

## Structural Changes of Poly(*p*-phenylene sulphide) on Doping

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Structural and morphological changes of poly(*p*-phenylene sulphide) (PPS) crystals on doping were examined by X-ray diffraction, infrared spectroscopy and electron microscopy. When a PPS crystal was doped with strong oxidizing agents such as  $\text{SbF}_5$  and  $\text{MoCl}_5$ , the dopants invaded into the PPS crystalline region, destroying the crystalline structure gradually from the surface of the crystals. Correspondingly the morphology changed from an as-grown sheaf-like structure to a featureless appearance. The dopants were not structured in the PPS crystal as in intercalated compounds. When PPS was lightly doped with  $\text{SbF}_5$ , X-ray measurement revealed the shortening of the identity period of the PPS sample probably due to the formation of thiophene rings as observed in the case of doping with  $\text{AsF}_5$ . The molecular conformation of PPS changes into the planar one by this treatment. Doping with mild oxidizing agents such as iodine or tetracyanoethylene caused no structural changes of PPS crystal.

KEY WORDS: Poly(*p*-phenylene sulphide)/ Doping/ Electrically conductive polymer/ Morphology/

### I. INTRODUCTION

Many investigations of electrically conductive polymers have been made from various points of view<sup>1)</sup>. We have already studied on the morphologies and crystalline state of some conductive polymers especially by high-resolution electron microscopy: polythiazyl (SN)x<sup>2)</sup>, poly(*p*-phenylene)<sup>3)</sup> and poly(*p*-phenylene sulphide) (PPS)<sup>4,5)</sup>. It is expected that extensive studies on structural changes of electrically conductive polymers caused by doping should give basic information to understand their conduction mechanism. For example, we succeeded in making clear the structural changes of (SN)x on doping with iodine by electron microscopic observation<sup>2)</sup>. In the process where the (SN)x crystals were gradually destroyed by iodine doping, the dopants invaded preferentially into the "skin" region of fibrous (SN)x crystal and formed the one-dimensional column structure on the (102) plane of (SN)x. The repeating distance of the iodine atoms structured at the intermediate state of doping is 0.9nm, in which three iodine atoms are contained, i.e.,  $\text{I}_3$  molecules are formed. Further doping leads to the complete destruction of the crystal structure.

PPS is receiving attention for its high stability at elevated temperatures, small moulding contraction and very low hygroscopicity<sup>6,7)</sup> because it surpasses other engineering plastics in these properties. Moreover, PPS is well known as a melt-processible conductive polymer and its conductivity increases up to  $1 \text{ Scm}^{-1}$  by doing with  $\text{AsF}_5$ <sup>8,9)</sup>. In this paper the structural changes of PPS and its oligomer on doping

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with some oxidizing agents are examined by X-ray scattering, infrared (IR) spectroscopy and electron microscopy.

## II. EXPERIMENTAL

For X-ray scattering and IR spectroscopy, uniaxially oriented crystalline films (13  $\mu\text{m}$  thick) provided by Kureha Chemical Industry Company Ltd. were used. The films were doped with  $\text{SbF}_5$  in vapour at  $80^\circ\text{C}$  for various periods ranging from 4 hrs to 5 days in a glass tube. X-ray scattering experiments of the films thus prepared were carried out using  $\text{CuK}\alpha$  radiation with Rigaku RU-3H as an X-ray source.

For electron microscopy, crystals 100 to 300 nm wide and 11.5 nm thick were grown from a dilute solution in  $\alpha$ -chloronaphthalene<sup>4</sup>. Carbon-coated *Pt-grids* were used to prevent from their breaking by oxidization on doping. The solution-grown crystals thus deposited on the *Pt-grid* were exposed to vapour of following oxidizing agents in a glass tube at various conditions;  $\text{SbF}_5$  (at ambient temperature for several seconds to a few minutes),  $\text{MoCl}_5$  (at temperatures 120 to  $210^\circ\text{C}$  for 3 min to 30 min), iodine (at  $90^\circ\text{C}$  for 22 hrs to 65 hrs) and tetracyanoethylene (TCNE) (at temperatures 120 to  $180^\circ\text{C}$  for 15 hrs to 1 week). The morphological observations and electron diffraction experiments of specimens were carried out using transmission electron microscopes, JEOL JEM-200CS (200 kV) and JEM-7A (80 kV).

Before the doped specimens were examined, dopant compounds adhered on surfaces of the specimens were washed away in hydrochloric acid and water in the case of the doping with  $\text{SbF}_5$ , and in hot water only in the case of the doping with  $\text{MoCl}_5$ .

