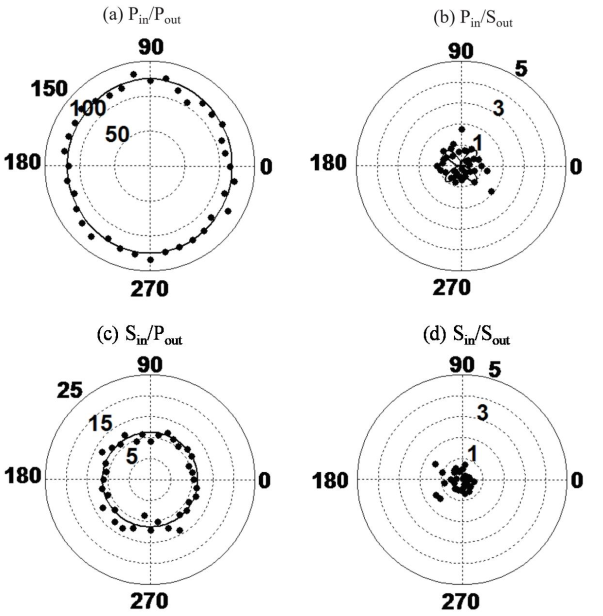


Figure 2: SHG intensity from an unrubbed polyimide film with the molar fraction 30% of steroidal side-chain diamine as a function of the sample rotation angle and the combination of the input and output polarization. This figure is reproduced from the publication by Ullah *et al.* [6].

technique is extremely surface sensitive because SHG occurs only at non-centrosymmetric parts in materials [5]. With results from different input/output polarization combinations, it provides information about the orientation of molecules on the surface. Ullah *et al.* observed that the SHG intensity of rubbed polyimide with steroidal side chains as shown in Figure 1 for the molar fraction 30% of side-chain diamine in polyimide shows anisotropic SHG intensity patterns as a function of the angle of the sample rotation angle [6]. In their work they assumed that only the steroidal side chains have microscopic optical nonlinearity and explained the result, but they did not check the validity of this assumption.

In this research, we will try to decide whether this assumption was correct or not. For this purpose, we observed SHG from polyimide surfaces before rubbing at several different molar fractions of side-chain diamine in polyimide. Unrubbed polyimides show isotropic SHG intensity patterns, as they are displayed in Figure 2. This means that smaller number of independent $\chi^{(2)}$ elements are involved in the pattern formation. The reason why we use unrubbed films is that we can exclude more ambiguity in the analysis of the obtained SHG intensity patterns. Based on the SHG signals from the surface of these polyimide films, we will deduce the contribution of main chains and side chains.

II. THEORETICAL BACKGROUND

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 $\alpha^{(2)}_{\xi\xi\xi}$ along the long molecular axis ξ, the macroscopic nonlinear susceptibility responsible for the SHG is given by

$$\chi^{(2)}_{ijk} = N_s\langle(\hat{\boldsymbol{i}}\cdot\hat{\boldsymbol{\xi}})(\hat{\boldsymbol{j}}\cdot\hat{\boldsymbol{\xi}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{\xi}})\rangle\alpha^{(2)}_{\xi\xi\xi}\,, \tag{1}$$

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:

$$\chi^{(2)}_{zzz} = N_s\langle\cos^3\theta\rangle\alpha^{(2)}_{\xi\xi\xi}$$

$$\chi^{(2)}_{zii} = \chi^{(2)}_{izi} = \chi^{(2)}_{iiz} = \frac{1}{2}N_s\langle\sin^2\theta\cos\theta\rangle\alpha^{(2)}_{\xi\xi\xi}\,, \tag{2}$$

where $(i, j) = (x, y)$ and θ is the angle between $\hat{\boldsymbol{\xi}}$ and $\hat{\boldsymbol{z}}$. Here, $\hat{\boldsymbol{z}}$ 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,

