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X-ray Photoelectron Spectroscopic Studies of Polypyrrole Synthesized with Oxidative Fe(III) Salts

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ABSTRACT: Conductive polypyrrole (PPY) complexes obtained from chemical polymerization and oxidation of pyrrole by Fe(III) oxidants, such as $FeCl_3$ and $Fe(ClO_4)_3$, have been studied by X-ray photoelectron spectroscopy (XPS). The Cl2p core-level spectrum of the PPY/chloride complexes reveals the presence of the "dopant" in three distinct chemical states. Thus, any reaction stoichiometry derived from the total chlorine balance of the complex alone can be misleading. As in the case of the nitrogens in polyaniline, proton modifications of the pyrrolylium nitrogens give rise to a number of intrinsic oxidation states, ranging from that consisting of about 25% oxidized imine-like (=N—) structure, observed in the present study, to the fully reduced PPY (all —NH— structure). The former is obtained by deprotonation of the oxidized and positively charged pyrrolylium nitrogens and is susceptible to reprotonation by protonic acids, while the latter is obtained from the reduction of the deprotonated structure by phenylhydrazine and is susceptible to reoxidation by electron acceptors. From the actual chloride anion content of a complex and the corresponding intrinsic oxidation state of the polymer, a reaction stoichiometry that accounts for 25% oxidized pyrrole units is favored. Similar intrinsic structures are observed in PPY complexes synthesized with $Fe(ClO_4)_3$. In this case, although the dopant exists predominantly as perchlorate species, a small amount of the dopant also exists as the chloride species.

Introduction

In recent years, the synthesis and characterization of electroactive polymers have become important research areas in polymer science.[1] Among these polymers, polypyrrole (PPY) and its derivatives have received a good deal of attention because of their high electrical property, environmental stability, and ease of synthesis.[2-11] Highly conductive PPY complexes have been prepared by various methods, such as electrochemical polymerization,[2-4] chemical polymerization,[5-10] and chemical vapor deposition.[11,12]

The majority of recent research on PPY has been centered on the as-grown films obtained from electrochemical polymerization and oxidation. For instance, most of the X-ray photoelectron spectroscopy (XPS) studies on PPY have been devoted to materials prepared by electrochemical method.[13-18] We reported recently on the XPS studies of some chemically synthesized PPY/halogen[19] and PPY/organic acceptor[20] complexes. XPS has been found to be a useful tool for studying polymer-dopant charge-transfer (CT) interactions because of its ability to elucidate the structural changes and the charge redistribution in the complexes associated with these interactions.[13-21] It has also provided a convenient means for the quantitative differentiation of the various anion species present in the polymeric complexes. By far, the Fe(III) salts are the most commonly used oxidant for the chemical synthesis of highly conductive PPY complexes.[5,6,8,10] Accordingly, it should be interesting to carry out a detailed XPS study on this family of chemically synthesized and oxidized PPY complexes. This paper thus deals with the XPS study of the CT interaction in some PPY complexes prepared via the oxidative polymerization of pyrrole by $FeCl_3$ and $Fe(ClO_4)_3$. For comparison purposes, the use of other transition-metal salts, such as $AgNO_3$ and $Cu(ClO_4)_2$, has also been included.

The chemical synthesis of PPY with oxidative transition-metal ions has been widely reported in the literature. For example, the optimum reactant Fe(III)/monomer ratio for the polymerization of pyrrole by Fe(III) chloride has been suggested to be about 2.4.[10] Furthermore, conductivity as high as 190 S/cm has recently been reported for the PPY complex synthesized in the methanol solution of $FeCl_3$.[6] On the other hand, considerable discrepancies in the chemical compositions of the PPY complexes, as well as the reaction stoichiometries, still exist in the published literature.[6,8,10,22]

Experimental Section

Polymer Synthesis. Pyrrole (Merck) was vacuum distilled before use. The polymerization and oxidation of pyrrole by ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were carried out at 0–5 °C and under a nitrogen atmosphere in various solvents, such as methanol, ethanol, water, acetone, acetonitrile, and chloroform. Except in the case of chloroform, in which a saturated ferric chloride solution was used, all polymerizations were carried out in 2.5 M $FeCl_3 \cdot 6H_2O$ solutions at various monomer/metal salt mole ratios according to the procedures reported in the literature.[6,8,10] All reaction products were filtered and washed thoroughly with copious amounts of the respective solvent used for polymerization and then rinsed with excess methanol before being dried by pumping under reduced pressure. The effect of polymerization media on the electrical properties of the complexes obtained from the polymerization of pyrrole by ferric chloride had been reported in an earlier study.[6]

Polymerizations by hydrated ferric perchlorate [$Fe(ClO_4)_3 \cdot 9H_2O$] and copper perchlorate [$Cu(ClO_4)_2 \cdot 6H_2O$] were carried out both in aqueous and in acetonitrile solutions and also with various initial monomer/metal salt ratios. Again each of the complexes was washed thoroughly with the respective polymerization solvent before being dried by pumping under reduced pressure. Polymerization by $AgNO_3$ was carried out in aqueous medium according to the method of Chao et al.[8] Due to the sluggishness of the reaction, the reaction was allowed to proceed for at least 1 week.

