

ESCA Analysis of Polymer–Acceptor Interactions in Chemically Synthesized Polypyrrole–Halogen Complexes

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ABSTRACT: X-Ray photoelectron spectroscopy (XPS) studies have been performed on conductive polypyrrole (PPY)–halogen complexes, such as PPY–I₂, PPY–Br₂, and PPY–Cl₂ complexes, prepared by the simultaneous chemical polymerization and oxidation of pyrrole by the respective halogens. Substantial halogenation of the pyrrole ring was observed in the case of PPY–Cl₂ and PPY–Br₂ complexes. In the case of PPY–Br₂ complex, the ratio of covalent to ionic bromide content can be effectively varied over a wide range by varying the bromine to monomer ratio used for polymerization. The increase in covalent bromide content causes a decrease in the electrical conductivity of the complex. The N1s spectra suggest the presence of positively charged nitrogen species and their possible contribution to the electrical conductivity of the complexes. The Cls spectra for all the complexes reveal that close to 1/3 of the carbon atoms may have been associated with structural disorder, as in the case of electrochemically prepared PPYs.

KEY WORDS X-Ray Photoelectron Spectroscopy / Polypyrrole–Halogen Complexes / Chemical Synthesis / Structural Disorder / Electrical Conductivity /

Electroactive polymers have attracted a great deal of attention during the past decade because of their unusual electrical/electronic properties. A survey of the literature^{1–3} reveals that most of the recent interest on conductive polyheterocycles, polypyrrole (PPY) in particular, are devoted to the materials obtained from electrochemical polymerization and oxidation. For example, most of the Electron Spectroscopy for Chemical Applications (ESCA) studies were centered on electrochemically prepared polypyrrole and related polyheterocycles.^{4–8} These ESCA studies provided information pertaining to the nature of interactions between polymeric cations and their counter anions, and the structural disorder in these polymers arising from these interactions. However, there are still certain discrepancies^{4,6} between the results reported.

Rather conductive PPY complexes have also

been synthesized chemically in the presence of various Fe(III) oxidants, such as Fe(ClO₄)₃ and FeCl₃.^{9–11} A simple method for the simultaneous chemical polymerization and oxidation of pyrrole by halogens, such as I₂, Br₂, and Cl₂, and by organic acceptors, such as DDQ and chloranil in aqueous media and in organic solvents has also been developed recently in our laboratory.¹² The PPY–halogen complexes prepared by this chemical method are stable in the atmosphere. Their electrical conductivity and conduction behavior are comparable to those of the PPYs obtained from electrochemical polymerization and oxidation.¹³ Thus, it would be of great interest to carry out an ESCA study on this new family of chemically synthesized PPY complexes. It is hoped that the results obtained therefrom may help to provide a better understanding of the nature of interaction between PPY and the various electron acceptors.

EXPERIMENTAL

Polymer Samples

The polypyrrole samples used for this study consist of various polypyrrole-halogen complexes, such as PPY-I₂, PPY-Br₂, and PPY-Cl₂ complexes. All samples were prepared *via* the simultaneous chemical polymerization and oxidation of pyrrole by the respective halogen acceptor according to the methods reported earlier.^{12,13} The PPY-Br₂ and PPY-Cl₂ complexes were prepared in acetonitrile while the PPY-I₂ complex was prepared in an aqueous medium. In the case of PPY-Br₂ complexes, and to a lesser extent the PPY-Cl₂ and PPY-I₂ complexes, the amount of acceptor incorporated in the final complexes can be effectively varied by varying the monomer to halogen ratio used for the polymerization process. The final physicochemical and electrical properties of the PPY complexes are strongly affected by the type of acceptor incorporated and the nature of the polymer-acceptor interactions.

ESCA Measurements

X-Ray photoelectron spectroscopy (XPS) measurements were made on powder polymer samples. The measurements were carried out on an ESCA 750 spectrometer with a monochromatized MgK α X-ray source (1253.6 eV photons) through the courtesy of Toray Research Center, Inc., Shiga, Japan. The pressure in the spectrometer during measurements was typically 6×10^{-5} Pa or below. All spectra were referenced to the Cls neutral carbon peak at 284.6 eV. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors.