$$\chi^{(2)}_{zzz} = N_{\mathrm{M}}\langle\cos^3\theta_{\mathrm{M}}\rangle\alpha^{(2)}_{\mathrm{M}\xi\xi\xi} + N_{\mathrm{X2}}\langle\cos^3\theta_{\mathrm{X2}}\rangle\alpha^{(2)}_{\mathrm{X2}\xi\xi\xi} \tag{3}$$

$$\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy} = \frac{1}{2}N_{\mathrm{M}}\langle\cos\theta_{\mathrm{M}} - \cos^3\theta_{\mathrm{M}}\rangle\alpha^{(2)}_{\mathrm{M}\xi\xi\xi} + \frac{1}{2}N_{\mathrm{X2}}\langle\cos\theta_{\mathrm{X2}} - \cos^3\theta_{\mathrm{X2}}\rangle\alpha^{(2)}_{\mathrm{X2}\xi\xi\xi}\,. \tag{4}$$

The hyperpolarizabilities $\alpha^{(2)}_{\mathrm{M}\xi\xi\xi}$ and $\alpha^{(2)}_{\mathrm{X2}\xi\xi\xi}$ are those of units without and with the steroidal structure side chains in Figure 1, respectively.

In the following, the suffices '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]

$$I(2\omega) \propto \left|\chi^{(2)}_{\mathrm{eff}}\right|^2 I^2(\omega)\,. \tag{5}$$

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

$$\chi^{(2)}_{\mathrm{eff}} = [\hat{\boldsymbol{e}}(2\omega)\cdot\boldsymbol{L}(2\omega)]\boldsymbol{\chi}^{(2)}:[\boldsymbol{L}(\omega)\cdot\hat{\boldsymbol{e}}(\omega)][\boldsymbol{L}(\omega)\cdot\hat{\boldsymbol{e}}(\omega)]. \tag{6}$$

Here, $\hat{\boldsymbol{e}}$ are unit polarization vectors for input beam at ω and output beam at 2ω, and $\boldsymbol{L}$’s are the local-field factor or Fresnel factor tensors for SHG field and fundamental beam, respectively. Using $\chi^{(2)}_{\mathrm{eff}}$ determined by SHG measurements and $\boldsymbol{L}$, 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 an imidization reaction. The thickness of the polyimide layer was controlled by the spinning rate. We used polyimide samples with the film thickness of about 100 nm.

The SHG experimental arrangement has been described elsewhere [6]. Briefly, a picosecond $\mathrm{Nd^{3+}}$:YAG laser (EKSPLA, PL2143B) operating at 10 Hz was used in conjunction with a harmonic unit to generate a visible beam at 532 nm. The beam irradiated an unrubbed sample mounted on a sample stage with pulse energy of about 20 μJ/pulse. The SHG output was detected by a photomultiplier in the reflection direction and a Boxcar integrator. We collected SHG data for two input/output polarization configurations: $\mathrm{S_{in}/P_{out}}$ (S-polarized fundamental beam and P-polarized SHG) and $\mathrm{P_{in}/P_{out}}$. For each data point signal accumulation was done for 15000 laser shots. The sample holder held two samples at a time and their absolute SHG intensity was compared by using a sliding mechanism. At each time, we measured SHG signal of a PI-60 film and then one of the polyimide films with different molar fractions of side-chain diamine (PI-0, PI-30, PI-60, PI-90, and PI-100). The SHG signal of the PI-60 film was used to normalize the SHG signal of the other samples. For each molar fraction of side-chain diamine, we prepared two samples and measured their SHG response.

IV. RESULTS AND DISCUSSION

Figure 3 shows a dependence of the SHG intensity from the unrubbed polyimide film in the $\mathrm{P_{in}/P_{out}}$ and $\mathrm{S_{in}/P_{out}}$ configurations 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. $\mathrm{S_{out}}$ 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 $\mathrm{P_{in}/P_{out}}$ and $\mathrm{S_{in}/P_{out}}$ polarization combinations at one fixed azimuthal angles of the samples.

