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Chemical nature of the nitrogens in polypyrrole and nitrogen-substituted polypyrrole: a comparative study by X-ray photoelectron spectroscopy

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The chemical nature of the nitrogens in polypyrrole (PPY) and poly(N-methylpyrrole) (PMPY) has been critically compared using X-ray photoelectron spectroscopy as a primary tool. Treatment of PPY/perchlorate complex with NaOH results in a deprotonation process which gives rise to a PPY base (DP–PPY) having an intrinsic oxidation state consisting of 25% oxidized imine-like (=N–) structure, similar to that observed in the 50% oxidized emeraldine state of polyaniline. This intrinsic oxidation state, however, does not exist in the nitrogen-substituted PPY. As a result, the charge-transfer (CT) mechanisms involving the two base polymers and the various oxidants and electron acceptors are vastly different. The PMPY base undergoes strong CT interactions with metal oxidants, such as $Cu(ClO_4)_2$, but interacts only weakly with organic electron acceptors, such as the halobenzoquinones and cyanobenzoquinones. The reverse is true for DP–PPY. Both polymer complexes also exhibit different thermal degradation behaviour.

1. Introduction

The synthesis and characterization of electroactive polymers have become one of the most important research areas in polymer science (e.g. [1]). Of these polymers, the polyheterocycles, such as polypyrrole (PPY) and its derivatives [2], are of particular interest because of their high electrical conductivity, environmental stability and interesting redox properties associated with the chain heteroatoms. A large number of studies using X-ray photoelectron spectroscopy (XPS) has been devoted to the chemically and electrochemically synthesized PPY complexes [3–11]. However, little attempt has been made to compare directly the chemical nature of the nitrogens in PPY and its nitrogen-substituted derivatives, although it is expected that the heteroatoms will have a significant bearing on the physicochemical properties of each polymer. For example, our recent study [12] has indicated that the electrical conductivity and thermal stability of the pyrrole-N-methylpyrrole copolymers are strongly influenced by the copolymer compositions. Accordingly, this study is devoted to the comparison of the chemical nature of nitrogens in PPY and its nitrogen-substituted derivative, such as poly(N-methylpyrrole) (PMPY), using XPS as a primary tool. Pyrrole and some of its nitrogen-substituted derivatives have been known to undergo chemical polymerization and oxidation in the presence of a large number of oxidants, such as the transition metal salts [13, 14] halogens [15] and organic electron acceptors [16].

2. Experimental procedure

The monomers, pyrrole and N-methylpyrrole, were obtained commercially. Polypyrrole (PPY) and poly(N-methylpyrrole) (PMPY) complexes were prepared via the simultaneous polymerization and oxidation of the respective monomers by $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile and under a nitrogen atmosphere [14]. It was found that changes in the reactant (oxidant/monomer) mole ratios between 0.24 and 4.0 did not cause either a significant variation in the final complex composition, in particular the Cl/N ratio, or a significant variation in the electrical conductivity of the complex. All samples were washed thoroughly with copious amounts of acetonitrile before being dried by pumping under reduced pressure. The PPY/perchlorate and PMPY/perchlorate complexes so produced had the typical bulk compositions of $C_4H_{3.2}N_{1.0}O_{0.4}(ClO_4)_{0.35-0.41}$ and $C_5H_{5.3}N_{1.0}O_{0.4}(ClO_4)_{0.24-0.26}$. Part of each oxidized polymer complex was then treated with excess 0.5M NaOH. The polymer bases so obtained were then treated with protonic acids, exposed to oxidants, such as $Cu(ClO_4)_2 \cdot 6H_2O$, or treated with electron acceptors, such as *o*-chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in acetonitrile solutions.

The electrical conductivities of the complexes were measured using the standard collinear four-probe or two-probe technique. X-ray photoelectron spectroscopy (XPS) measurements were made on a VG ESCALAB MkII spectrometer with an MgK_α X-ray source (1253.6 eV photons). The X-ray source was

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operated at a reduced power of 120 W (12 kV and 10 mA). All binding energies were referenced to the C 1*s* neutral carbon peak at 284.6 eV. In spectral deconvolution, the widths (full width at half maximum or FWHW) 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.

