

NOTES

X-Ray Photoelectron Spectroscopy of Electron-Acceptor Doped Poly(*p*-phenylene sulfide)

Hiroshi SHIMIZU, Yoshikazu TANABE, and Hisaaki KANETSUNA

*Research Institute for Polymers and Textiles,
1-1-4 Higashi, Yatabe-machi, Tsukuba-gun,
Ibaraki 305, Japan*

(Received July 12, 1985)

KEY WORDS XPS / Poly(*p*-phenylene sulfide) / Conductive Polymer /
Doping Mechanism /

Considerable attention has been paid to a variety of conductive polymers such as polyacetylene, poly(*p*-phenylene), polypyrrole, and polythiophene in connection with practical applications and theoretical interests in conduction mechanisms. Compared with the above-mentioned conjugated polymers, poly(*p*-phenylene sulfide) (PPS) is a non-conjugated polymer and has a characteristics of the processibility. Frommer *et al.* have reported a remarkably high conductivity, 200 S cm^{-1} , for AsF_5 -doped PPS film cast from AsF_3 solution.¹ For the conduction mechanism of AsF_5 -doped PPS, several ideas such as the formation of benzothiophene structure² and intermolecular crosslinking³ have been proposed from the results of elementary analysis and IR spectral measurements. However, it is necessary to obtain more detailed information on the doping mechanism of electron-acceptor doped PPS in order to discuss the conduction mechanism. Recently we have reported the existence of the two conduction mechanisms in SO_3 or SbF_5 doped PPS from optical absorption measurements.⁴ At lower doping levels, bipolaron states exist and these are unstable in the atmosphere. At higher doping levels, other conduction mechanism appears which is stable in the atmosphere.

Only the latter conduction mechanism exists in the atmosphere.

In this note we measured XPS (X-ray photoelectron spectroscopy) spectra of PPS films heavily doped with electron acceptors: these films have only the stable conduction mechanism. From XPS spectra the doping mechanism, of these films is discussed, which depends on dopants. XPS is useful for the investigation of charge-transfer complexes and organic ions.⁵⁻⁷

EXPERIMENTAL

Thin transparent films of PPS (15—25 μm thick) were offered from Kureha Chemical Industry Co., Ltd. PPS films were doped with electron acceptors such as SbF_5 , SO_3 , and I_2 in the vapor phase under a pressure of *ca.* 4 torr. XPS spectra were measured using Shimadzu Electron Spectrometer ESCA 750. The binding energies E_b (defined as differences between the Fermi level and the atomic level energies) are given by the equation

$$E_b = E_{h\nu} - E_k - \Phi_s \quad (1)$$

where $E_{h\nu}$ is the energy (1253 eV) of the X-ray excitation (Mg-K_α radiation), E_k is the measured kinetic energy of the photoejected elec-

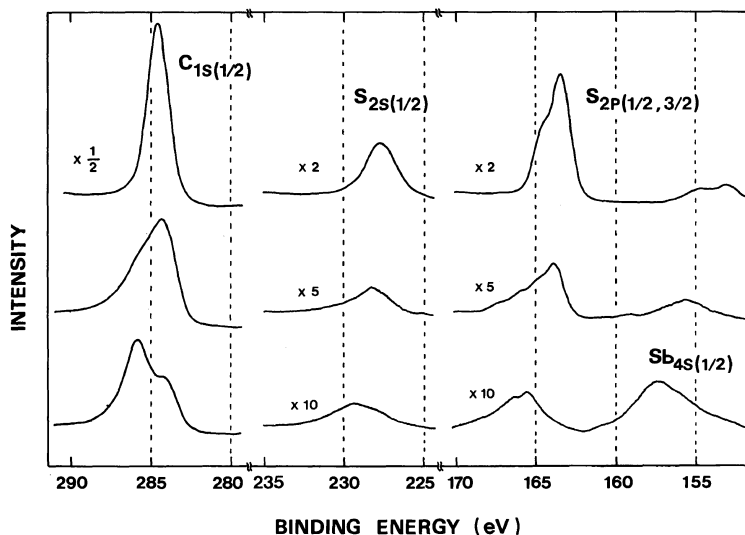


Figure 1. XPS core level spectra of undoped PPS (top) and SbF_5 -doped PPS (middle and bottom). The dopant concentrations of the middle and bottom curves are about 50 mol% and about 150 mol%, respectively.

tron and Φ_s is the spectrometer work function (the energy necessary to bring the electron from the Fermi level to the free-electron level). All measurements of XPS were performed under a pressure of about 1×10^{-7} torr. The binding energies were calibrated by the peak position of $\text{Au}_{4f(7/2)}$ band. All spectra were measured after the conductivity of doped-PPS reached the steady value in the atmosphere.