Conductivity Measurements

Electrical conductivity of the polymer samples was measured using the standard collinear four-probe technique on compressed pellets. The measuring circuit consisted of a Keithley 614 digital electrometer and a

Hewlett-Packard model 6212 d.c. power supply. The current passed was 10 mA.

RESULTS AND DISCUSSION

Figure 1 shows curve fitted Br3d XPS core-level spectra for four PPY-Br₂ complexes with a wide range of acceptor levels. The peak at about 68 eV is attributable to bromide anion while the peak at a higher binding energy of 70 eV corresponds to bromine covalently bonded to the pyrrole ring. The polymerization conditions and resulting physicochemical properties of the respective complexes are given in Table I. Also shown in Table I are the experimental parameters for the PPY-I₂ and PPY-Cl₂ complexes and the XPS results derived from the various core-level spectra. It is clear from Figure 1 that substantial amount of bromine is covalently bonded to the pyrrole moiety. The ratio of covalent to ionic bromide in the polymer complex increases upon increasing the halogen to monomer ratio used for the polymerization. The increase in the amount of covalently bonded bromine causes a decrease in the electrical conductivity. This is consistent with the fact that poly(bromopyrrole) has electrical conductivity substantially lower than that of PPY polymerized and oxidized under the same condition.¹⁴ In the oxidative polymerization of pyrrole, polymerization occurs primarily through the α, α' linkage of the pyrrole moiety.¹⁵ Thus, one can expect the halogen addition to occur mainly at the β -carbon. This is supported by the infrared (IR) absorption spectra. The intensity of the IR absorption band at 1040 cm⁻¹, attributable to C $_{\beta}$ -H in-plane vibration,¹⁶ decreases as the proportion of covalently bonded bromine increases. Furthermore, for samples with high covalent to ionic ratio, the hydrogen content decreases substantially from the theoretical C:H:N ratio of 4:3:1 for a linear chain of disubstituted pyrrole rings.

Figure 2 shows the Cl2p core-level spectrum for a typical PPY-Cl₂ complex. For the PPY-

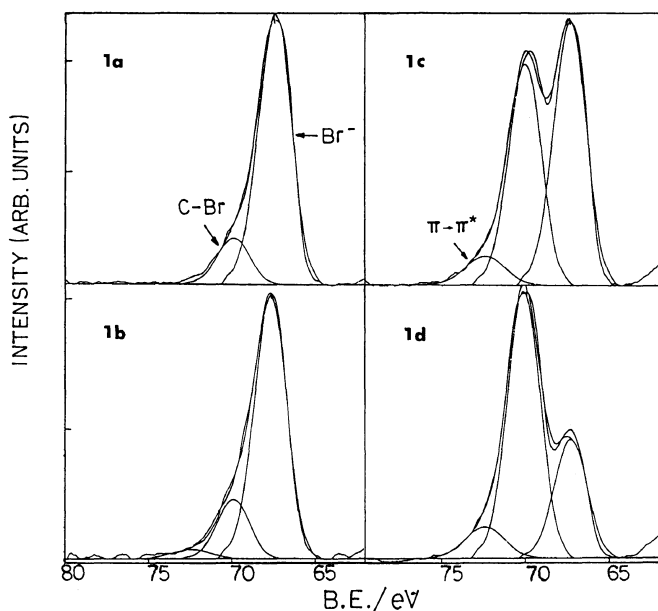


Figure 1. Br3d XPS core-level spectra of the polypyrrole-bromine complexes.

Table I. Experimental parameters and results for the various PPY-halogen complexes

