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XPS studies of iodine complexes of pyrrole – N-methylpyrrole copolymer

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SUMMARY

Simultaneous chemical copolymerization and oxidation of pyrrole and N-methylpyrrole by iodine has been carried out. The electrical conductivity, the I_3^- content and the amount of positively charged pyrrolylium nitrogen decrease with increasing N-methylpyrrole content in the copolymer complexes.

INTRODUCTION

The synthesis and oxidation of heterocyclic polymers, such as polypyrrole(PPY) and its derivatives, by electrochemical method have become a well-established common practice(1-2). Electrochemical copolymerization of pyrrole with its N-substituted derivatives has been used to some extent for the controlling of the electrical properties in this family of electroactive polymers(3-5). Highly conductive PPY complexes have also been synthesized chemically in the presence of various Fe(III) oxidants, such as $Fe(ClO_4)_3$ and $FeCl_3$(6-8). A relatively simple chemical method for the simultaneous polymerization and oxidation of pyrrole by halogens, such as I_2, Br_2 and Cl_2 has also been developed recently in our laboratory(9,10). The PPY-halogen complexes so prepared have electrical conductivity and conduction behavior comparable to those of PPYs prepared by electrochemical method. Thus, it would be of great interest to extend the chemical method to the copolymerization and oxidation of pyrrole and its N-substituted derivatives. This report deals with the XPS studies of the charge transfer interaction in pyrrole - N-methylpyrrole copolymer-I_2 complexes prepared by the iodine induced chemical polymerization and oxidation.

EXPERIMENTAL

Pyrrole(PY) and N-methylpyrrole(MPY) monomers were purified by distillation under reduced pressure. The copolymer-iodine complexes were prepared via the iodine induced simultaneous polymerization and oxidation of pyrrole in aqueous medium according to the method reported earlier for PPY-I_2 complexes(9,10). The copolymer compositions were determined from elemental analysis. The composition of the copolymer can be effectively controlled by varying the monomer feed ratio. The reactivity ratios for PY and MPY have been determined to be 1.13 and 0.35, respectively. The electrical conductivity measurements were carried out on compressed pellets using the standard collinear four-probe and two-probe techniques. The measuring circuit consisted of a Keithley 614 digital electrometer and a Hewlett-Packard Model 6212 d.c. power supply. Detailed chemical synthesis and characterization procedures for the copolymer complexes will be reported separately(11). X-ray photoelectron spectroscopy (XPS) measurements for the copolymer complexes were made on a VG Scientific ESCALAB MKII spectrometer with a Mgkα X-ray source (1253.6 eV photons). The powder polymer samples were mounted onto standard sample holder by using double-sided Scotch tape. 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.

RESULTS AND DISCUSSION

The XPS core-level spectra were obtained for the nitrogen, iodine and carbon of the copolymer complexes. Figure 1 shows the I3d5/2 and Nls core-level spectra for two typical copolymer complexes and the N-methylpyrrole homopolymer complex. All Spectra were fitted with Gaussian component peaks. The corresponding core-level spectra for the pyrrole homopolymer complex have been reported earlier(12). The composition and electrical conductivity of the copoloymer complexes are given in Table 1.

Deconvolution of the I3d5/2 core-level spectra gives two major peaks with binding energies (B.E.) of about 618.6 and 620.5 eV. In iodine doped polyacetylene(13,14) and substitued polyacetylene(15), the peaks corresponding to these B.E. have been assigned to the I_3^- and $I_2 + I_3^- = I_5^-$ species, respectively. The component peaks at the high B.E. tail in all the I3d5/2 core-level spectra are as yet to be identified. The high B.E. nature suggests an iodine environment associated with electron withdrawing group, such as iodine covalently bonded to the polymer through ring substitution or addition. However, in iodine-doped polyacetylene, the high B.E. tail for the high resolution I3d5/2 core-level spectra has been resolved into two shake-up satellite structures associated with the I_3^- and I_5^- species(14). We do not favor the formation of covalently bonded iodine to a significant extent since the infrared absorption spectra for all the copolymer and homopolymer complexes reveal the presence of strong absorption band at about 1040 cm^{-1} attributable to C_β-H in-plane vibration(16) of the pyrrole moiety.

Since a substantial amount of iodine in the present complexes can be removed after prolonged pumping in the ultra-high vacuum environment of XPS, all samples have been measured within the shortest time possible in the spectrometer. Similar experimental observations and procedures have been reported for the case of polyacetylene-I_2 complexes(17). For most of the present samples, the iodine concentration at the surface, as measured by XPS, is slightly less than that of the bulk composition determined from chemical analysis. However, in the case of MPY homopolymer (PMY-I_2), the iodine is more concentrated at the surface, with a surface composition which is almost twice that of the bulk. Table 1 and the line shape of the I3d5/2 core-level spectra suggest that both the ratio of I_3^-/I_5^- and the electrical conductivity decrease with increasing MPY content in the copolymer complex. These appear to be consistent with an increase in the difficulty of oxidation, due to steric effect arising from the methyl substituent in MPY. The steric effect would probably cause a substantial amount of the dopant to exist as I_2 molecule, which in turn would interact with I_3^- in an equilibrium process to form the I_5^- species. This may then help to account for the decrease in conductivity with

