SHORT COMMUNICATIONS

X-Ray Analysis of Poly(thiophene-*alt*-thiophene-1,1-dioxide)

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Electrically-conductive polymers containing thiophene unit demonstrate high chemical stability, and have been the subject of many papers. The results of X-Ray crystallographic analysis of polythiophene (PTh) have been reported.[2,3] PTh and its derivatives comprising rigid π-conjugated backbone are hard to melt on heating, and low in solubility and also in thermal processibility. Their chemical modification possibly alters the manner of interactions between the π-conjugated moieties, and also the conduction and processing properties.

Polymers of thiophene-1,1-dioxide have also attracted attention.[4,5] However, successful preparation of the dioxide polymer has not been reported due to synthetic difficulties. We recently reported preparation of alternating copolymer of thiophene and thiophene-1,1-dioxide by Stille coupling reaction between organic halide and organic stannyl compound.[6]

These polymers are generally poorly crystalline probably because of the molecular rigidity and the strong intermolecular interactions. Exhibition of only several X-Ray reflections indicates the lack of orders of ordinary crystalline polymers, but even such data claim some essential molecular arrangements. The normal X-Ray crystal structure analysis is practically difficult, but the Rietveld whole-fitting technique has addressed the problem. It has been successfully applied to analyses of PTh,[3] poly-(*p*-phenylene) (PPP),[7] poly(3-methylthiophene) (P 3 MeTh),[8,9] and many other polymers.

In this study, the structure of poly(thiophene-*alt*-thiophene-1,1-dioxide) (PTTO) was analyzed with the aid of linked-atom Rietveld method (LARV), in which bond lengths and bond angles can be constrained to their standard values. Even if X-Ray reflections are overlapped for the powder sample and the diffraction pattern is too simple, the LARV simulation using a small number of parameters can reject the false structure and manifest the essential structure with a certain reliability, since undesirable peaks invariably emerge in the calculated scattering curve of the false structure.
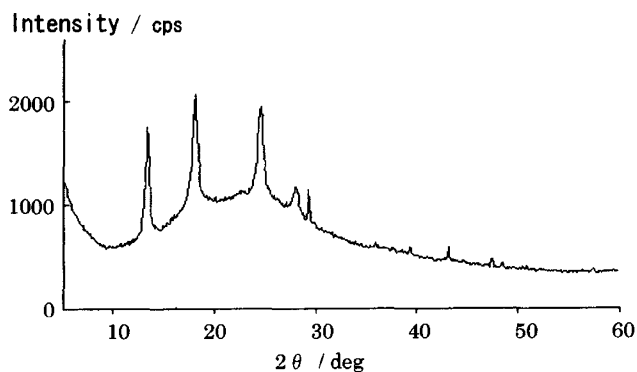

Figure 1. Powder X-Ray diffraction pattern of PTTO.

EXPERIMENTAL

The sample of PTTO was prepared according to the previously reported procedure.[6] The density of the PTTO powder sample was tried to measure by the flotation method at 25°C. However, it was surely higher than 1.63 g cm^{-3}, since the sample precipitated even in carbon tetrachloride.

The specimen for X-Ray measurement was prepared by scattering the fine powder on a non-reflective silicon plate with dilute adhesive solution. The diffraction curve was measured by a symmetrical-reflection powder diffractometer with graphite-monochromatized Cu-K_α radiation. The data were accumulated over three-times scans with a step of 0.1° in the range of diffraction angle $2\theta = 5$—60°. The diffraction pattern was also taken with a planar image-plate detector, and it was converted into the diffraction curve. The image-plate pattern was essentially identical, but rather poor in the resolution and the S/N quality as a general feature of the transmission method.

The observed profile measured by the diffractometer is shown in Figure 1. The weak and extraordinarily sharp reflections in the range of $2\theta > 29$° are considered to come from impurities such as triphenylphosphine or its

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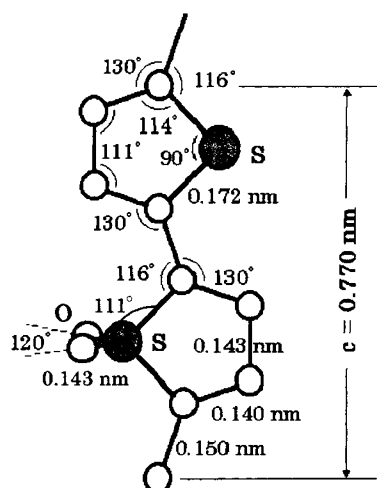
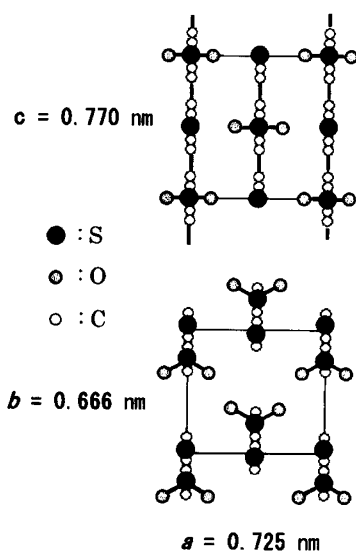**Figure 2.** Molecular geometry, bond lengths, and bond angles.