Crystals of a model compound with low molecular weight, di-(*p*-phenyl thio)-benzene (DPTB), were obtained in powdery form and were also doped with  $\text{SbF}_5$  in the same way as above. The structural change was examined by the X-ray scattering method. The method of synthesizing DPTB will be reported elsewhere.

## III. RESULTS AND DISCUSSION

### 1. X-ray scattering

The X-ray diffraction pattern of the as-doped specimen with  $\text{SbF}_5$  showed several rings probably due to the dopant compounds adsorbed on the surface of PPS film. After the PPS sample was washed in hydrochloric acid and water and subsequently dried in a vacuum, the diffraction rings were not observed because the dopant compounds on the surface was removed by washing. The X-ray diffraction works were done on the PPS samples which were doped with  $\text{SbF}_5$  and treated in the above way. From now on, the results on the PPS were mainly discussed. As doping of a uniaxially oriented crystalline film of PPS proceeded, the intensity of each crystalline reflection from PPS decreased from that of the pristine PPS. New diffuse reflections appeared at a stage where samples are moderately doped. One of the reflections is on the meridian and others on the equator and at the off-axial positions as seen in Fig. 1(b) and modeled in Fig. 1(c). The change of the X-ray diffraction pattern suggests that a PPS molecular chain was chemically modified by doping. The new reflection on the

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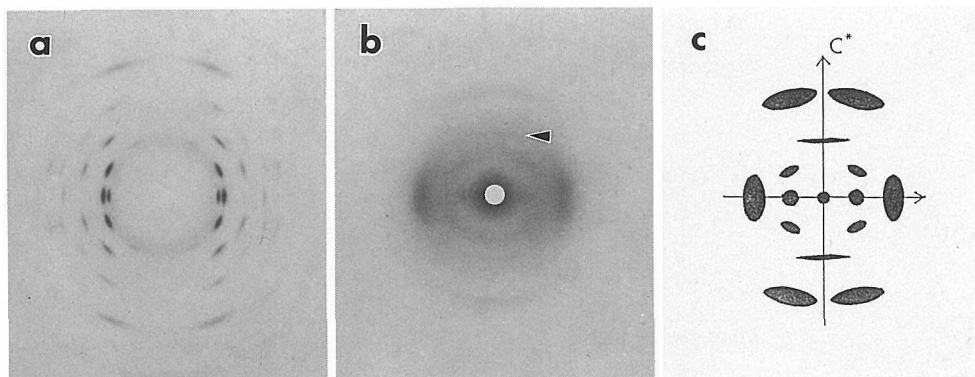


Fig. 1. X-ray diffraction patterns of PPS: (a) uniaxially oriented crystalline film of pristine PPS, (b) PPS doped with  $\text{SbF}_5$  and washed in hydrochloric acid and water and dried in a vacuum and (c) schematic representation of the pattern of (b).

meridian shown by an arrow in Fig. 1(b) corresponds to the lattice spacing of about 0.4 nm and indicates that the repeating period of the molecular chain changed from 1.026 nm<sup>10)</sup> of a pristine PPS to 0.8 nm. Clearly, shortening of the repeating length in a PPS chain occurs. It may be caused by intrachain bridging, the evidence of which is shown by elemental analysis and IR-experiment as discussed below.

The result of elemental analysis (Table 1) revealed that the number ratio of hydrogen atoms normalized to six carbon atoms in monomeric unit of PPS decreased after doping. This indicates that the chemical reactions to remove hydrogen atoms from a polymer chain take place. If such reactions occur in a chain, the formation of thiophene rings is most probable as shown in the case of doping with  $\text{AsF}_5$ <sup>11)</sup> (Fig. 2). Generally, a network of overlapping intra- or intermolecular  $\pi$ -orbitals is needed for a polymer to be electrically conductive. Pristine PPS has neither successive conjugated  $\pi$ -orbitals nor planar molecular structure giving rise to their overlapping. When PPS is doped with  $\text{AsF}_5$ , however, the thiophene rings are formed by bridging between carbon atoms of adjacent phenylenes, and resultingly, the aromatic rings in PPS are forced to be coplanar due to this chemical modification<sup>11)</sup>. This modification of molecular structure generates overlapping of intramolecular orbitals. Generally the overlapping leads to a large band width in the chain direction and consequently a considerable increase in charge carrier mobility, so that the modification of molecular structure must contribute to the increase in electrical conductivity<sup>12)</sup>.

Table 1. The number of atoms of each species, which is normalized to six carbons per repeat unit calculated from elemental analysis data.