Polymer Characterization. XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV of photons). The energy analyzer was set at a constant retardation ratio of 40. The polymer samples in powder form were mounted on the standard VG sample studs by means of double-sided adhesive tapes. To minimize radiation damage to the sample, the X-ray source was run at a reduced power of

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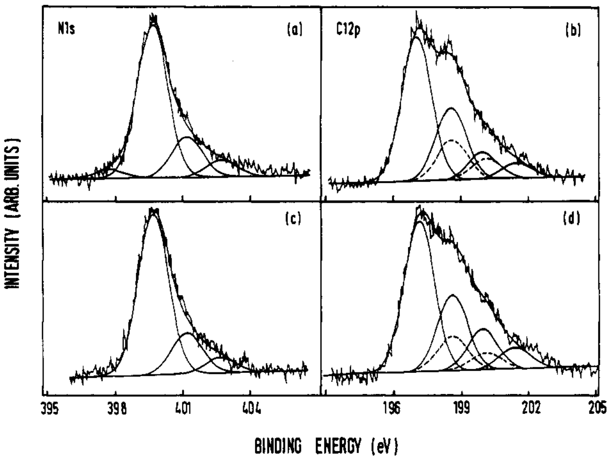

Figure 1. N1s and Cl2p core-level spectra of PPY complexes prepared with initial $FeCl_3$/monomer ratio of a and b 0.24 and c and d 4.0 in aqueous medium.

120 W (12 kV and 10 mA). This power rating did not cause any detectable damage to the present samples. This was suggested by the fact that almost identical spectra were always obtained when the binding energy scans for each sample were repeated. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during the measurements. To compensate for surface charging effects, the binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. However, for the oxidized and highly conductive samples, the main C1s peak component remains unshifted at 284.6 eV. In spectral deconvolution, the widths (full widths at half-maximum or fwhm) of Gaussian peaks were maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were obtained from peak area ratios, corrected with the experimentally calibrated sensitivity factors, and might be liable to a maximum of ±10% error.

Bulk elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The electrical conductivities of the samples were measured by using either the standard collinear four-probe or the two-probe techniques on compressed pellets. The infrared (IR) absorption spectra were measured on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr.

Results and Discussion

PPY Synthesized from Ferric Chloride. Parts a–d of Figure 1 show the respective N1s and Cl2p core-level spectra for two PPY complexes prepared in aqueous medium with initial $FeCl_3$/monomer ratios of 0.24 and 4.0. In general, increase in the initial $FeCl_3$/monomer ratio between these two limits results in an increase in the yield of the complex. For example, the yields for complexes prepared from the present two ratio limits differ by as much as 4 times. On the other hand, the electrical conductivities (σ) of the complexes prepared with various initial $FeCl_3$/monomer ratios do not vary significantly from one to another. This is consistent with the fact that the N1s line shape of the various complexes is almost independent of the initial $FeCl_3$/monomer ratio. In particular, the proportions of the positively charged nitrogens, as revealed by the high binding energy (BE) tail of the N1s spectrum above 401 eV,[17] do not differ appreciably for the various reactant ratios studied in this work. However, for complexes prepared with low initial $FeCl_3$/monomer ratio, a small low BE component, which is shifted by about −2 eV from the main pyrrolylium nitrogen component at about 399.7 eV, is also discernible (Figure 1a). A similar N1s peak component has been observed in electrochemically grown PPY films at low current densities,[18] as well as in PPY complexes "compensated" with a base,[21] and has been attributed to the formation of deprotonated pyrrolylium nitrogen or imine-like (=N—) structure.[15,18,21] Thus, under the less oxidative environment, PPY is susceptible to some degree of deprotonation. This is further supported by the fact that for PPY complexes prepared in the presence of a less oxidative transition-metal salt, such as $AgNO_3$, and at low oxidant/monomer ratio, the low BE =N— structure in the N1s core-level spectrum is substantially enhanced.

The chemical compositions, σ, and XPS results for complexes prepared with various initial $FeCl_3$/monomer ratios in aqueous and organic solvent media are summarized in Table I.