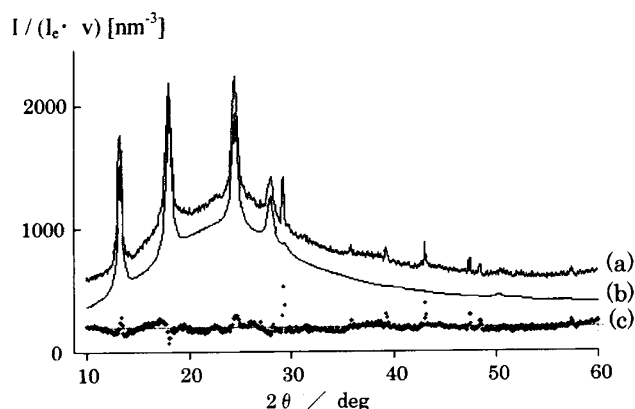**Figure 3.** A closest packing model (Pmnm) for PTTO.

Figure 4. Comparison between (a) observed and (b) calculated profiles. Curve (c) indicates the difference (a−b) profile. Curve (b) is shifted downward while (c) upward for visual obviousness.

Table I. X-Ray Data of PTTO

System	rectangular pmg (orthorhombic Pmnm)
Cell dimension	$a = 0.725$ nm $b = 0.666$ nm, $(c = 0.770$ nm)
Calc. density	1.75 g cm^{-3}

Spacing and indices of reflections

d_{obs} / nm	d_{calc} / nm	hkl
—	0.725	100
0.666	0.666	010
0.491	0.490	110
0.362	0.362	200
—	0.333	020
0.318	0.318	210

by using a palladium compound containing triphenylphosphine.

RESULTS AND DISCUSSION

The PTTO molecular model was constructed by assuming the same planar backbone conformation as that of PTh[3] with dimensions given in Figure 2. The dioxide unit was additionally attached for C_{2v} symmetry with the unique C_2 axis that is normal to the chain axis and passes through the sulfur atom. The calculated repeat distance for the two thiophene units along the chain axis was $c = 0.770$ nm.

By taking into account the closest packing of the models with the atomic shells of van der Waals radii, the diffraction curves were calculated for several crystal-structure models. The simulations suggested that the four main reflections are equatorial ones, since the nonequatorial reflections cannot be so strong in the powder pattern that is the one averaged spherically in the 3-D reciprocal spcace. The four inherent reflections were indexed for the most probable packing model as the equatorial ones of a rectangular unit cell with dimensions $a = 0.725$ nm and $b = 0.666$ nm (Table I). The high density comparable to the value 1.64 g cm^{-3} for PTh[3] is due to the compact thiophene unit and the dense molecular packing. The ideal closest packing model is illustrated in Figure 3. In the pmg structure, the symmetry is defined by the mirror planes normal to the a axis and the glide planes normal to the b axis, and therefore the molecular positions are highly confined in the unit cell.

As was the case of PTh,[3] nonequatorial reflections seemed to be absent. A very weak peak at $2\theta = 23.0°$ is possibly 002 reflection which supports the c dimension of the present model. Other nonequatorial reflections could not be clearly identified. The feature suggests the two-dimensional packing order in the c-axis projection, but indicates the shift disorder along the c axis.

The diffraction curve was calculated by the LARV method for this model in the 2θ range of 10—60°. Hydrogen atoms were neglected in the structure factor calculation. Contributions from the missing $hk0$ reflections were included, while nonequatorial ones were initially neglected. The observed (I_o) and calculated (I_c) profiles are compared in Figure 4.

