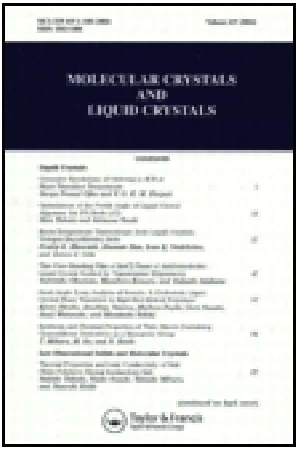


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# Molecular Orientation of Poly(2,2′;-Bipyridine-5,5′-Diyl) Film Prepared by Vacuum Deposition on the Glass Substrate as Determined with SHG Technique

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# Molecular Orientation of Poly(2,2′-Bipyridine-5,5′-Diyl) Film Prepared by Vacuum Deposition on the Glass Substrate as Determined with SHG Technique

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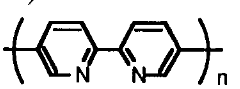
We have found that vacuum-deposited poly(2,2′-bipyridine-5,5′-diyl) PBPy aligns along glass substrate surface using SHG technique. The SHG activity originates from the interface where the PBPy molecules coordinate to acidic Si-O-H group on the glass surface.

*Keywords: poly(2,2′-bipyridine-5,5′-diyl), vacuum-deposition, molecular orientation, SHG, coordination*

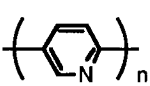
## INTRODUCTION

Preparation and properties of electrically conducting π-conjugated polymers are the subject of recent interest.[1,2] The π-conjugated polymers are essentially regarded as one-dimensional conductors, and alignment of the π-conjugated polymer molecules is considered to be an important and crucial step for revealing their basic properties (e.g., mobility of carrier, and optical properties).

So far the following properties have been reported: (a) Poly(2,2′-bipyridine-5,5′-diyl) PBPy[3] and poly(pyridine-2,5-diyl) PPy[4] prepared by organometallic techniques using nickel complex[5,6] take rigid and linear rod-like structures in solutions (e.g., in formic acid).



PBPy
n = ca. 20



PPy
n = ca. 50

b) PBPy, PPy, and similar rigidly linear π-conjugated polymers such as poly(p-phenylene) PPP and poly(thiophene-2,5-diyl) PTh form thin films on various substrates when deposited under vacuum.[7] The polymer molecules in the films have the same chemical structure as those of the source materials for the vacuum deposition, and they are oriented perpendicularly to the surface of the substrate when they are deposited on nonpolar substrates such as amorphous carbon, aluminum, and gold.[8]

In the course of the study on the vacuum deposition of the π-conjugated polymers, we have found that some of the deposited films are SHG (second harmonic generation) active when they are formed on glass substrate, which has polar surface due to the presence of Si-O-H functional group on the surface. We now report the SHG properties of the films and propose that the SHG activity of the film originates from an orientation of the polymer molecules on the interface between the polymer and the glass.



## EXPERIMENTAL AND ANALYSIS

PBPy,[3] PPy[4] and PTh were prepared as previously reported. The polymer was vacuum-deposited on a glass substrate (S-3313: Matsunami Glass Ind. with dimensions of 0.7 × 10 × 10 mm) from a heated (200–400°C) tantalum boat at 1.5 × $10^{-4}$ Pa. The fundamental Nd:YAG laser beam (1064 nm), whose power was about 3 mJ/pulse, was focused on the vacuum-deposited polymer film with a spot size of about 300 μm in diameter. The SHG was measured for various combinations of polarizations, P- and S-polarized light, as the sample film was rotated around the Z axis shown in Figure 1 (Incident angle $\theta$ = 45° in the present case). Refractive index of PBPy at 589 nm (Na-D line) was 2.18 as kindly measured by Messrs. Y.

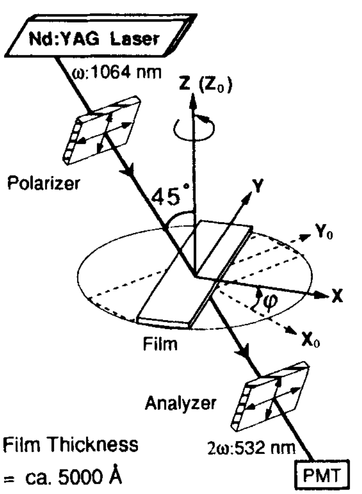



FIGURE 1 The schematic experimental geometry. Irradiation of polarized light to the vacuum-deposited PBPy film which can be rotated around the $Z$ axis. Coordinates ($X_0$, $Y_0$, $Z_0$) are those of laboratory frame.

Tsutsui and M. Hasegawa of Tosoh Co. Ltd. Since vacuum deposited PBPy films on the glass substrate have the absorption edge at 430 nm and are transparent enough in the region between 532 and 1064 nm, Fresnel's factors were calculated using the refractive index at 589 nm for analysis of the SHG data.