The SHG intensity in the $\mathrm{P_{in}/P_{out}}$ 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 not zero, or $I_{\mathrm{pp}}(\mathrm{PI\text{-}0}) \neq 0$. We can say that the nonlinear hyperpolarizability of the main chain without the side chains is non-zero, i.e., $\alpha^{(2)}_{\mathrm{M}} \neq 0$. We note that $\alpha^{(2)}_{\mathrm{X2}}$ 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 Sin/Pout 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 $\mathrm{S_{in}/P_{out}}$ SHG intensity divided by $\mathrm{P_{in}/P_{out}}$ SHG intensity for all the films. In Figure 3(c), the SHG intensity ratio is the smallest for the PI-0 sample, $I_{\mathrm{SP}}(\mathrm{PI}\text{-}x)/I_{\mathrm{PP}}(\mathrm{PI}\text{-}x)$ is more than 5% for $x \geq 30$, while it is around 4% for $x = 0$. The corresponding ratio of the nonlinear susceptibility elements $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}(\mathrm{PI\text{-}0})$ should be the

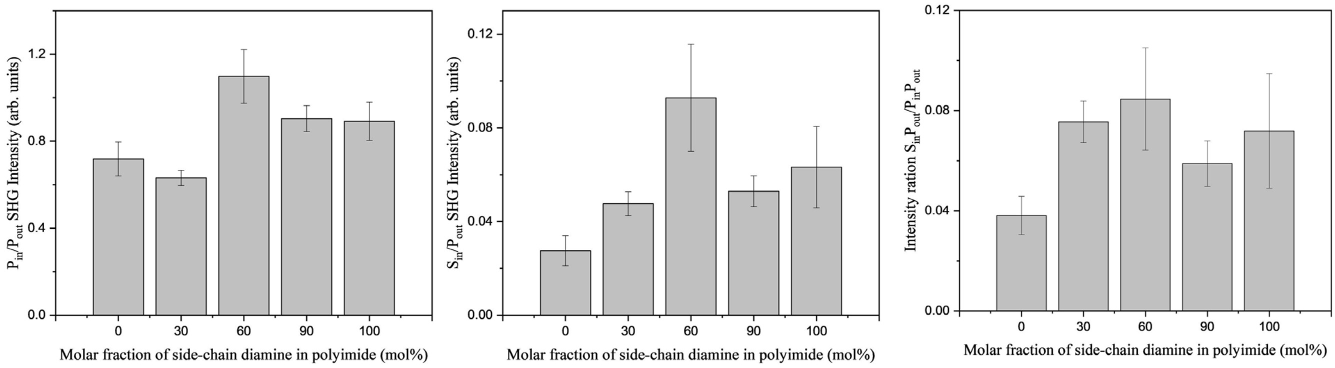


Figure 3: SHG intensity of unrubbed polyimide films of the structure shown in Figure 1 as a function of the molar fraction of side-chain diamine for (a) $\mathrm{P_{in}/P_{out}}$ configuration, (b) $\mathrm{S_{in}/P_{out}}$ configuration, and (c) $\mathrm{S_{in}/P_{out}}$ configuration normalized by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

Table 1: $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ of unrubbed polyimide films with different molar fraction of side-chain diamine in polyimide.

Molar fraction of side-chain diamine in polyimide (mol%)	$\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$
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

smallest among the different molar fractions of side-chain diamine in polyimide. Here we first consider the reason for the smallest values of I_{SP}(PI-0)/I_{PP}(PI-0) and $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ (PI-0).