Polymer complex	Reagent mole ratio monomer: halogen	Polymer composition (elemental analysis)	Conductivity $\sigma/S\text{cm}^{-1}$	Deconvoluted halogen spectra ^a			XPS surface stoichiometry N: halogen ratio	N1s spectra components (B.E. > 401 eV)
				%Br ⁻ or %Cl ⁻	%C-Br or %C-Cl	% $\pi\rightarrow\pi^*$		
1a. PPY-Br ₂	1:0.45	C _{4.0} H _{3.1} N _{1.0} Br _{0.34} O _{0.45}	10	86	14	0	1:0.30	29.6%
1b. PPY-Br ₂	1:0.68	C _{4.0} H _{3.1} N _{1.0} Br _{0.38} O _{0.58}	25	79	18	3	1:0.34	39.4%
1c. PPY-Br ₂	1:1.35	C _{4.0} H _{2.9} N _{1.0} Br _{0.48} O _{0.46}	4	50	43	7	1:0.51	28.6%
1d. PPY-Br ₂	1:2.03	C _{4.1} H _{2.6} N _{1.0} Br _{0.80} O _{0.35}	1	28	63	9	1:0.61	21.4%
2. PPY-Cl ₂	1:1.0	C _{4.0} H _{2.9} N _{1.0} Cl _{0.66} O _{0.55}	0.5	22	73	5	1:0.90	25.4%
3. PPY-I ₂	1:1.2	C _{4.1} H _{3.1} N _{1.0} I _{0.48} O _{0.30}	16	—	—	—	1:0.40	35.9%

^a XPS Br3d or Cl2p core-level spectra.

Cl₂ complex, the acceptor exists predominantly as covalently bonded chloride, regardless of the initial halogen to monomer ratio used during polymerization. The presence of a large proportion of covalently bonded chloride is accompanied by a substantial reduction in intensity of IR absorption band at 1040 cm⁻¹ due to the C_β-H in-plane vibration and a reduction in electrical conductivity. Again, significant halogen addition at the β-

carbon may have occurred.

Figure 3 shows the I3d_{5/2} core-level spectrum for the PPY-I₂ complex. The spectrum was fitted to Gaussian component peaks. Deconvolution gives two major peaks with binding energies of 620.6 and 618.6 eV. In iodine doped polyacetylene, peaks corresponding to these binding energies have been assigned to the I₅⁻ and I₃⁻ species, respectively.¹⁷ The presence of thermally less stable I₅⁻ spe-

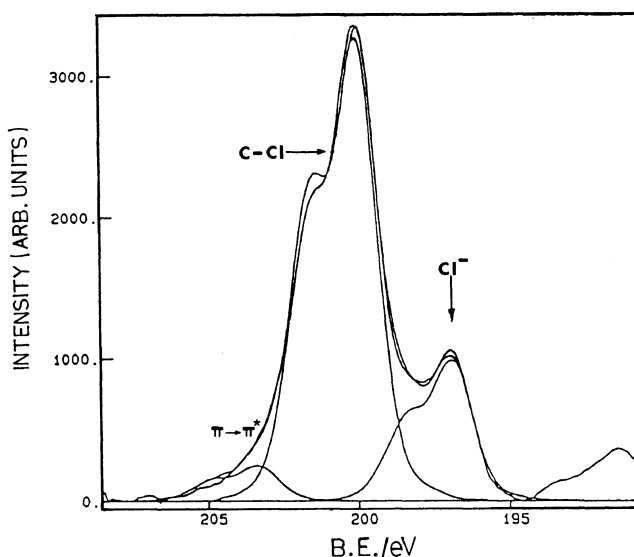


Figure 2. Cl2p XPS core-level spectrum of the polypyrrole-chlorine complex.

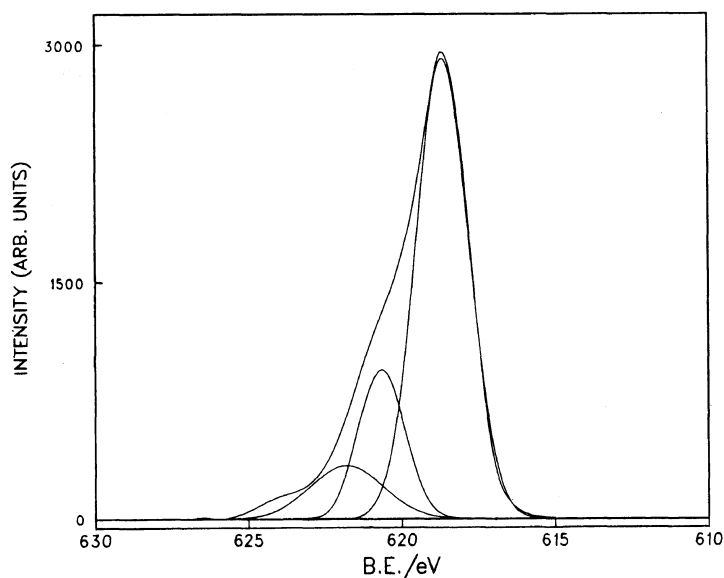


Figure 3. I3d5/2 XPS core-level spectrum of the polypyrrole-iodine complex.