Considerable discrepancies still exist in the published chemical compositions and reaction stoichiometries for PPY complexes synthesized from $FeCl_3$. For example, Cl/N ratios of 0.30 ± 0.4 have been reported by Armes[10] for complexes synthesized with initial Fe(III)/pyrrole mole ratios between 0.1 and 4.0, while a Cl/N ratio of only 0.21 was reported by Pron et al.[22] for a complex prepared with an initial Fe(III)/pyrrole mole ratio of about 0.2. Furthermore, the amounts of Fe incorporated in the polymer complexes also vary from one study to another. A limiting Fe content of 2.4% has been suggested in one study,[8] although other studies suggest negligible Fe content.[6,22] The data in Table I suggest that for the present samples prepared in aqueous medium the chemical compositions, and the Cl/N ratios in particular, are consistent with those reported by Armes[10] and Machida et al.[6] The amount of chlorine incorporated can also vary somewhat with the extent and method of washing,[8] although the general line shape of the Cl2p core-level spectrum remain unchanged. Furthermore, substantial variations in the Cl/N ratio and electrical conductivity are observed for samples prepared in different solvent media. The Cl/N ratios for the present complexes prepared in methanol and acetonitrile are somewhat higher than the values of 0.33 reported by Machida et al.[6] These authors have also reported a substantial lower electrical conductivity for complexes prepared in acetonitrile than for those prepared in the aqueous and alcohol media. However, comparable electrical conductivities are observed for samples prepared in all three solvents in the present study. This discrepancy could be attributed in part to the fact that anhydrous $FeCl_3$ was used by Machida et al. while hydrated $FeCl_3$ was used in the present work, although both types of $FeCl_3$ give rise to complexes with high conductivity in aqueous medium.[5,6,10] It has also been suggested that anhydrous $FeCl_3$ can react with acetonitrile.[6] The use of other organic solvents, such as acetone and chloroform, results in PPY complexes with CHN ratios deviated substantially from the ideal value. As a result, the complexes prepared in these two media are much less conductive.

The elemental analysis results in Table I also show an excess of both hydrogen and oxygen in all samples studied. This has also been widely observed in other PPY complexes prepared chemically or electrochemically.[3,9,20] The presence of excess oxygen is consistent with the presence of a fairly strong O1s spectral signal in each sample. The presence of excess oxygen has been widely attributed to the surface oxidation products, such as those resulted from the charge-transfer complexing with oxygen, as PPY has a relatively low oxidation potential.[3,22,23] For all complexes studied in this work (Table I), the Cl/N ratio at the surface, as reviewed by XPS, agrees fairly well with those obtained from the bulk analysis. Thus, the surface compositions and states analyzed by XPS should constitute a fair representation of the bulk properties.

Table I
XPS Results of PPY Complexes Synthesized from $FeCl_3 \cdot 6H_2O$ under Various Conditions

sample	solvent	reactant ratios $FeCl_3$/monomer	PPY compositions (bulk)	total Cl/N ratios (XPS)	chemical states[a]			proportions[b] of			conductivity σ, S/cm
					Cl^-/N	Cl*/N	–Cl/N	=N–	–NH–	N^+	
1	H_2O	0.24	$C_{4.0}H_{3.3}N_{1.0}Cl_{0.30}O_{0.61}$	0.28	0.19 (68%)[c]	0.05 (19%)	0.04 (13%)	0.04 [0.21][d]	0.70 [0.72]	0.26 [0.07]	16
2	H_2O	1.0	$C_{4.0}H_{3.4}N_{1.0}Cl_{0.30}O_{0.45}$	0.33	0.23 (69%)	0.06 (19%)	0.04 (12%)	0.0 [0.21]	0.73 [0.72]	0.27 [0.07]	21
3	H_2O	2.4	$C_{4.0}H_{3.3}N_{1.0}Cl_{0.35}O_{0.50}$	0.33	0.22 (66%)	0.06 (19%)	0.05 (15%)	0.0 [0.22]	0.73 [0.70]	0.27 [0.08]	24
4	H_2O	4.0	$C_{4.0}H_{3.4}N_{1.0}Cl_{0.35}O_{0.47}$	0.31	0.21 (67%)	0.04 (15%)	0.06 (18%)	0.0 [0.22]	0.74 [0.70]	0.26 [0.07]	20
5	methanol	2.4	$C_{4.0}H_{3.4}N_{1.0}Cl_{0.39}O_{0.55}$	0.41	0.24 (58%)	0.12 (29%)	0.05 (13%)	0.0 [0.23]	0.70 [0.71]	0.30 [0.06]	30
6	ethanol	2.4	$C_{4.0}H_{3.3}N_{1.0}Cl_{0.39}O_{0.56}$	0.41	0.21 (52%)	0.14 (34%)	0.06 (14%)	0.03 [0.22]	0.68 [0.71]	0.29 [0.07]	38
7	acetonitrile	2.4	$C_{4.0}H_{3.4}N_{1.0}Cl_{0.48}O_{0.30}$	0.48	0.19 (39%)	0.20 (42%)	0.09 (19%)	0.02 [0.20]	0.68 [0.74]	0.30 [0.06]	40
8	acetone	2.4	$C_{4.0}H_{5.0}N_{0.6}Cl_{0.16}O_{0.21}$	0.11	0.06 (53%)	0.0	0.05 (47%)	0.04	0.92	0.04	$\leq 10^{-8}$
9	chloroform	~0.4	$C_{4.0}H_{4.6}N_{0.9}Cl_{0.35}O_{0.44}$	0.32	0.27 (83%)	0.0	0.05 (17%)	0.05	0.75	0.20	10^{-2}

[a] From Cl2p core-level spectra. The $Cl2p_{3/2}$ B.E. for Cl^- = 197.1 eV, Cl* = 198.6 eV, –Cl = 200.1 eV. [b] From deconvoluted N1s core-level spectra. [c] Number in parentheses is the percentage of each chloride species. [d] Number in brackets is the value after treatment with excess 0.5 M NaOH.