3. Results and discussion

Earlier XPS studies [3–11] have shown that the oxidized PPY complexes exhibit a major N 1*s* core-level spectral component at a binding energy (BE) of about 399.7 eV, characteristic of the pyrrolylium nitrogens (–NH– structure), and a high BE tail attributable to the positively charged nitrogens ($-N^+H-$ structure). Fig. 1a shows the N 1*s* core-level spectrum of a PPY/perchlorate complex with a surface perchlorate/nitrogen ratio of 0.35. The fraction of the positively charged nitrogens corresponds roughly to the dopant level. The N 1*s* core-level spectrum of similar lineshape, but with a slightly lower BE for the main component (399.6 eV) is observed for the PMPY/perchlorate complex prepared under similar conditions (Fig. 1c). However, the dopant level or the perchlorate/nitrogen ratio in the nitrogen-substituted polymer is reduced to about 0.25. This is accompanied by a corresponding decrease in the proportion of the positively charged nitrogens in the complex. The electrical conductivities of the PPY and PMPY complexes are 10 and 10^{-2} S cm^{-1}, respectively.

Fig. 1b and d show the respective Cl 2*p* core-level spectra for the PPY and PMPY complex. Properly deconvoluted Cl 2*p* core-level spectra for the PPY complex and, to a lesser extent, for the less-conductive PMPY complex, suggest that the perchlorate species can exist in at least two environments, the Cl $2p_{3/2,1/2}$ doublet at BE about 207.4 eV and 208.9 eV is attributable to the perchlorate anion $(ClO_4)^-$ [17].

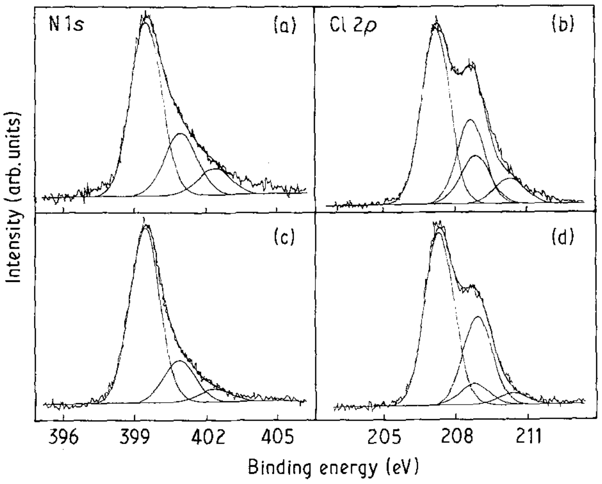

Figure 1 N 1*s* and Cl 2*p* core-level spectra of (a, b) PPY/perchlorate complex (perchlorate/nitrogen = 0.35), (c, d) PMPY/perchlorate complex (perchlorate/nitrogen = 0.25).

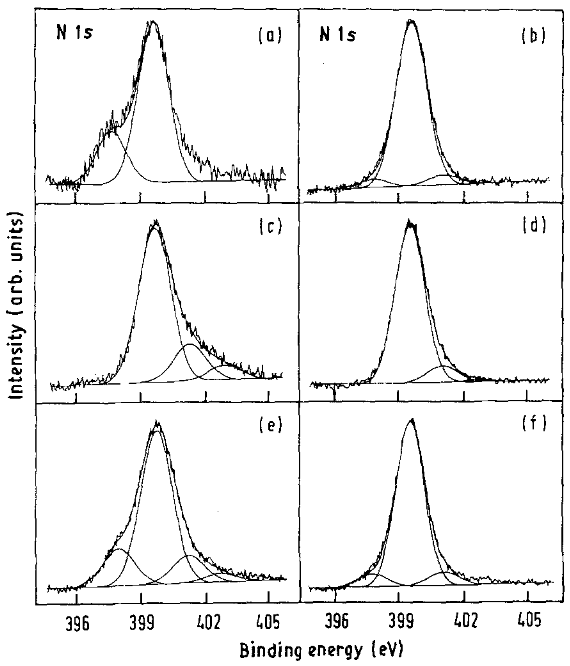

Figure 2 N 1*s* core-level spectra of (a) DP–PPY, (b) PMPY base, (c) DP–PPY after treatment with 1 M H_2SO_4, (d) PMPY base after treatment with 1 M H_2SO_4, (e) PPY/perchlorate heated to 280 °C in nitrogen gas, and (f) PMPY/perchlorate heated to 300 °C in nitrogen gas.