RESULTS AND DISCUSSION

After heavy doping of SbF_5 and SO_3 , electrical conductivities of PPS films reached 10^{-2} and $10^{-5} \text{ S cm}^{-1}$, respectively. Though the conductivity of these films decreased by a factor of *ca.* 10^3 after exposing to the atmosphere, reduced ones were relatively stable in the atmosphere for a long time (one month or so). In case of PPS doped with I_2 , the conductivity was lower than $10^{-12} \text{ S cm}^{-1}$. These differences of conductivities reflect the various doped states.

1) SbF_5 -Doped PPS

Figure 1 shows XPS spectra of undoped (top) and SbF_5 -doped PPS film (middle and bottom). The middle spectra of Figure 1 correspond to the films in which dopant concentration is about 50 mol% (conductivity is about $10^{-9} \text{ S cm}^{-1}$) and the bottom ones correspond to those doped with about 150 mol% SbF_5 (as high as $10^{-7} \text{ S cm}^{-1}$). Undoped PPS film has three bands at 284.5, 227.8, and 163.5 (164.5) eV, which were assigned to carbon 1s (C_{1s}), sulfur 2s (S_{2s}), and sulfur 2p (S_{2p}) [1/2, 3/2 spin] electrons, respectively. The C_{1s} band corresponds to carbon atoms of phenyl rings in PPS, while S_{2s} and S_{2p} bands are attributed to the divalent sulfur atoms. The S_{2p} band of undoped PPS exhibits satellite peaks at 155 and 153 eV. As shown in middle and bottom curves of Figure 1, XPS spectra of SbF_5 -doped PPS changed in binding energy, in band intensity, and in band shape with doping. These spectral changes were correlated with the band intensity of Sb_{4s} (observed at 157.5 eV) which was related to the doping level of SbF_5 . When the band intensity of Sb_{4s} was relatively small,

very broad C_{1s} and S_{2p} bands with pronounced shoulder on the side of higher binding energy were observed (middle of Figure 1).

As shown in the bottom curves of Figure 1, the C_{1s} spectrum of SbF_5 -doped PPS exhibited two distinct carbon 1s electron lines (284.5 and 286 eV) with relative separation of 1.5 eV. The peak with higher binding energy suggests the formation of cationic species,^{5,6} where positive charges are delocalized over the corresponding

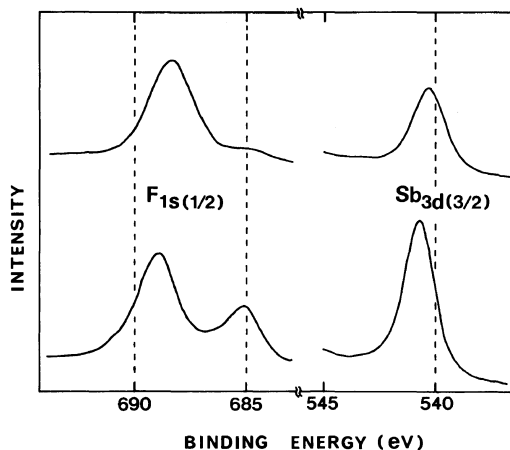


Figure 2. $F_{1s(1/2)}$ and $Sb_{3d(3/2)}$ XPS core level spectra of SbF_5 -doped PPS, in which the same samples were used as ones shown in Figure 1. The upper and lower spectra correspond to the middle and bottom curves of Figure 1, respectively.

phenyl rings. In the case of S_{2s} and S_{2p} XPS bands of PPS heavily doped with SbF_5 , only peaks with higher binding energy were observed at 229.5 and 165.5 eV, respectively. The chemical shift of S_{2s} and S_{2p} electrons (1.7 and 2.0 eV respectively) also suggests the localized positive charges on sulfur atoms^{8,9} resulting in the formation of the divalent and/or trivalent sulfur cations.

Figure 2 shows the XPS spectra of the dopant, $F_{1s(1/2)}$ and $Sb_{3d(3/2)}$ electrons in SbF_5 -doped PPS films. In this figure, the same samples were used as ones shown in Figure 1. Hence, the doping levels of the upper and lower spectra are same as the middle and bottom curves of Figure 1, respectively. As shown in lower curve of Figure 2, the two distinct F_{1s} bands separated by 3.9 eV were observed, and the peak position of Sb_{3d} slightly shifted to higher binding energy (0.4 eV) compared to that of upper line. In the two F_{1s} bands, the band observed at 685 eV indicates the enhancement of anionic character of F atom by the effect of charge transfer from PPS chain. The chemical shift of $Sb_{3d(3/2)}$ band would denote the increase in covalence of Sb atoms.

