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Pyrrole Copolymerization and Polymer Derivatization Studied by X-ray Photoelectron Spectroscopy

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Nitro-functionalized polypyrrole films have been deposited on gold surfaces by copolymerization with pyrrole or by derivatization of the polymer. Electrochemical copolymerization of 2- and 4-nitrostyrenes or 2- and 4-nitrobenzaldehydes with pyrrole indicates that lower polymerization yields result from the 2-nitro aromatics due to steric factors. Copolymerization of pyrrole in the presence of 2- or 4-nitrotoluene or isomeric chloronitrotoluenes does not incorporate the nitroaromatics into the polypyrrole matrix, but does affect the oxidation state of the resulting polymer. N-Arylation or N-acylation of preformed polypyrrole films were performed using 2,4-dinitrofluorobenzene, 4-nitrobenzoyl chloride, or 5-nitro-2-furoyl chloride. Electropolymerization of (2,2′-dipyrrolyl)(nitrophenyl)methanes were also performed for comparison purposes. X-ray photoelectron spectroscopic analysis of the derivatized polymers shows that the nitro substituents exhibit varying degrees of stability toward oxidation, reduction, and aging.

INTRODUCTION

The unique characteristics of conducting organic polymers have spurred a range of studies in an effort to develop materials suitable for diverse applications. The conductivity of these materials can be switched between approximately 10 orders of magnitude by applying an appropriate potential, while also displaying electrochromic changes.[1,2] Other desirable characteristics include stability, light weight (with respect to other conducting materials), ease of formation, and often the presence of functional groups to allow derivatization of the polymer. With a view to utilize these properties, research has been undertaken to incorporate organic polymers into switching devices,[3] protective coatings,[4] rechargeable batteries,[2] and chemical sensors.[5]

Many studies have been carried out documenting the effect of reaction conditions on electrochemically-prepared polymers.[6–9] The nature of the synthesized material has been found to depend on solvent, temperature, applied potential, choice of counteranion, and concentration of reactants. In addition to controlling the characteristics of the polymer through these means, it is the goal of many researchers to prepare interfaces with various functionalities in an attempt to produce chemical sensors with greater selectivity. Of particular significance is the conducting polymer polypyrrole which finds increasing utility in the area of chemical sensors due to its capability of ready transformation between oxidized and neutral states. Furthermore, the pyrrole nucleus is amenable to a variety of derivatization reactions. The common procedure to form derivatized polypyrrole consists of polymerizing an appropriately derivatized pyrrole monomer. These polymerizations are usually carried out in the presence of pyrrole since N-substituted pyrroles do not normally produce even coatings by themselves. Ferrocene,[10] alkyl and aromatic groups,[11] phenothiazine,[12] sulfopropane,[13] glucose oxidase,[14] and amino ligands[15] have all been reacted with pyrrole before polymerization in an effort to obtain polymers incorporating electroactive agents,[16] active enzymes, and ionic sites. Functionalization at the 3-position, which requires extra synthetic steps in order to avoid reaction at the 2-position, has been performed in order to produce polymers with unique properties such as solubility,[17] self-doping,[18] ionic sites,[19] and amphiphilicity.[20]

An alternate approach used to form polypyrrole derivatives is through copolymerization with organic compounds. Josowicz et al.[21] have reported coating polypyrrole derivatives on the gate of a suspended-gate field effect transistor and obtained chemical selectivity to adsorption of various chemical species from these films. Copolymerization of pyrrole with either 2-nitrotoluene or 4-nitrotoluene resulted in films that behaved oppositely to toluene vapor; the pyrrole/4-nitrotoluene copolymer underwent a work function decrease upon exposure to toluene vapor while the pyrrole/2-nitrotoluene copolymer experienced a work function increase. The products of the copolymerizations were proposed to be as shown for the para isomer in Figure 1 and the work function changes were attributed to $N-\pi$ interactions between toluene and the nitroarene moiety in the copolymer.