For this purpose, we first assume that

$$\alpha^{(2)}_{\mathrm{M}} \approx \alpha^{(2)}_{\mathrm{X2}} \tag{7}$$

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 $\alpha^{(2)}_{\mathrm{M}}$ and $\alpha^{(2)}_{\mathrm{X2}}$ 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 $\alpha^{(2)}_{\mathrm{M}}$ and $\alpha^{(2)}_{\mathrm{X2}}$ are similar. If $\alpha^{(2)}_{\mathrm{M}}$ and $\alpha^{(2)}_{\mathrm{X2}}$ 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 $\alpha^{(2)}_{\mathrm{M}}$ and $\alpha^{(2)}_{\mathrm{X2}}$ of the two components. However, the experimental data of the PI-60 show that this value is far from zero. Hence, $\alpha^{(2)}_{\mathrm{M}}$ and $\alpha^{(2)}_{\mathrm{X2}}$ have the same sign and the relation can be assumed [Eq. (7)].

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

$$\frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zzz}} = \frac{1}{2}\frac{N_{\mathrm{M}}(\cos\theta_{\mathrm{M}} - \cos^3\theta_{\mathrm{M}}) + N_{\mathrm{X2}}(\cos\theta_{\mathrm{X2}} - \cos^3\theta_{\mathrm{X2}})}{N_{\mathrm{M}}\cos^3\theta_{\mathrm{M}} + N_{\mathrm{X2}}\cos^3\theta_{\mathrm{X2}}}. \tag{8}$$

Because of 0° ≤ θ_{M}, θ_{X2} ≤ 90°, the value of Eq. (8) takes a real positive value. Hence, the real part of $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ has real positive values.

Based on the result of SHG measurements, we calculated the Fresnel factors and the $\chi^{(2)}$ element ratio $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ 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 $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ has real positive value from the discussion of the previous paragraph.

Putting $N_{\mathrm{X2}} = 0$ in Eq. (8), we have

$$\frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zzz}} = \frac{1}{2}\frac{\langle\cos\theta_{\mathrm{M}} - \cos^3\theta_{\mathrm{M}}\rangle}{\langle\cos^3\theta_{\mathrm{M}}\rangle}. \tag{9}$$

Here, let us roughly assume that the statistical average of $\langle\cos^3\theta\rangle$ with respect to the orientation angle θ of effective molecules is approximately unity because the effective molecules are standing almost upright. The statistical average of $\langle\cos\theta - \cos^3\theta\rangle$ should be zero when all the molecules are standing exactly upright or $\cos\theta = 0$. The experimental result that the $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ is not zero but the smallest among the different molar fractions of side-chain diamine in polyimide then means that $\langle\cos\theta_{\mathrm{M}} - \cos^3\theta_{\mathrm{M}}\rangle$ 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 $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ 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 $\alpha^{(2)}_{\mathrm{X2}\xi\xi\xi}/\alpha^{(2)}_{\mathrm{M}\xi\xi\xi}$ is not known. Still we can say that the angles θ_{X2} of the microscopic nonlinear polarization are larger than θ_{M} to explain the $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ for the molar fraction of side-chain diamine larger than 30 mol%. We might also be able to say that the reason why $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ is smaller for PI-90 than for PI-60 will be that the microscopic nonlinear polarization of the side chains are less randomly oriented. This in turn may be because there is not enough space for the random orientation of the side chains in the surrounding neighborhood for PI-90. The intensity ratio $\mathrm{S_{in}P_{out}/P_{in}P_{out}}$ for PI-100 films in Figure 3(c) has a relatively large error, so it does not give any physical information about this sample.

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 $\mathrm{S_{in}/P_{out}}$ polarization configuration normalized by that of $\mathrm{P_{in}/P_{out}}$ 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

Table A1 shows the refractive indices of five unrubbed polyimide films measured by spectroscopic ellipsometry.

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	$1.7523 + 0.2733i$
30	$1.5919 + 0.0002i$	$1.6479 + 0.2239i$
60	1.5755	$1.6100 + 0.2103i$
90	1.5673	$1.5506 + 0.2027i$
100	$1.5602 + 0.0063i$	$1.6328 + 0.0975i$

Note

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