Due to the discrepancy in the observed Cl/N ratios of the polymer complexes prepared from $FeCl_3$, at least two reaction stoichiometries have been proposed:

$$n(C_4H_3N) + 2.33nFeCl_3 \rightarrow [(C_4H_3N)^+ 0.33\ Cl^-]_n + 2.33nFeCl_2 + 2nHCl \quad \text{(ref 6)}$$

$$4(C_4H_5N) + 9FeCl_3 \rightarrow [(C_4H_3N)_4{}^+Cl^-] + 8HCl + 9FeCl_2 \quad \text{(ref 22)}$$

The former is taken to give rise to a complex with a pyrrole/Cl^- ratio of 3:1, while the latter a ratio of 4:1. The discrepancy can be resolved from the properly deconvoluted Cl2p core-level spectra. The Cl2p core-level spectra of the present complexes are best resolved with three spin-orbit split doublets ($Cl2p_{3/2}$ and $Cl2p_{1/2}$), with the BE for the $Cl2p_{3/2}$ peaks lying at about 197.1, 198.6, and 200.1 eV. This readily indicates that the chlorine incorporated exists in three distinct chemical states. The BE values of the $Cl2p_{3/2}$ components at about 197.1 and 200.1 eV are suggestive of the presence of ionic and covalent chlorine species, respectively.[24] The data in Table I indicate that the proportion of covalent chlorine increases with increasing $FeCl_3$/monomer ratio used for the synthesis. Thus, more than 10% of the incorporated chlorine can exist as covalent or neutral species for samples prepared with high $FeCl_3$/monomer ratio.

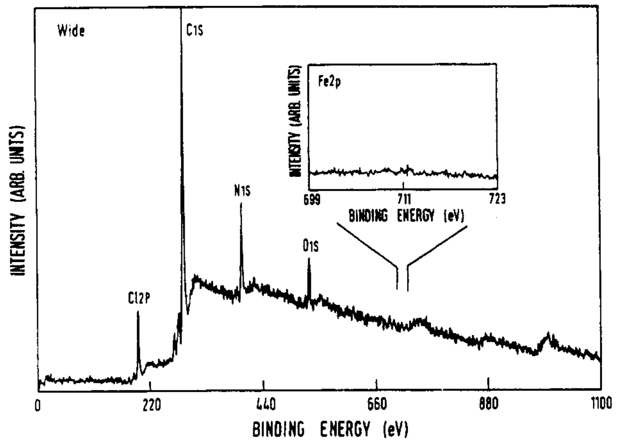

Figure 2. Wide and narrow energy scans of a PPY complex prepared with an initial $FeCl_3$/monomer ratio of 2.4 in methanol.

The presence of chlorine species with a $Cl2p_{3/2}$ BE (~198.6 eV) between those of the ionic and covalent components in most of the $FeCl_3$ polymerized samples deserves special consideration. The proportion of this intermediate chloride species (Cl*) is in the order of 20% of the total chlorine incorporated for samples prepared in the aqueous medium. It is somewhat independent of the initial $FeCl_3$/monomer ratio but varies to some extent with the preparation media (see Table I). In fact, the difference in the amount of this intermediate BE species accounts for the variations in the total amount of chlorine incorporated for complexes prepared in different media. For instance, the Cl2p core-level spectra for a typical PPY complex prepared in methanol exhibits an even higher proportion of the Cl* species than that of the sample prepared in the aqueous medium. A survey of the Cl2p BE values in the literature[25] suggests that the BE of this intermediate species is similar to those of the chloride ions in metal chlorides, including $FeCl_3$ and $FeCl_2$. Furthermore, Pron et al.[22] have shown that exposure of PPY to $FeCl_3$/nitromethane solution can result in the incorporation of iron-based counteranions, such as $FeCl_4^-$. Since a trace amount of Fe has been reported in virtually every study[6,8,10] on the $FeCl_3$ polymerized PPY complexes, the partial contribution of the iron-based chloride species to the Cl* component in some samples has to be taken in account. On the other hand, wide and narrow BE scans of the present $FeCl_3$ polymerized samples do not reveal the presence of a significant amount of iron, in particular $FeCl_3$ and $FeCl_2$ species with $Fe2p_{3/2}$ BE values in the region of 711 eV.[25] Figure 2 shows a typical wide survey spectrum of the PPY complex prepared in the methanol solution of $FeCl_3$. Thus, most of the present intermediate chloride species is more appropriately associated with anionic chloride species resulted from the charge-transfer interactions between the halogen and the metal-like conducting state of the polymer chain. This is consistent with the observation that high electrical conductivity is usually associated with high Cl* content. The reduced negative BE shift observed for this intermediate chloride species suggests the present of chloride anion in a more positive environment, as a result of increase in the number of positively charged nitrogens in the polymer chain associated with the formation of polarons and bipolarons.[26]

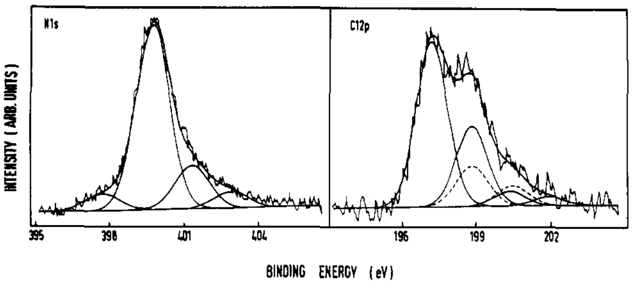

Figure 3. N1s and C12p core-level spectra of a PPY/chloride complex obtained via the anion exchange of the PPY/iodide complex in 1 M HCl.