Thus, for the PPY complex, the actual $(ClO_4)^-$/N ratio is only in the order of 0.28. The perchlorate species whose BE is shifted by about + 1.5 eV suggests the presence of perchlorate anion in a more positive environment, probably as a result of increase in the number of positively charged nitrogens in the polymer chain associated with the formation of polarons and bi-polarons [18].

Treatment of the present PPY and PMPY complexes with 0.5 M NaOH results in the loss of the perchlorate anions. In the case of PPY complex, Fig. 2a indicates that the NaOH treatment also results in the appearance of a low BE component at about 397.7 eV in the N 1*s* core-level spectrum. This is attributable to the dehydrogenation of a certain fraction of the pyrrolylium nitrogens [5, 8]. Thus, treatment of oxidized PPY complex with the base gives rise to a partially deprotonated polymer consisting of about 25% oxidized imine-like structure. In general, treatments of other PPY complexes, such as the PPY/iodide [15] or PPY/chloride [13] complexes with NaOH also result in the appearance of 20%–25% imine nitrogens. Similar BE shifts have also been observed for the imine and amine nitrogens in the emeraldine oxidation state of polyaniline [19]. It has been found that the deprotonated PPY (DP–PPY) is not completely stable. The proportion of the imine nitrogens decreases by half when exposed to laboratory atmosphere for over 2 months.

However, in the case of PMPY, the loss of the perchlorate species is not accompanied by an appreciable degree of demethylation. This is readily suggested by the fact that the N 1*s* core-level spectrum becomes fairly symmetrical, as shown in Fig. 2b. Thus, the nitrogens of PMPY do not exist in a number of intrinsic oxidation states as in the case of PPY. As a result, unlike the DP–PPY which is readily reprotonated by a protonic acid such as H_2SO_4, to give rise to a complex with conductivity of about 5 S cm^{-1}, the PMPY base cannot be reprotonated by acids. This is readily supported by the lack of an appreciable amount of the S 2*p* core-level signal and the positively charged nitrogens in the N 1*s* core-level spectrum of the latter after treatment with 1M H_2SO_4 (Fig. 2c and d).

Both the PPY/perchlorate and PMPY/perchlorate complexes undergo thermal "undoping" upon exposure to high temperature in nitrogen gas. This is readily suggested by the loss of the perchlorate species and the proportion of the positively charged nitrogens. The decomposition of the perchlorate species is also accompanied by the formation of some covalently bonded chlorine species. Fig. 2e and f show the respective N 1*s* core-level spectra of the PPY and PMPY complexes after having been heated to around 300 °C in nitrogen gas. The PPY/perchlorate complex degrades thermally via a deprotonation process, as suggested by the appearance of the N 1*s* low BE shoulder at 397.7 eV. Similar degradation behaviour is also observed for other PPY complexes, such as the PPY/halide complexes synthesized in the presence of iodine or $FeCl_3$. On the other hand, the PMPY/perchlorate complex degrades predominantly via the decomposition of the perchlorate species and the N 1*s* spectrum of the thermally degraded complex is not unlike that of the NaOH-compensated PMPY complex except for the formation of a small amount of imine-like nitrogens.

The two polymer bases also exhibit distinct behaviour towards charge-transfer (CT) interactions with various oxidants. Fig. 3a and b compare the N 1*s* core-level spectra of the two base polymers after having been treated with $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile. Thus, treatment with the metal perchlorate has resulted in the reappearance of the positively charged nitrogens in both polymers. In the case of the DP–PPY complex, the CT interaction occurs preferentially through the imine units, as suggested by the loss of the low BE shoulder in the N 1*s* spectrum. The electrical conductivities of the resulting PPY/perchlorate and PMPY/perchlorate complexes are 10^{-3} and 10^{-2} S cm^{-1}, respectively. The perchlorate/nitrogen ratios in the corresponding complexes are about 0.25 and 0.35. These results suggest that the PMPY base can be reoxidized more readily by copper perchlorate. Furthermore, treatment of the DP–PPY with copper perchlorate gives rise to a perchlorate complex significantly different from the initial PPY-/perchlorate complex. Similar CT behaviour has also been observed recently for complexes involving copper perchlorate and the emeraldine (50% =N– structure) and leucoemeraldine (all –NH– structure) oxidation states of polyaniline [20].