cies in the present complex is consistent with the lack of electrical stability of the complex at temperature above 75°C, although the complex does not suffer any weight loss in the thermogravimetric analysis until the vaporization temperature of iodine at 184°C.¹⁸ The iodine core level spectrum readily suggests that

the acceptor is incorporated in the polymer complex predominantly as ionic iodide.

Comparison of the atomic ratios of halogens in the bulk and at the surface in Table I reveals that the halogens are uniformly distributed in most of the present PPY complexes, except in the case of samples with high covalent halide

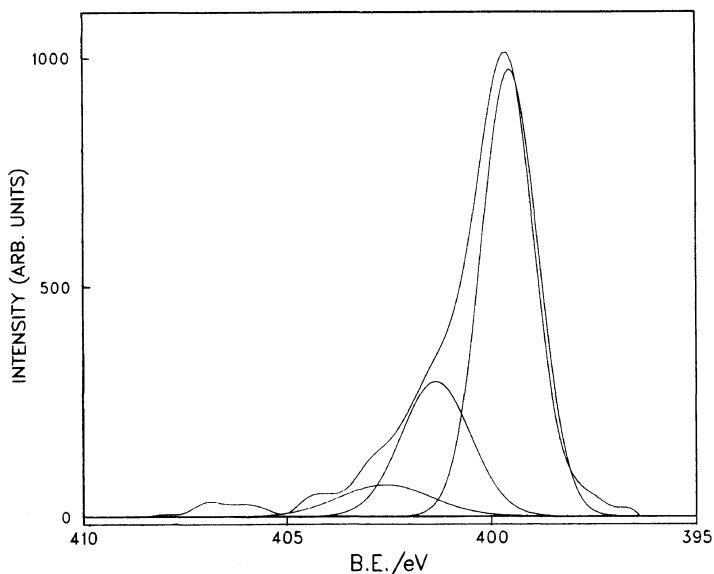


Figure 4. N1s XPS core-level spectrum of the polypyrrole-iodine complex.

content. Thus, the use of high halogen to monomer ratio during polymerization, which gives rise to high covalent to ionic halide ratio in the final complexes, may have introduced substantial modifications of the polymer surface structure/state. Alternatively, exposure of these complexes under high vacuum during drying or XPS measurements may cause halogen accumulation at or removal from the surface. Our thermogravimetric analysis data¹⁸ indicate that the onset temperature for major weight loss decreases as the covalent to ionic halide ratio of the complex increases.

Figure 4 shows the N1s core-level spectrum of PPY-I₂ complex. Similar line shape is also obtained with the spectra of other complexes. The spectrum was fitted to Gaussian component peaks. The position, intensity and peak width of the component peaks were optimized to give the best fit to the experimental spectrum. The main component peak at 399.5 eV is attributable to the neutral nitrogen of the pyrrole moiety. The peaks corresponding to the higher binding energies can be assigned to nitrogen atoms associated with positive charge. Table I shows the percentage of the total

N1s envelope that arises from components with peaks at a higher binding energy than 401 eV. For a family of polymer complexes with the same acceptor, such as the PPY-Br₂ complexes, electrical conductivity seems to increase with increase in the proportion of the N1s spectra having binding energy greater than 401 eV. This relation, however, should be regarded only as qualitative at this stage since the effect of various degrees of halogenation of the pyrrole ring on the electrical conductivity of the complex cannot be precisely determined. Using a model compound such as tetrabutylammonium perchlorate, which has a unit positive charge, a recent study on the electrochemically prepared PPY complexes has assigned the high binding energy components of the N1s spectra to oxidized nitrogen atoms having a unit positive charge.⁴ In the case of PPY-ClO₄ and PPY-BF₄ complexes obtained from electrochemical polymerization and oxidation,⁵ the N1s line shape with high binding energy shoulder has been attributed to three electrostatically inequivalent *N* sites created by the polymer-anion interaction. The two high binding energy components were