The intermediate chloride species is also observed in PPY complexes prepared from iron-free oxidants. For example, the PPY/iodide complex prepared via the simultaneous chemical polymerization and oxidation of pyrrole by iodine[7] readily undergoes anion exchange in 1 M HCl to give rise to a PPY/chloride complex. The N1s and C12p core-level spectra of the PPY/chloride complex so produced (Figure 3) are not unlike those of the $FeCl_3$ polymerized samples shown in Figure 1. Furthermore, similar intermediate chloride species have also been observed in the C12p core-level spectrum of the HCl protonated emeraldine oxidation state of polyaniline.[27]

In this connection, it is interesting to note that an earlier XPS study[28] on the reaction of evaporated metal films with Cl_2 gas has also revealed the presence of three chlorine species. The species have been attributed to the metal chlorides, the chlorine ions adsorbed at the metal surface arising from different potential effect or bonding nature of the ion to the metals, and the neutral Cl_2 or Cl absorbed on the chlorides. For metals with low oxidation potential, the BE for the absorbed chlorine ions is similar to that of the Cl^* species observed in the present study.

For complexes with moderate Cl^* content (e.g., samples 1–6, Table I), fairly close balance between the amount of chloride anion (Cl^- and Cl^* species) and the pyrrolylium nitrogen cation is observed, if it is assumed that the pyrrolylium nitrogen carries a unit positive charge. The presence of unit positively charged nitrogens has also been favored in a number of earlier studies,[16,18] although other studies suggest partial or delocalized charges.[14,15] For complexes with high Cl^* content (e.g., sample 7, Table I), the sum of the chloride anion species is somewhat larger than the amount of nitrogen cation. Thus, the high Cl^* content in some complexes is probably associated with the incorporation of a small amount of iron-based chloride species which do not undergo charge-transfer interaction with the pyrrolylium nitrogens.

Earlier studies[15,21] have suggested that treatment of oxidized PPY complexes with excess base results in the dehydrogenation of a certain fraction of the pyrrolylium nitrogens. Subsequent rearrangement of the pyrrole bonds to satisfy the three nitrogen valences gives rise to a =N— type structure. These deprotonated nitrogens are revealed by a low BE shoulder in the N1s spectrum which is shifted by about −2 eV from the pyrrolylium nitrogen peak at 399.7 eV. Table II shows the effect of progressive NaOH treatments on a PPY/chloride complex synthesized in ethanol and with an initial complex Cl/N ratio of about 0.41. The N1s and C12p core-level spectra of the corresponding samples are shown in Figure 4. Thus, in the presence of limited NaOH, the Cl^* species is preferentially removed over the Cl^- species by NaOH (compare the Cl^*/N and Cl^-/N ratios of samples 1 and 2 in Table II). The data in Table II further indicate that a decrease in the Cl^-/N ratio, but not the Cl^*/N ratio, is accompanied by a corresponding increase in the proportion of the =N— component. These readily suggest that each Cl^- species is associated with a specific nitrogen cation and the Cl^* species is less tightly binded.

With the exception of some covalent chlorine species, the Cl^- and Cl^* species in various PPY/chloride complexes are removed in the presence of excess NaOH. This is accompanied by the loss of the N1s high BE tail attributable to the N^+ component and the appearance of about 20–25% of the deprotonated pyrrolylium nitrogens (Figure 4d). The residual amount of the N^+ component is probably associated with the surface oxidation products as mentioned earlier. Despite a substantial variation in the total Cl/N ratio of the various samples, similar amounts of the =N— structure are obtained in all of the NaOH-treated PPY/chloride complexes of well-defined structure and composition, such as samples 1–7 of Table I. This coincides with the fact that all of these complexes have similar Cl^-/N ratios which fall in the range 0.19–0.24. Furthermore, a similar fraction of the =N— structure is also observed in other NaOH-treated PPY/halides complexes, such as the PPY/iodide complex prepared by the simultaneous polymerization and oxidation of pyrrole by iodine.[7] Finally, our recent results suggest that the PPY/halide complexes degrade thermally in N_2 via a deprotonation process to give rise to a similar fraction of the =N— structure.