Interesting CT interactions are also observed between DP–PPY (and to a lesser extent the PMPY base) with various organic electron acceptors. Fig. 4a–d show the respective N 1*s* and Cl 2*p* core-level spectra for a DP–PPY/*o*-chloranil and a DP–PPY/DDQ complex. The electrical conductivities of the respective complexes are 10^{-1} and 10^{-2} S cm^{-1}. The Cl 2*p* core-level spectrum of the *o*-chloranil complex reveals the presence of both ionic and covalent species, with the Cl $2p_{3/2}$ BE of the respective species at about 196.8 and 200.4 eV. Furthermore, the CT interaction between the polymer and the acceptor occurs preferentially through the imine units, as suggested by the disapperance of the low BE shoulder in the N 1*s* spectrum. To account for the formation of chloride anions and pyrrolylium cations, and the disappearance of the imine units,

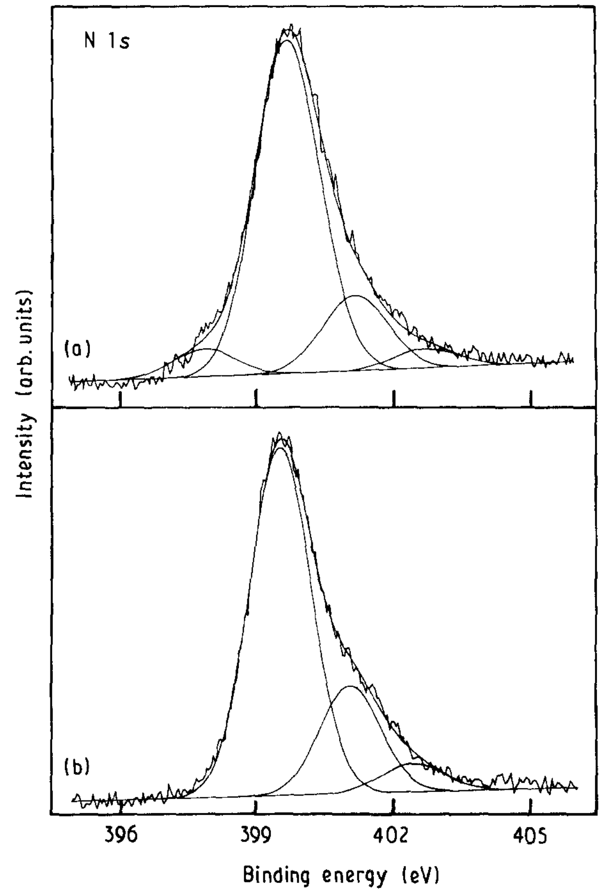

Figure 3 N 1*s* core-level spectra of (a) DD–PPY, and (b) PMPY base after treatment with $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile.

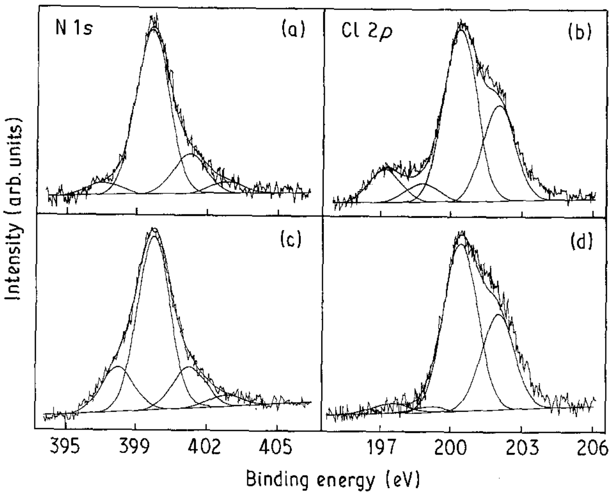

Figure 4 N 1*s* and Cl 2*p* core-level spectra of (a, b) DP–PPY/*o*-chloranil complex (acceptor/monomer = 0.26), and (c, d) DP–PPY/DDQ complex (acceptor/monomer = 0.20).

