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 I₂ 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(ClO₄)₃ and FeCl₃(6-8). A relatively simple chemical method for the simultaneous polymerization and oxidation of pyrrole by halogens, such as I₂, Br₂ and Cl₂ 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-I₂ 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-I₂ 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 C1s 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 13d5/2 and N1s 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 copolymer complexes are given in Table 1.

Deconvolution of the 13d5/2 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 substituted 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 13d5/2 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 13d5/2 core-level spectra has been resolved into two shake-up satellite structures associated with the I_5 and I_3 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_8H 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 13d5/2 core-level spectra suggest that both the ratio of I_2/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