The deprotonated pyrrolylium nitrogens can be reprotonated by protonic acids, such as HCl, H_2SO_4, and HBr. Reprotonation results in a diminished =N— component and the reappearance of the N^+ component in the N1s spectrum, consistent with the earlier study.[21] Again, the properly deconvoluted C12p core-level spectrum of the 1 M HCl reprotonated sample (Cl/N = 0.23) reveals the presence of a significant amount of the Cl^* component. The acid/base treatment, however, may have involved a small degree of hydrolysis and ring opening,[29] as suggested by a slight increase in H/N and C/N ratios of the polymer. Alternatively, the deprotonated pyrrolylium nitrogen can also be treated with phenylhydrazine to give rise to a fully reduced PPY (all -NH- structure). Figure 5a shows the N1s core-level spectrum of a deprotonated PPY after reduction by phenylhydrazine. The low BE =N— component has diminished substantially without any increase in the high BE tail. The fully reduced PPY can in turn be oxidized by electron acceptors, such as halogens. Figure 5b shows the N1s core-level spectrum of the polymer after partial reoxidation by iodine in acetonitrile solution to give rise to a I/N ratio of about 0.15. The reoxidized polymer again exhibits an enhanced N1s high BE tail characteristic of the $-N^+H-$ component. Treatment of this complex with NaOH readily results in the reappearance of the deprotonated pyrrolylium nitrogens in approximate proportion to that of the partial oxidation level (Figure 5c).

Thus, the pyrrolylium nitrogens can exist in a number of intrinsic oxidation states, ranging from that consisting of about 25% oxidized neutral imine-like (=N—) structure observed in this study to that consisting entirely of reduced amine-like (—NH—) structure. The chemical nature of these redox states is not unlike those observed in the aniline family of polymers. In polyaniline, the 50% oxidized emeraldine oxidation state (50% =N— structure) is susceptible either to protonation by protonic acids or to reduction by phenylhydrazine to the fully reduced leucoemeraldine (all —NH— structure).[30] The latter in turn can be oxidized by electron acceptors such as chlorine to give rise to a structure equivalent to that of the HCl protonated emeraldine.[30,31] The various intrinsic oxidation

Table II
Effect of Progressive NaOH Treatments on a PPY Complex Synthesized from $FeCl_3{\cdot}6H_2O$ in Ethanol As Revealed by XPS

		chemical states[a]			proportions[b] of			
sample	total Cl/N (XPS)	Cl^-/N	Cl^*/N	–Cl/N	=N–	–NH–	N^+	conductivity σ, S/cm
1 (untreated)	0.41	0.21	0.14	0.06	0.03	0.68	0.29	38
2	0.24	0.17	0.04	0.03	0.08	0.68	0.23	3
3	0.15	0.10	0.03	0.02	0.14	0.69	0.17	0.1
4	0.01	0.0	0.0	0.01	0.22	0.71	0.07	$\leq 10^{-6}$

[a,b] See footnotes of Table I.

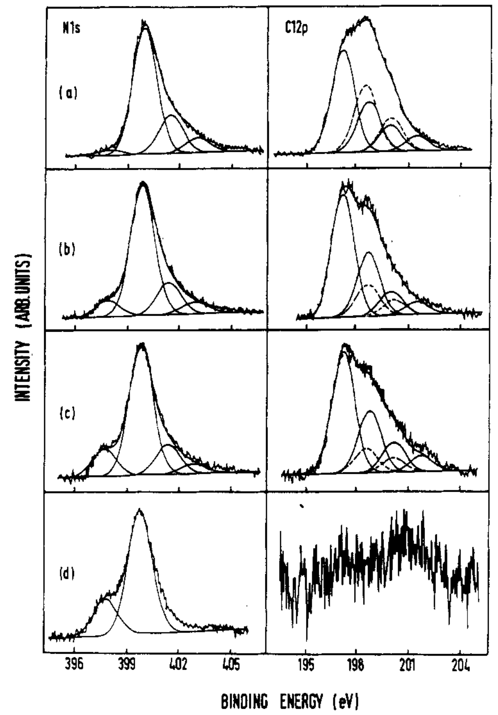

Figure 4. N1s and Cl2p core-level spectra of a PPY/chloride sample prepared in ethanol upon progressive NaOH treatments: (a) before treatment, Cl/N = 0.41; (b) Cl/N = 0.24; (c) Cl/N = 0.15; (d) Cl/N = 0.01.

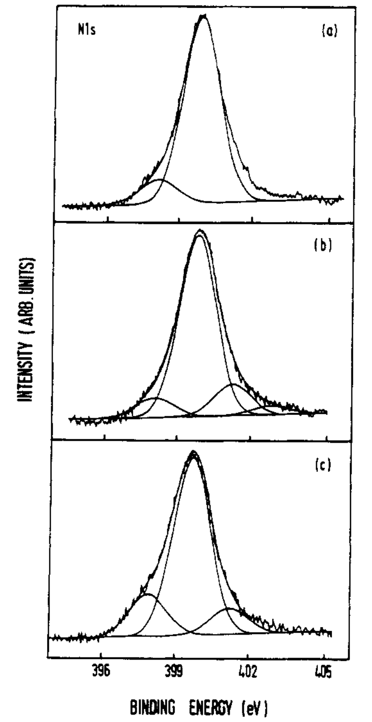

Figure 5. N1s core-level spectra of (a) a deprotonated PPY after reduction by phenylhydrazine, (b) the reduced PPY after partial reoxidation by iodine to I/N = 0.15, and (c) the partially reoxidized PPY after treatment with excess NaOH.