	C	H	O	S	F
PPS	6	3.70	0.0	1.00	
PPS- $\text{SbF}_5$	6	3.48			0.049

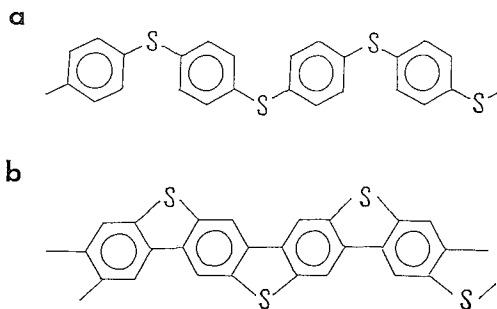


Fig. 2. Molecular structures of (a) PPS and (b) poly (benzothiophene).

When powdery DPTB crystals were doped with  $\text{SbF}_5$ , the intensities of the X-ray crystalline reflections decreased and no new reflections appeared. The dopant invades as well into the DPTB crystal, destroying the crystalline structure as in the case of PPS. Probably more complicated chemical reactions such as intra- and intermolecular bridging occur in the crystal. Since the crystal structure of DPTB has not yet been analysed, the destruction process is not detailed at the present time. Though speculatively, the process is as follows; since DPTB molecules rotate around their axis and are displaced easily from their original position during such a chemical reaction, the crystals transform to an amorphous state without taking any intermediate structure such as a thiophene ring.

## 2. Infrared spectroscopy

Figure 3 shows the IR spectra of a uniaxially oriented crystalline film of pristine PPS and of a PPS specimen moderately or heavily doped with  $\text{SbF}_5$  and treated as above to remove the dopant compounds. The doped PPS used for the IR spectroscopic investigation did not show any longer crystalline reflections in the X-ray diffraction. Some extra absorption peaks not observed in a pristine film appeared in the IR spectra of the doped films. For example, the band at  $1300\text{ cm}^{-1}$  appeared probably due to quinoidal structure, which is related to polaron or bipolaron formation in the main chain. The band at  $600$  to  $700\text{ cm}^{-1}$  seems to be related to sulphur groups, but the assignment is not established. The intensities of these new peaks increased as the doping proceeded, and the peaks originally observed in pristine PPS decreased in intensity. The bands at  $1700$  to  $2000\text{ cm}^{-1}$  which correspond to the deformation vibration (overtone) mode of para-substituted benzene rings decreased in intensity with an increase in the extent of doping. A new band at  $853\text{ cm}^{-1}$  appeared due to the out-of-plane deformation vibration mode of 1, 2, 4-trisubstitution in a benzene ring, and conversely the gradual decrease in intensity was found in the band at about  $812\text{ cm}^{-1}$  which was due to the out-of-plane deformation vibration mode of two adjacent C-H groups in a benzene ring. These results may support the formation of thiophene rings between adjacent phenylene groups (Fig. 2). This coincides well with the result of X-ray diffraction.

Heavily doped samples showed no absorption peaks of characteristic bands at  $1700$

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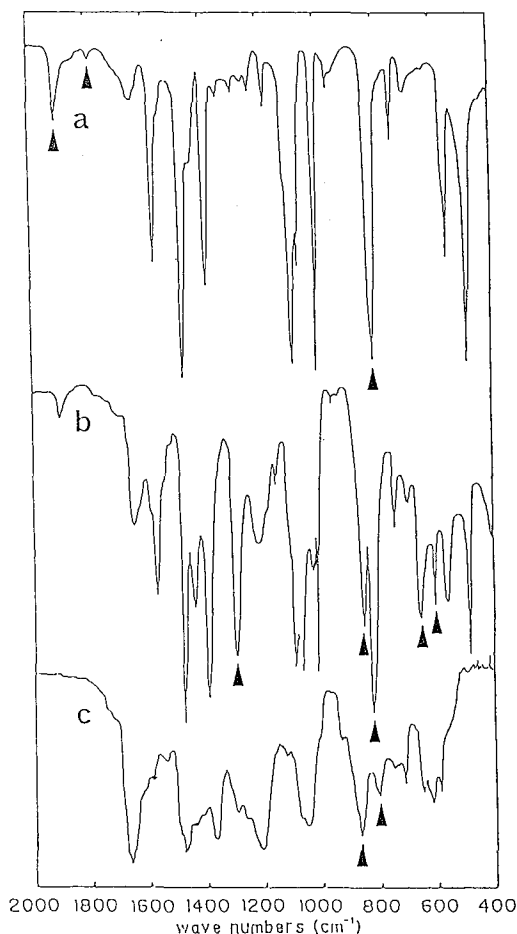