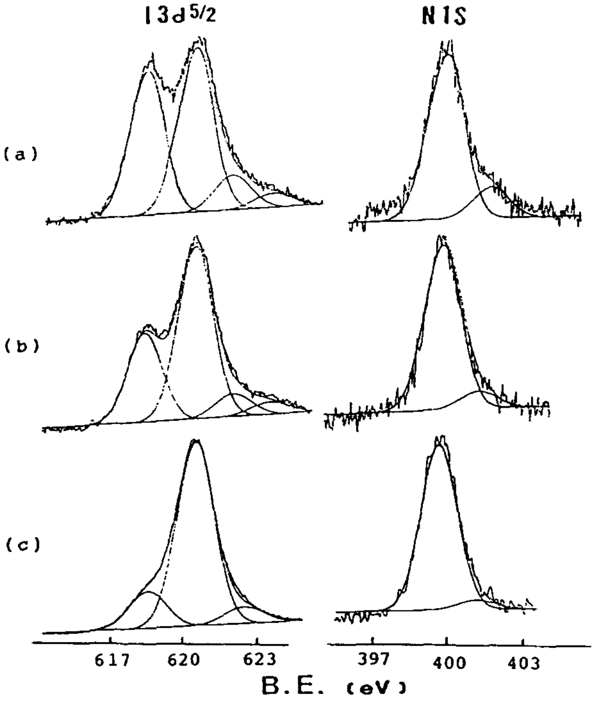

Figure 1 I3d5/2 and XPS core-level spectra for the copolymer and homopolymer complexes: (a) PY mole fraction is 0.76, (b) PY mole fracation is 0.55 and (c) N-methylpyrrole homopolymer.

Table 1 Experimental parameters and results for the various pyrrole - N-methylpyrrole copolymer complexes

Polymer Complex	Mole Fraction PY in Copolymer	Electrical Conductivity σ, S/cm	XPS Surface Stoichiometry N : I	I3d5/2 Spectra I_3^-/I_5^- ratio	N1s Spectra % N^+ Components
PPY-I_2	1.0	20	1 : 0.4	4.0/1.0	36
Copolymer 1	0.84	3.7	1 : 0.5	0.9/1.0	19
Copolymer 2	0.76	2.1	1 : 0.6	0.9/1.0	16
Copolymer 3	0.70	1.1	1 : 0.5	0.8/1.0	14
Copolymer 4	0.55	0.1	1 : 0.7	0.5/1.0	10
PMPY-I_2	0.0	4.2×10^{-5}	1 : 1.5	0.2/1.0	6

decreasing I_3^-/I_5^- ratio. The data in Table 1 readily suggest that the electrical conductivity of the present complexes is related to the proportion of I_3^- species present. This relation, however, should be regarded only as qualitative since the role of absorbed iodine and other iodine species cannot be precisely determined. In other conjugated polymers, such as polythiophene(18) and some monosubstituted polyacetylene(15), the role of polyiodine species in the conductivity of the polymer has been suggested. Furthermore, the electrical conductivity of poly(tert-butylacetylene)- I_3^- complex has been found to increase rapidly upon absorption of free iodine(19).

The N1s core-level spectra for all the present complexes are skewed towards the high B.E. side and can be fitted with at least two Gaussian component peaks. The main component peak at 399.5 eV is attributable to the neutral nitrogen of the PY and MPY. The peak at the higher B.E. can be assigned to nitrogen atoms associated with positive charge(20). The proportion of positively charged nitrogen in each complex is shown in Table 1. A strong correlation between the amount of positively charged nitrogen in the complex and electrical conductivity is observed. At low conductivity level where the amount of positively charge nitrogen is small, the conductivity shows the strongest dependence on the amount of positively charged nitrogen. These observations are probably consistent with the occurrence of interchain charge carrier transport process. They also appear to be consistent with the proposed formation of less conducting polarons at low doping level and highly conducting bi-polarons at high dopant concentration in polypyrrole chains(21). Recently, it has also been shown that all oxidized PPY nitrogen atoms bear a unit positive charge(20). Thus, one may be tempted to speculate that the positive charges of polaron and bi-polaron in PPYs are likely to be localized on the nitrogen atoms.

CONCLUSION

The charge transfer interactions in chemically synthesized PY-MPY copolymer-I_2 complexes have been studied by XPS. The results suggest that the iodine at the surface exists mainly as I_3^- and I_5^- anions. The ratio of I_3^-/I_5^- and the electrical conductivity of the copolymer complexes decrease with increasing MPY content. The electrical conductivity of the complexes can be qualitatively correlated with the proportion of positively charged pyrrolylium nitrogen in each complex.

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