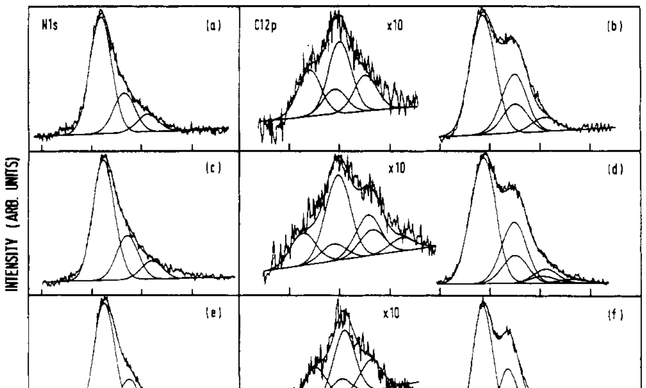

Figure 6. N1s and Cl2p core-level spectra of PPY complexes prepared with initial $Fe(ClO_4)_3$/monomer ratio of a and b 0.24 and c and d 4.0; and e and f with initial $Cu(ClO_4)_2$/monomer ratio of 2.4.

states of present PPY are not clearly distinguishable from the IR absorption spectra. However, the IR absorption spectra indicate that the process of deprotonation by NaOH and subsequent reduction by phenylhydrazine does not result in a substantial alteration of the polymer structure. This is suggested by the persistence of the IR absorption bands at about 1540, 1480, 1300, 1180, 1040, and 920 cm^{-1}, which are characteristic of PPY,[3,4] in both states. The presence of a strong C_β–H in-plane vibration at about 1040 cm^{-1} in both the deprotonated and reduced polymers suggests that most of the β-carbons remain intact during the redox process.

The observation that only one of the four pyrrolylium nitrogens can exist in the form of oxidized imine-like structure, at least in the present PPY/halide complexes, and the fact that the Cl^-/N ratio is always in the order of 0.25, regardless of the total amount of chlorine incorporated, readily suggested that the reaction scheme which gives rise to a product with a pyrrole/Cl^- ratio of 4:1 is more appropriate. Furthermore, the degree of oxidation of the PPY complexes obtained from the polymerization and oxidation of pyrrole by $FeCl_3$ should not be derived from the total chlorine balance alone.

PPY Synthesized from Ferric Perchlorate. Parts a–d of Figure 6 show the respective N1s and Cl2p core-level spectra for two PPY/perchlorate complexes synthesized with the initial $Fe(ClO_4)_3$/monomer ratio of 0.24 and 4.0 in aqueous medium. Again, changes in the reactant mole ratios between these two limits cause neither a significant variation in the final Cl/N ratio of the complexes nor a significant variation in the types of chlorine species present. Most of the chlorines exist as the perchlorate species with a characteristic Cl2p BE in the region of 207 eV.[14] The lower BE Cl2p spectrum, which is partially attributable to the X-ray satellite lines

Table III
XPS Results of PPY Complexes Synthesized from $Fe(ClO_4)_3{\cdot}9H_2O$ in Aqueous Medium

sample	reactant ratio Fe(III)/monomer	amount and chemical states of dopant[a]						proportions[b] of			conductivity σ, S/cm
		Cl^-/N	Cl^*/N	$-Cl/N$	$(ClO_4)^-/N$	$(ClO_4)^*/N$	$-(ClO_4)/N$	=N-	-NH-	N^+	
1	0.24	0.01	0.02	0.0	0.29	0.07	0.0	0.0	0.65	0.35	4
2	1.0	0.01	0.02	0.01	0.29	0.08	0.02	0.0	0.63	0.37	7
3	2.4	0.01	0.01	0.01	0.31	0.08	0.02	0.0	0.62	0.38	13
4	4.0	0.01	0.02	0.01	0.28	0.06	0.02	0.0	0.66	0.34	7

[a] From C12p core-level spectra. The $C12p_{3/2}$ B.E. for Cl^- = 197.1 eV, Cl^* = 198.8 eV –Cl = 200.4 eV, $(ClO_4)^-$ = 207.4 eV, $(ClO_4)^*$ = 208.9 eV, and $-(ClO_4)$ = 210.4 eV. [b] From deconvoluted N1s core-level spectra.

of the perchlorate species, can itself be resolved into three components with characteristic $C12p_{3/2}$ BE of about 200.6, 199, and 197.3 eV. The first and the last components are attributable to the covalent chlorine and chloride anion, respectively, while the intermediate component is probably of similar nature as that of the Cl* species observed earlier in the PPY/chloride complexes. The presence of the chloride species is consistent with the fact that perchlorate anion has a high reduction potential and may undergo reaction to form the chloride species.[32] The latter in turn interacts with the polymer to give rise to the observed C12p spectrum in the 200-eV BE region.