Fig. 3. IR spectra of PPS: (a) uniaxially oriented crystalline film of pristine PPS, (b) PPS film moderately doped with SbF<sub>5</sub> and (c) PPS film heavily doped with SbF<sub>5</sub>. Samples in (b) and (c) were washed in hydrochloric acid and water and dried under vacuum after doping.

to 2000 cm<sup>-1</sup> as shown in Fig. 3(c). The band at about 812 cm<sup>-1</sup> almost disappeared and every peak became broader. Since various types of chemical reactions take place probably in the PPS sample, it is disordered in the chemical structure and in the solid state by heavy doping with SbF<sub>5</sub>.

### 3. Electron microscopy

Doping with SbF<sub>5</sub> causes the destruction of the crystal structure of PPS probably by the formation of thiophene rings in the main chain as described above. In order to clarify the microscopic doping process, the structural and morphological changes of solution-grown PPS crystals on doping with various dopants were investigated by electron microscopy.

When a PPS solution-grown crystal was heavily doped with MoCl<sub>5</sub>, its morphology

changed from a sheaf-like structure to a featureless appearance as shown in Figs. 4(a) and (b). Many dark speckles are seen on the surface of as-doped PPS, but they disappear after washing in hot water and drying in a vacuum. Probably they are  $\text{MoCl}_5$  dopants themselves or other molybdenum compounds adsorbed on the PPS surface as mentioned above for the case of the doped film. Whether this specimen was washed or not, it did not show any crystalline reflections of PPS, but halo rings in the electron diffraction pattern. It means that the dopant destroys the PPS crystalline structure at the stage of doping as in Fig. 4(b).

In order to obtain information on structural changes at an earlier stage of doping, PPS was lightly doped with  $\text{MoCl}_5$  at  $120^\circ\text{C}$  for a few minutes. Figure 4(c) shows the morphology of the doped sample. The electron diffraction (the diameter of the selected-area aperture corresponds to 500 nm on the specimen) from the A-region which