## RESULTS AND DISCUSSION

Figure 2 shows SHG response of the vacuum-deposited thin films of PBPy in P-P (irradiation light = P polarized light; detected SH light = P component of the SH light), S-S, S-P, and P-S combinations. As shown in Figure 2, the PBPy film is SHG active and SH intensity is predominantly observed in the P-P combination. The SH intensities in the other three combinations are about 1/10 compared with that in the P-P combination. This observation implies that there exists a large nonlinear susceptibility component perpendicular to the surface plane.

As is clear from Figure 2(a), one of the interesting features of the SHG of the PBPy film is anisotropy of the SHG concerning the rotation around the $Z$ axis: the point symmetry is $C_s$ with only one mirror in the $X$-$Z$ plane. This feature strongly suggests that all the PBPy molecules which contribute to SHG align to a certain, but unspecified, direction and the molecule plane tilts from the surface normal. However, the vacuum-deposited PBPy film does not show observable dichroism in its UV-visible spectrum, while it was clearly observed for aligned PBPy molecules in stretched polymer (e.g., poly(vinyl alcohol)) film.[4] Therefore, we can conclude that most of the PBPy molecules in the vacuum-deposited PBPy film are essentially randomly oriented and the SH light is mainly generated from the interface between the glass substrate and its neighboring layer of PBPy. Since there are no position dependence in the SHG profiles, all the PBPy molecules on the surface of the glass substrate are considered to be aligned along the same direction all over the area of 10 × 10 mm.

Based on the SHG data and molecular structure of PBPy, we assume $C_s$ symmetry for the present system. Taking the $Z$ axis along the surface normal and the $X$-$Z$

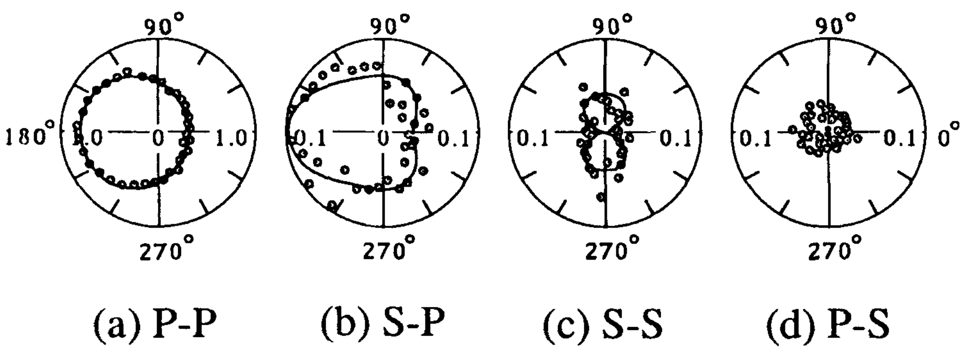



FIGURE 2 SHG from vacuum-deposited PBPy film on a glass substrate at P-P, S-S, S-P, and P-S combinations. (⊗ : observed data, —: best theoretical fit). Relative scale of the SHG intensity is shown on the radial line.

plane as the mirror plane, we obtain the following ten non-zero elements in the second-order susceptibility tensor.[11]

$$\begin{pmatrix} \chi_{XXX} & \chi_{XYY} & \chi_{XZZ} & 0 & \chi_{XZX} & 0 \\ 0 & 0 & 0 & \chi_{YYZ} & 0 & \chi_{YXY} \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & 0 & \chi_{ZZX} & 0 \end{pmatrix}$$

Since Kleinman's condition holds for the present PBPy film, the number of the element can be reduced to six;

$$\chi_{XXX}, \chi_{XYY} = \chi_{YXY}, \chi_{XZZ} = \chi_{ZZX}, \chi_{XZX} = \chi_{ZXX}, \chi_{YYZ} = \chi_{ZYY}, \chi_{ZZZ}.$$

The induced second order nonlinear polarization is expressed as $\mathbf{P}_i(2\omega) = \chi_{ijk}:\mathbf{E}_j(\omega)\mathbf{E}_k(\omega)$. The SH light intensity is given by square of $\mathbf{P}_i(2\omega)$, and those in the P-P, S-P, P-S, and S-S combinations are given by the following equations, respectively,