These results (Figures 1 and 2) clearly suggest the formation of charge-transfer structure

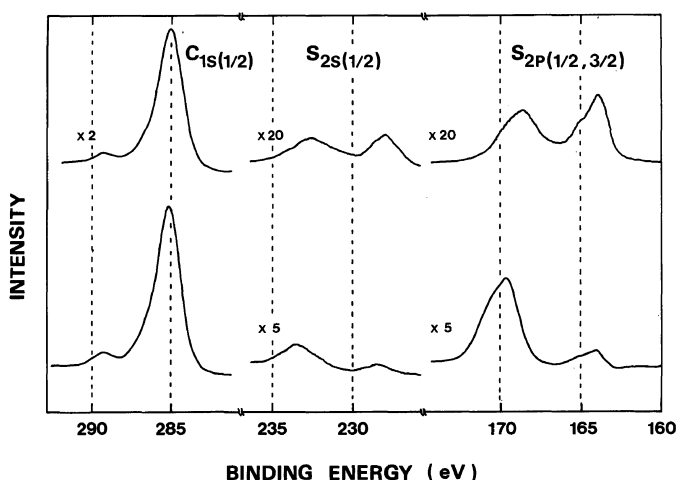


Figure 3. XPS core level spectra of SO_3 -doped PPS. The concentrations of SO_3 are about 60 mol% (upper curves) and about 200 mol% (lower curves).

such as $(\text{PPS})^+(\text{SbF}_6)^-$ for the SbF_5 -doped PPS films.

2) SO_3 -Doped PPS

The XPS spectra of SO_3 -doped PPS are shown in Figure 3. The concentrations of SO_3 are about 60 mol% for the upper spectra and about 200 mol% for the lower spectra. In these spectra (especially lower curves), a new S_{2p} band with the separation of 6 eV from the original band of undoped PPS (see Figure 1) was observed at 169.5 eV. The S_{2s} spectrum showed also the new band (5.7 eV higher than that of undoped one). From the comparison of these spectra with those of polyethersulfone, phenyl *p*-toluenesulfonate, and sodium *p*-styrenesulfonate, the new bands were assigned to the hexavalent sulfur atom resulting in the formation of sulfone and/or sulfonate.

The chemical shifts of S_{2s} (228.5 eV) and S_{2p} (164 eV) bands were 0.7 and 0.5 eV respectively, which shift to higher binding energy. The chemical shift of C_{1s} line was 0.5 eV. These results suggest that weak charge-transfer structure is also formed in this PPS- SO_3 system.

The small C_{1s} band at 289.2 eV would reflect the presence of the sulfonate resulting in the formation of the interchain crosslinking rather than presence of the trivalent carbocation.

From the above-mentioned results, the doping of SO_3 seems to mainly induce the sulfonation on PPS chain, although charge-transfer structure appears weakly.

3) I_2 -Doped PPS

The C_{1s} , S_{2s} , and S_{2p} spectra of PPS were little affected by the doping of I_2 , while the complicating XPS bands of $\text{I}_{3d(3/2)}$ and $\text{I}_{3d(5/2)}$ were observed. This means that iodine hardly contributes to form the charge-transfer structure in PPS chain.

In conclusion, the XPS spectra of doped PPS are different each other depending on the dopant species. These results reflect the different doping mechanisms, the formation of charge-transfer structure (for SbF_5), the occurrence of side reaction (for SO_3) and so on. Since the PPS films doped with SbF_5 have the highest conductivity in the atmosphere among our samples, charge-transfer structure seems to be important for increasing the conductivity in stable state.

Acknowledgments. Thanks are due to Dr. N. Maruyama (Kureha Chemical Industry Co., Ltd.) for kind supplying the transparent PPS films.

REFERENCES

1. J. E. Frommer, R. L. Elsenbaumer, and R. R. Chance, American Chemical Society Symposium Series No. 242, p 447, Washington, 1984.
2. L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, *J. Chem. Phys.*, **75**, 1919 (1981).
3. T. C. Clarke, K. K. Kanazawa, V. Y. Lee, J. F. Rabolt, J. R. Reynolds, and G. B. Street, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 117 (1982).
4. Y. Tanabe, H. Shimizu, and H. Kanetsuna, *Rep. Prog. Polym. Phys. Jpn.*, **28**, 381 (1985).
5. G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Am. Chem. Soc.*, **92**, 7231 (1970).
6. G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **94**, 2529 (1972).
7. G. D. Mateescu, J. L. Riemenschneider, J. J. Svoboda, and G. A. Olah, *J. Am. Chem. Soc.*, **94**, 7191 (1972).
8. A. Fahlman, K. Hamrin, J. Hedman, R. Nordberg, C. Nordling, and K. Siegbahn, *Nature*, **210**, 4 (1966).
9. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordling, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells Boktryckeri Ab, Uppsala, 1967, p 125 and 139.