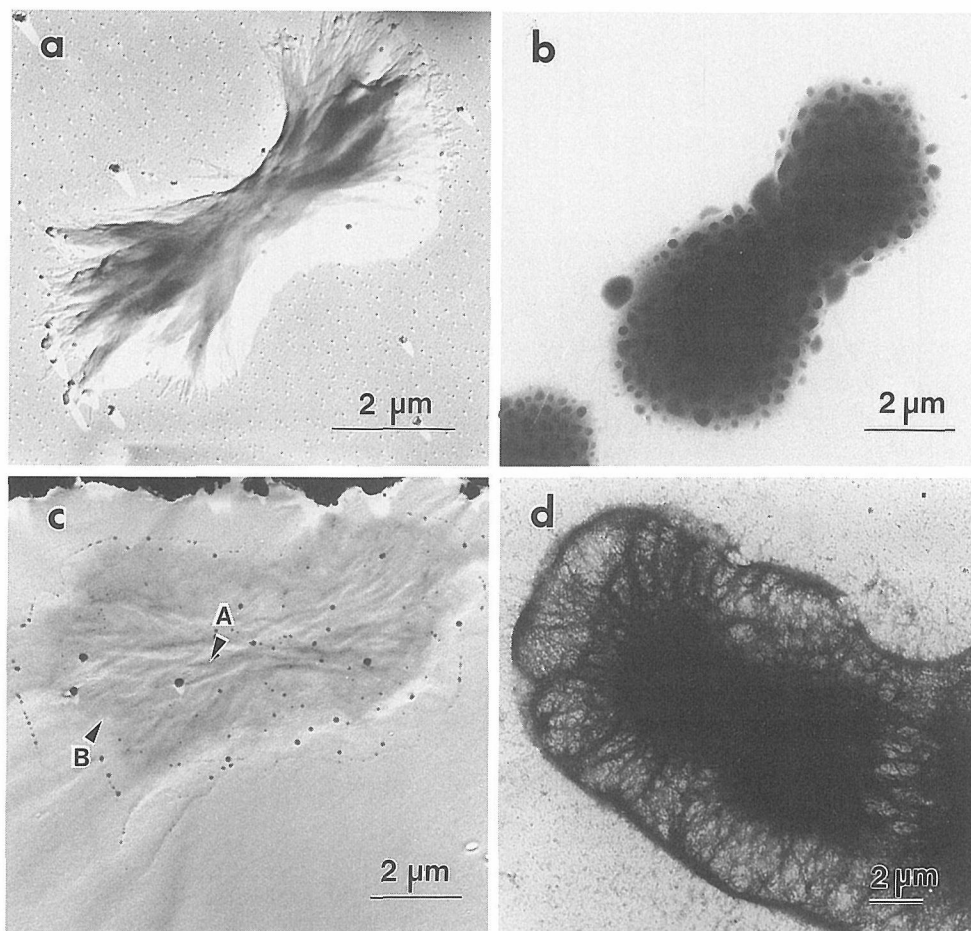


Fig. 4. Electron micrographs of solution-grown crystals: (a) sheaf-like pristine PPS, (b) PPS heavily doped with  $\text{MoCl}_5$ , (c) PPS lightly doped with  $\text{MoCl}_5$  and shadowed with Pt-Pd and (d) PPS doped with  $\text{SbF}_5$ .

corresponds to the periphery of the pristine crystal did not show any longer the PPS crystalline reflection. To the contrary, as the B-region where several fibrillar crystals are stacked is thicker than the A-region, the B-region gives the crystalline reflections of PPS, and the crystals are still alive in the interior deep from the surface though the crystals at the surface may be already dead. This shows that the dopant invades into the PPS crystalline region gradually from the surface.

Even when a PPS solution-grown crystal was only slightly exposed to the stronger electron acceptor  $\text{SbF}_5$  at ambient temperature for several seconds, its morphology changed easily as shown in Fig. 4(d) and the crystalline structure was completely destroyed at the state. In the figure, some fibrillation was observed at the periphery. The morphology evidences that the strong oxidizing agent such as  $\text{SbF}_5$  invades into the PPS crystalline region, destroying the crystalline structure gradually from the periphery. Thiophene rings will possibly be formed, though the molecular conformation of PPS cannot be estimated because the electron diffraction pattern gives no peak that informs the changes in the repeating distance.

On the other hand, doping with some mild oxidizing agents, TCNE and iodine, results also in an increase of conductivity<sup>13)</sup> but causes no structural changes of the PPS crystal itself. The increase of conductivity is mainly due to a certain structural change in the amorphous phase.

High-resolution electron microscopic images of a polymer crystal in two different crystallographic directions are very useful to determine the three-dimensional structure and also to study the dopant distribution relative to the position of polymer chains in the doped polymer crystal, if the dopants are structured as iodine in  $(\text{SN})x^{2)}$ . We have succeeded in obtaining two kinds of high-resolution electron microscopic images of a pristine PPS solution-grown crystal<sup>5)</sup>. When a PPS is doped with  $\text{SbF}_5$  or  $\text{MoCl}_5$ , however, the dopant is not structured in the PPS crystal as shown above. At first we expected the high-resolution electron microscopic image of doped PPS in which the PPS crystal lattice, the dopants structured in the PPS crystal and the structural relation between the two were imaged in the same area. Since doping with a strong oxidizing agents, however, damages easily the PPS crystalline structure to destroy regular alignment of lattice planes and the dopants are not structured in the sample, the doped PPS becomes amorphous. Normally, in such an amorphous sample we cannot obtain high-resolution electron microscopic images resolving the structure in molecular dimension. Therefore we could not obtain the structural relation between the PPS molecular chain and the dopants from the high-resolution images.

#### IV. CONCLUDING REMARKS

When a PPS crystal is doped with strong electron acceptors such as  $\text{SbF}_5$  and  $\text{MoCl}_5$ , the morphology changes from a sheaf-like structure to a featureless appearance. The dopants invade into the PPS crystalline region and destroys the crystalline structure gradually from the surface. However, the dopant is not structured in a PPS crystal in contrast to the case of  $(\text{SN})x$  doped with iodine. Doping with  $\text{SbF}_5$  or possibly with  $\text{MoCl}_5$  causes shortening the repeating distance in chain length probably

due to the formation of thiophene rings between adjacent phenylene rings in a chain as in the case of doping with  $\text{AsF}_5$ . Each aromatic ring in PPS is forced to be coplanar due to this chemical modification, which leads to higher electrical conductivity. As PPS doped with  $\text{MoCl}_5$ , however, shows low conductivity, much less thiophene rings may be formed by the  $\text{MoCl}_5$  doping than the  $\text{SbF}_5$  doping, though we could not give a definite conclusion on the  $\text{MoCl}_5$  doping from X-ray scattering and IR spectroscopy. Doping with a mild oxidizing agent, TCNE or iodine causes no structural changes of the PPS crystal. The increase of conductivity is mainly due to a certain structural change in the amorphous phase.

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