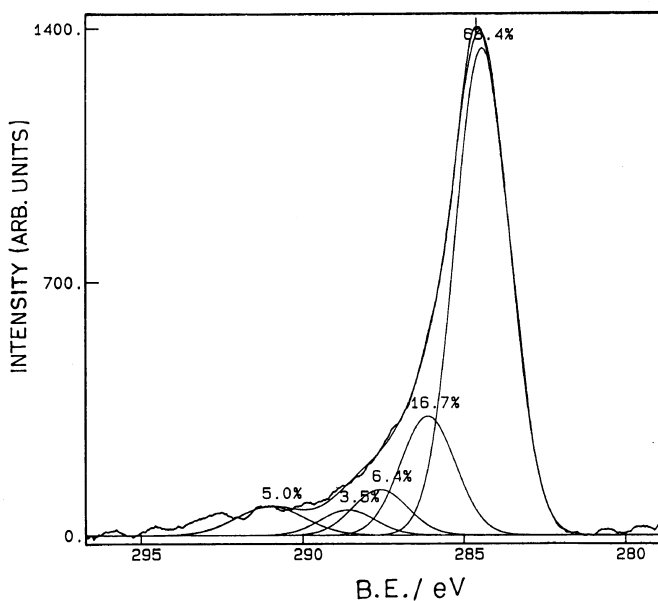


Figure 5. C1s XPS core-level spectrum of the polypyrrole-iodine complex.

assigned fractional positive charge. Yet in another study, Salaneck *et al.*⁷ found essentially single-component N1s spectra for polypyrrole tetrafluoroborate obtained from electrochemical polymerization.

The C1s spectrum of the PPY-I₂ complex is shown in Figure 5. The spectrum is skewed towards the high energy side with the main component peak at 284.4 eV having well defined position, intensity and line width. The C1s envelope is essentially similar in width and line shape for all the other PPY-halogen complexes. The high energy tail can be deconvoluted into four peaks. The peak at 286.1 eV can be assigned to the C-N, C-O and/or the covalent carbon-halogen bonds, the peak at 287.6 eV to the carbonyl structure, and the third peak at 288.6 eV to the carboxyl groups. Finally, at 291.0 eV, a low-intensity, shake-up satellite arising from the aromatic ring can be resolved. Thus, the asymmetry of the C1s spectra observed in the present complexes may be attributed mainly to disorder phenomena, as in the case of PPY prepared by electrochemical method.^{5,6} In fact, the C1s spec-

trum of electrochemically prepared PPY-ClO₄ complex also suggests that as much as 1/3 of the pyrrole rings were affected by structural disorder.⁵ The amount of structural disorder revealed by the present C1s spectra appears to be high, despite the bulk elemental analysis results which suggest that the C:H:N mole ratio in most of the complexes does not deviate substantially from the theoretical value of 4:3:1 for a long linear chain of disubstituted pyrrole ring. This anomaly may be explained by suggesting that the defects are most probably related to the surface states rather than bulk structural defects. The presence of the carbonyl and related structures in the PPY-halogen complexes is consistent with the presence of O1s XPS core-level spectrum at about 532.5 eV and the trace amount of oxygen given by the elemental analyses of all the samples. However, the carbonyl structure is not readily visible in the infrared absorption spectra of all the complexes.¹² This discrepancy can be explained by the fact that the carbonyl absorption band at around 1700 cm⁻¹ may have been masked by the broad absorption tail,

extending from 4000 cm^{-1} to 1600 cm^{-1} and are characteristic of oxidized and conductive PPY.¹⁹ Alternatively, the carbonyl structures are probably more characteristics of the surface state rather than the bulk state, as a result of interactions between the PPY surface and oxygen. Similarly, neutral and oxidized PPYs obtained from electrochemical polymerization are also 'doped' to a small extent by oxygen.^{19,20} This interaction with oxygen can produce chemical changes in the polymer, such as the formation of carbonyl and hydroxyl groups, in addition to the oxidation process which removes π -electrons from the polymer.^{20,21} Finally, the presence of pyrrolidinone structure has been widely observed in the chemical oxidation of pyrrole.^{15,22}