$$\begin{aligned} P_{P\text{-}P} &= \{A_0[\chi_{YYZ}, \chi_{ZZZ}] + A_1[\chi_{XYY}, \chi_{XZZ}]\cdot\cos\varphi + A_2[\chi_{XZX}, \chi_{YYZ}]\cdot\cos^2\varphi \\ &\quad + A_3[\chi_{XXX}, \chi_{XYY}]\cdot\cos^3\varphi\}\cdot E_0^2 \\ P_{S\text{-}P} &= \{B_0[\chi_{ZXX}] + B_1[\chi_{XXX}, \chi_{XYY}]\cdot\cos\varphi + B_2[\chi_{ZXX}, \chi_{ZYY}]\cdot\cos^2\varphi \\ &\quad + B_3[\chi_{XXX}, \chi_{XYY}]\cdot\cos^3\varphi\}\cdot E_0^2 \\ P_{P\text{-}S} &= \{C_0[\chi_{XXX}, \chi_{XZZ}, \chi_{XYY}] + C_1[\chi_{XXX}, \chi_{XYY}]\cdot\sin^2\varphi \\ &\quad + C_2[\chi_{XZX}, \chi_{YYZ}]\cdot\cos\varphi\}\cdot\sin\varphi\cdot E_0^2 \\ P_{S\text{-}S} &= \{D_0[\chi_{XYY}] + D_1[\chi_{XXX}, \chi_{XYY}]\cdot\sin^2\varphi\}\cdot\sin\varphi\cdot E_0^2 \end{aligned}$$

where $A_m - D_m (m = 0, 1, 2, \ldots)$ are coefficients including Fresnel's factors and multiple reflection effects.[9–13] $A_m[\chi_{ijk}, \chi_{i'j'k'}, \ldots]$ are linear combinations of $\chi_{ijk}$, $\chi_{i'j'k'}$, .... $\varphi$ stands for the rotation angle.

Fitting the theoretical equations to the observed data (Figure 2), with a least square method, gives relative values of the six tensor elements; $\chi_{ZZZ}$ is the dominant tensor element and other five elements are 20–50 times smaller than $\chi_{ZZZ}$. The theoretical best fitted SHG profiles shown in Figure 2, (solid lines), agree with the observed SHG profiles ( ⊙ marks), supporting the assumption of the Cx symmetry.

If the PBPy molecules are oriented perpendicularly to the surface of the glass substrate as in the case of the PBPy films deposited on the nonpolar substrates,[7,8] such SHG profiles as those shown in Figure 2 would not be expected. On the contrary, if one assumes orientation of the PBPy molecules along the surface of the $SiO_2$ glass as shown in Figure 3(a), the molecules are expected to have the component of the dipole moment perpendicular to the surface of the substrate.

The glass substrate is considered to have acidic Si-O-H group, and 2,2′-bipyridine, the unit of PBPy, is known to coordinate to acidic-H to form the *s*-cis conformation,[14] in spite of its *s*-trans conformation in ordinary state.[15] A model for the alignment of the PBPy molecules at the interface is depicted in Figure 4.

In contrast to PBPy, the vacuum-deposited PPy film was SHG inactive, which is considered to be due to difficulty for the PPy molecule to coordinate to the Si-

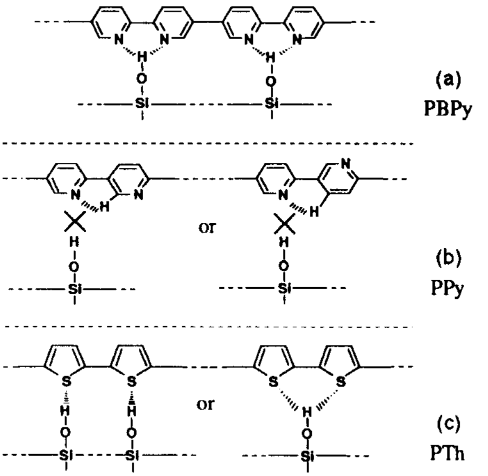



FIGURE 3 Coordination of PBPy (a) and PTh (c) molecules on the Si-O-H group on the surface of the glass substrate. In the case of PPy (b), such coordination does not take place.

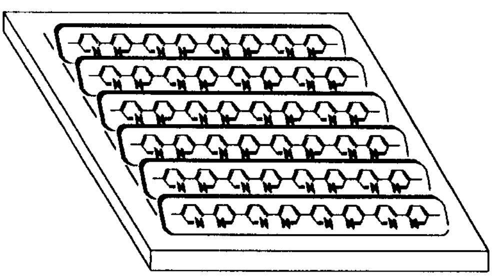


FIGURE 4 Alignment of the linear PBPy molecules at the interface and its neighboring layers on the glass substrate. The SH light is mainly generated from this part.

O-H group because of the head-to-tail structure of PPy (Figure 3(b)). It is reported that PBPy has strong ability of coordination toward transition metals whereas PPy does not.[3] The vacuum-deposited PTh film on the glass substrate had the SHG activity, which is also considered to be due to the coordination of the PTh molecule to the polar Si-O-H group (Figure 3(c)). The SHG phenomena of PTh will be reported elsewhere.

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