The parameters were refined according to the Rietveld original fashion as follows. Since X-Ray date were rather

oxide originating from the catalyst. The presence of these impurities was previously pointed out by NMR for a polymer prepared by using a metal compound containing triphenylphosphine,[10] and PTTO was also prepared
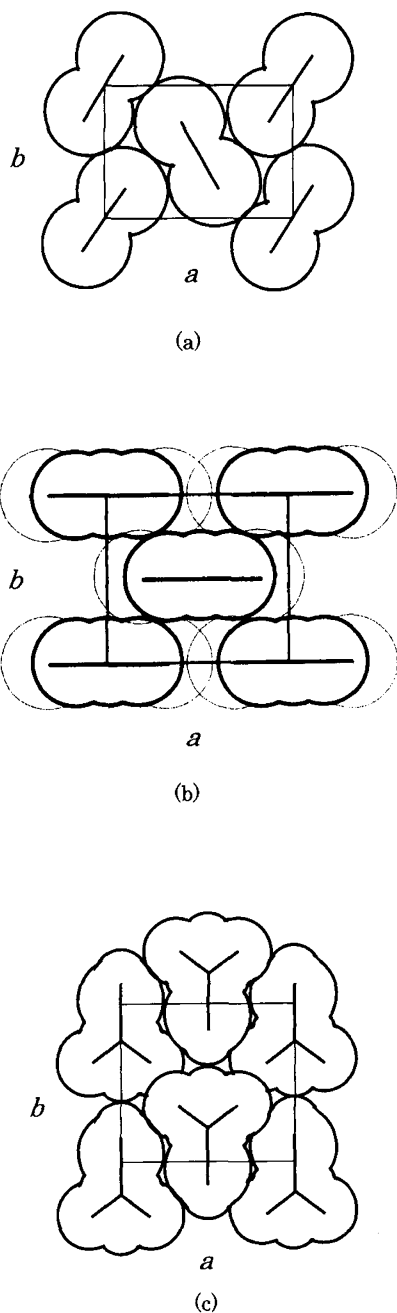
(a)

(b)

(c)

Figure 5. Molecular packing modes of (a) pgg (PTh), (b) cmm (P-3MeTh), and (c) pmg (PTTO). The outer envelopes are illustrated with respective van der Waals radii.

poor to refine the molecular conformation, the molecule was treated as a rigid body. The structural parameter is only the position of the molecule as a whole along the b axis (the final fractional coordinate $y/b = -0.25$ for the sulfonyl sulfur atom). The overall atomic temperature factor was held at a value of $B=0.07$ nm^2 . The first non-structural parameter was the scale factor to correct the observed intensity to absolute value expressed as $I/(I_e \cdot v)$, where I_e is the intensity scattered by a single electron and v is the scattering volume. The amorphous background curve was approximated by a linear function of 2θ (height 330 at $2\theta = 10°$ and 580 at $2\theta = 60°$) and a broad Cauchy function ($2\theta_{peak} = 22.9°$, half width 17.4° , and peak height 810). Reflection profiles were also described by Cauchy functions with half width of $\sqrt{(V \cdot \tan\theta)}$

deg (the final value $V=1.94$). The parameters of zero-angle correction and preferred orientation were fixed as 0. The final discrepancy factor $R = \Sigma \mid \sqrt{I_O} - \sqrt{I_C} \mid / \Sigma \sqrt{I_O}$ was 0.026 for the 501 data points.

As the next step, the diffraction curve was calculated for an ideal Pmnm packing model (Figure 3) by including nonequatorial reflections. The profile was certainly modified but essentially the same as that shown in Figure 4b. The weakness of the peak at $2\theta = 23.0°$ was elucidated by 002 reflection, and the weak intensity spreads at $2\theta = 32°$ and 38° were also attributable to 121 and 122 reflections, respectively. However, the total agreement between I_O and I_C was deteriorated. As in the case of PTh,[3] the shift disorder along the c axis is plausible from the features of the profile and the low crystallinity. Accordingly, the simulation for the ideal crystal structure has a problem, since the equatorial and the nonequatorial reflections cannot be treated with the same profile function in such a disordered structure. The well-defined Pmnm model illustrated in Figure 3 is possibly the essential structure, but the actual structure must be regarded to be disordered with respect to the displacement along the chain axis.

In PTh,[3] the molecules are packed in a rectangular pgg unit cell (Figure 5a). The packing mode is similar to those in PPP[7] and polyethylene, and has often been observed for slim molecules, where the molecular shape enveloping the atomic van der Waals radii is round or cylindrical. The attachment of pendant groups induces the parallel molecular arrangement. In P3MeTh (Figure 5b),[8,9] the molecules are packed in the face-centered cmm unit cell. In PTTO (Figure 5c), the molecules are stacked in face-to-face packing manner. A PTTO single chain is polar having the dipole moment normal to the chain axis. However, the moments are compensated by their alternate stacking. Positional relationship and interactions between the π-conjugated moieties are thus variable. It is significant to investigate the principles of structural order formation.

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