When the C1s spectra of the present complexes are compared with those of the electrochemically polymerized and oxidized PPY, the line shape is similar to that reported by Skotheim *et al.*,⁶ but differs somewhat from that observed by Pfluger and Street.⁵ The latter authors reported an asymmetric line shape which can be resolved into β and α carbon peaks at 283.6 and 284.5 eV respectively, as

well as a high energy peak at 285.4 eV attributable to disorder type carbon. However, the C1s spectra for all the complexes in our present study are more suitably fitted with a curve containing a main peak of 2.0 eV linewidth at 284.4 eV and an intensity equivalent to about 2/3 of the total spectral area. This relatively broad peak obtained for the carbon atoms of the pyrrole ring in the present complexes may result from the removal of the π -electrons and the formation of a carbonium-like polymeric pyrrole cation. This phenomenon may be explained with reference to the solid state ^{13}C NMR data. In the case of electrochemically polymerized PPY, the ^{13}C solid state NMR spectrum of the oxidized PPY¹⁹ shows only a broad peak while the downfield shifts for the α and β carbons are clearly distinguishable in neutral PPY. The solid state ^{13}C NMR spectrum of the present chemically synthesized PPY-I₂ complex as obtained by the cross polarization and magic angle spinning technique is shown in Figure 6. The spectrum similarly shows only a broad asymmetric peak shifted downfield relative to the neutral PPY peaks with no resolution for the α and β

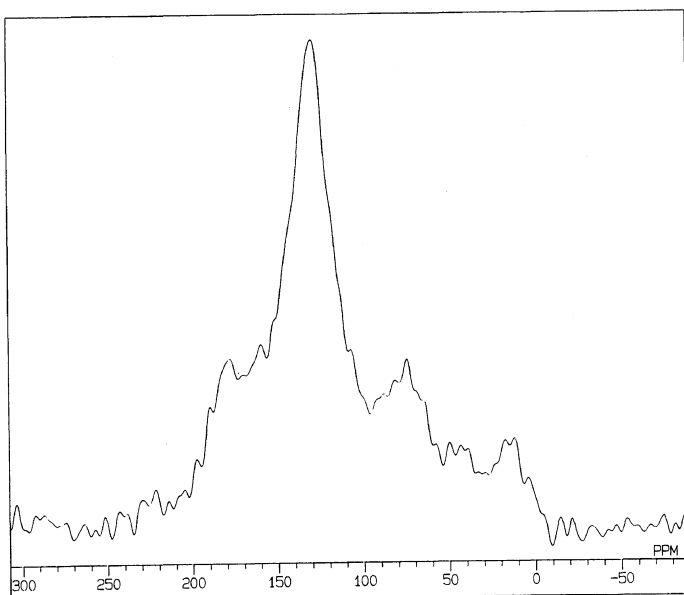


Figure 6. Solid state ^{13}C NMR spectrum of the polypyrrole-iodine complex.

carbon peaks.

CONCLUSION

XPS studies have been performed on PPY-I₂, PPY-Br₂, and PPY-Cl₂ complexes prepared *via* the simultaneous chemical polymerization and oxidation of pyrrole by the respective halogens. The halogen core-level spectra strongly suggest that the interaction between PPY and Br₂ or Cl₂ is more than just an oxidation process involving the removal of π -electrons from the polymer; but can also bring about a substantial degree of halogenation of the pyrrole ring. The structural disorder introduced by the halogen addition has a marked effect on the electrical conductivity of the complex. In most cases, the halogens are uniformly distributed in the bulk and at the surface. The N1s core-level spectra with high-energy shoulder is consistent with positively charged nitrogen in the oxidized polymer. The Cls spectra suggest that substantial structural disorder of the pyrrole ring in the polymer chain must have occurred during chemical polymerization and oxidation as in the case of electrochemical polymerization. Reduction of the structural disorder arising from, for example, covalently bonded halogens, and oxygen, may help to improve the electrical properties of the present complexes considerably.

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