cleavage of some of the C–Cl bonds of the acceptor, accompanied by the formation of linkages between the acceptor and the deprotonated pyrrolylium nitrogens through the cleavage sites must have occurred. Furthermore, the linkage is probably through the C_4 position of the acceptor, as this position is sterically less hindered. This is readily supported by the fact that for complex involving *p*-chloranil, the proportion of the chloride anion is substantially lower at comparable acceptor level. Finally, the O 1*s* core-level spectrum of the *o*-chloranil complex reveals the presence of a low and a high BE component of about equal size located at about 1.5 eV on either side of the carbonyl peak at about 532.5 eV. The two components are attributable, respectively, to the benzoquinone anions and oxygen bonded to an electron withdrawing group or the positively charged pyrrolylium nitrogens. Again, the linkage is through the deprotonated pyrrolylium nitrogens.

In the case of DP–PPY/DDQ complex the BE of the nitrogens of the neutral cyano group of the acceptor overlaps that of the neutral pyrrolylium nitrogens. The carefully deconvoluted N 1*s* spectrum of the complex reveals the appearance of the positively charged nitrogens and the displacement of the =N– peak component at 397.7 eV by a new component at about 398.2 eV. The latter, which is shifted by only about −1.5 eV from the neutral nitrogen species at 399.7 eV, must be attributable to the formation of the cyano anions. In other CT complexes involving organic cyano radical anions, such as TCNQ anions [21], a negative chemical shift of about 1.1–1.2 eV from the neutral nitrogen peak has also been observed. In addition, both the Cl 2*p* and O 1*s* core-level spectra reveal the presence of anionic species, as in the case of the chloranil complexes. However, the proportion of the chloride anions in the present DDQ complex is substantially lower than that of *o*-chloranil complex at comparable acceptor loading. This is consistent with the effect of steric hindrance proposed earlier.

The lack of imine-like nitrogens in PMPY base precludes the type of interactions observed between DP–PPY and the halobenzoquinones. As a result, only limited CT between PMPY and the halobenzoquinones exists, as suggested by the lack of an appreciable amount of the positively charged nitrogens or the halogen anions. This behaviour also differs significantly from the strong CT interactions observed between the amine nitrogens in the leucoemeraldine oxidation state of polyaniline and the organic acceptors [22]. However, in the presence of a strong acceptor, such as DDQ [23], the extent of CT interaction is discernible from the properly deconvoluted N 1*s* core-level spectrum of the PMPY complex. The N 1*s* and Cl 2*p* core-level spectra of a DMPY/DDQ complex are shown, respectively, in Fig. 5a and b. The N 1*s* core-level spectrum again suggests the presence of cyano radical anions at a BE of about 398.1 eV and a proportional amount of the positively charged nitrogens. Furthermore, the chlorine functional group of the acceptor probably does not contribute significantly to the CT process.

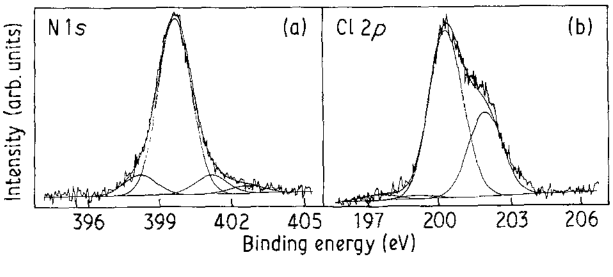

Figure 5 (a) N 1*s* (b) Cl 2*p* core-level spectra of a PMPY/DDQ complex (acceptor/monomer = 0.16).

4. Conclusion

XPS data suggest that the chemical nature of the nitrogens in polypyrrole (PPY) and nitrogen-substituted PPY, such as poly(N-methylpyrrole) (PMPY) is distinctly different. The nitrogens of PPY, but not PMPY, can exist in a number of intrinsic oxidation states, ranging from that consisting of at least 25% oxidized imine-like structure, obtained through the deprotonation of the PPY/anion complex by a base. As a result, the nitrogens of the two polymer bases exhibit different charge-transfer behaviour towards various oxidants and electron acceptors. The two polymer complexes also degrade thermally by distinctively different mechanisms.

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