The XPS data indicate the incorporation of about 0.36–0.41 perchlorate per nitrogen for the complexes prepared in aqueous medium with reactant ratios between the two limits. Similar polymer composition and complex stoichiometry are observed for complexes prepared in acetonitrile. The stoichiometry is also in agreement with that of the electrochemically prepared PPY/perchlorate complex in $AgClO_4$ solution.[14] However, the C12p core-level spectra of the present complexes suggest the presence of perchlorate species in at least two environments. The C12p doublet at about 207.4 and 208.9 eV is attributable to the perchlorate anion $(ClO_4)^-$.[14] Thus, for the present chemically synthesized complexes, the actual $(ClO_4)^-/N$ ratio is only in the order of 0.29. The species which has a BE shift of about +1.5 eV from that of the perchlorate anion and accounts for about 20% of the total perchlorate incorporated is probably similar to that of the intermediate chloride species observed earlier in the $FeCl_3$ polymerized samples. Again, fairly close balance between the total amount of perchlorate anions and the amount of positively charged nitrogens is observed. The XPS results for some of the complexes studied are summarized in Table III. The presence of a small C12p high BE tail in complexes prepared with high initial $Fe(ClO_4)_3$/monomer ratios is probably attributable to some adsorbed neutral perchlorate species at the surface.

The C:H:N mole ratios for the PPY/perchlorate complexes studied in this work are all very close to the theoretical value of 4:3:1. For instance, the C:H:N mole ratios for the two $Fe(ClO_4)_3$ complexes shown in Figure 6 are 4.0:3.2:1 and 3.9:3.3:1:0, respectively. The electrical conductivities for the perchlorate complexes prepared between the two reactant ratio limits are in the order of 10 S/cm. Treatment of the present PPY/perchlorate complexes with NaOH again results in the loss of the chloride and perchlorate species. It again gives rise to a partially deprotonated polymer consisting of about 25% of the oxidized imine-like species, as revealed by the appearance of a low BE shoulder at about 397.7 eV in the N1s core-level spectrum. Thus, the intrinsic polymer structure of the perchlorate complexes is approximately similar to that of the PPY/chloride complexes prepared from $FeCl_3$, where about one of every four pyrrole units exists in the oxidized state. However, an earlier study[8] has suggested three pyrrole units for every perchlorate, on the basis of the product composition analysis.

For comparison purposes, PPY complexes synthesized in the presence of other transition-metal perchlorates, such as $Cu(ClO_4)_2{\cdot}6H_2O$, were also investigated. An early study[9] has suggested that reaction of pyrrole with copper perchlorate gives rise to a PPY complex with the composition of $[(C_4H_3N)(ClO_4)_{0.35}{\cdot}0.25H_2O]_n$ and conductivity of 60 S/cm. A similar perchlorate/N ratio is observed for the present complexes synthesized with the initial $Cu(ClO_4)_2$/monomer ratio between 1 and 4. A somewhat lower perchlorate/N ratio is observed for complexes prepared with lower initial oxidant/monomer ratio. Parts e and f of Figure 6 show the respective N1s and C12p core-level spectra of a typical PPY complex synthesized with $Cu(ClO_4)_2$. Spectra of similar line shape and peak components are observed for complexes prepared with initial $Cu(ClO_4)_2$/monomer ratio between 0.24 and 4.0. The presence of the C12p core-level spectrum in two BE regions is not unlike that observed in the PPY/perchlorate complex synthesized from $Fe(ClO_4)_3$. Furthermore, the properly deconvoluted C12p core-level spectrum also suggests the presence of two or more perchlorate species. Again, the actual degree of doping in the $Cu(ClO_4)_2$ complexes should not be determined on the basis of the total chlorine or the total perchlorate balance alone. Finally, as in the case of $Fe(ClO_4)_3$ polymerized complexes, deprotonation of the PPY complexes prepared from $Cu(ClO_4)_2$ also gives rise to a N1s core-level spectrum consisting of about 25% oxidized imine-like structure.

Conclusion

Highly conductive PPY complexes obtained from chemical polymerization and oxidation of pyrrole by $FeCl_3$ and $Fe(ClO_4)_3$ have been studied by XPS. The C12p core-level spectrum of the $FeCl_3$ polymerized samples suggests that the chlorine dopant can exist in three chemical states. The XPS results also reveal that the proton modified pyrrolylium nitrogens can exist in a number of intrinsic oxidation states, ranging from that consisting of 25% oxidized imine-like (=N—) structure to that consisting of the fully reduced amine-like (—NH—) structure. The behavior of the pyrrolylium nitrogens at various redox states toward protonation/deprotonation or oxidation/reduction suggests that they are chemically similar to the nitrogens of polyaniline. From the actual chloride anion content of the complexes and the corresponding amounts of the oxidized imine-like structure after deprotonation, a reaction stoichiometry which gives rise to 25% oxidized pyrrole units in the complex is favored among those reported in the literature. Similar chemical structure is observed for the PPY complexes obtained by using $Fe(ClO_4)_3$ or $Cu(ClO_4)_2$ as oxidant.

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