One of the limitations of polymerization involving pyrrole is that copolymerization reagents may not contain a nucleophilic species as this will react with pyrrole radicals and prevent polymer propagation. An alternative scheme for incorporating functionalities into the polypyrrole matrix is to react the preformed polymer with appropriate reagents. As the polymerization occurs through the 2- and 5-positions,

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derivatization could be affected through the amine or by electrophilic substitution at the 3-position. Reaction at the 3-position is typically initiated by nitration and followed by conversion to an amine. Early work by Diaz et al.[22] covalently bound an electroactive derivative, tetrathiafulvalene, to polypyrrole and observed oxidation peaks in cyclic voltammograms from the attached molecule. Schuhmann and co-workers[23-25] have recently published several papers describing the immobilization of glucose oxidase by this route and report that the size-exclusion properties of the polypyrrole matrix allows more reliable glucose measurements of real samples to be made in comparison to other existing electrodes. This group has also bound chloranil and 2,3-dichloro-1,4-naphthoquinone to polypyrrole utilizing the 3-amino group and obtained a polymer which exhibited electrocatalytic properties for the oxidation of NADH.[26]

Fewer attempts have been made to functionalize polypyrrole through its amino site. O'Riordan and Wallace[27] have incorporated a carbodithioate in an effort to produce a modified electrode capable of complexing metal ions in solution, while Rosenthal et al.[28] have attached ferrocene to the surface and noted that this molecule retains its electroactivity. Although the latter work considers the degree of reaction to be a function of reaction temperature and steric factors, neither report has quantitated the reactivity of the amino group.

The current investigation involves the generation of nitrofunctionalized polypyrrole matrices either through copolymerization of pyrrole with nitroarenes or the derivatization of polypyrrole with nitro aromatic compounds and their characterization by XPS. The nitro groups were expected to provide highly polar surfaces capable of undergoing facile reduction to the corresponding amino derivative to permit the covalent binding of large receptors and other biomolecules. Quantitation of the nitro groups is straightforward since the chemical shifts of the two nitrogen types are readily distinguishable (about 400 eV for an amino group and 406 eV for the nitro group). Therefore, this spectroscopic study will facilitate the monitoring of the degree of derivatization and the stability of these surfaces to reaction conditions, such as the application of various electrochemical potentials.

EXPERIMENTAL SECTION

Materials and Reagents. The 9-MHz gold-plated piezoelectric quartz crystals were obtained from International Crystal Manufacturing Co.

Quinoline, pyrrole, furan, 3-methylthiophene, triethylamine, dimethylformamide, thionyl chloride, copper chromite, zinc dust, and all the nitro aromatic compounds used in the current work were purchased from Aldrich (Milwaukee, WI) and used as received with the exception of pyrrole and quinoline which were distilled prior to use. Tetrabutylammonium perchlorate was supplied by Fluka (Switzerland) and was of electrochemical grade. All the solvents utilized were of reagent grade procured from BDH (Toronto, Ontario).

Instrumentation. X-ray photoelectron spectra reported were recorded on a Leybold MAX-200 ESCA spectrometer using an unmonochromated Mg Kα source operated at 12 kV and 25 mA. The shape of the spectra indicated that no compensation for differential surface charging was needed. The binding energy scale was calibrated to 285.0 eV for the main C(1s) (C–C) feature. Spectra were run in both low-resolution (pass energy = 192 eV) and high-resolution (pass energy = 48 eV) modes for the C(1s), N(1s), and O(1s) regions. Each sample was analyzed at a 90° angle relative to the electron detector. An analysis area of 2 × 4 mm^2 was used for rapid data collection (typically 5 min for the C(1s) high-resolution spectrum).

Elemental compositions were calculated from the satellite-subtracted low resolution spectra normalized for constant transmission using the software supplied by the manufacturer.[29] The sensitivity factors employed in these computations, C(1s) = 0.34, N(1s) = 0.54, O(1s) = 0.78, and Cl (2p) = 1.08, were empirically derived for the MAX-200 spectrometer by Leybold.

Electrochemical oxidations and reductions were performed with a polarographic analyzer (Model 473) from ECO Instruments (Cambridge, MA).

Piezoelectric frequency measurements were made on a Universal frequency counter (Hewlett-Packard Model 5334B).

2- and 4-nitrostyrenes were synthesized by the decarboxylation of the corresponding nitrocinnamic acids (Aldrich), following the procedure reported by Wiley and Smith.[30] They were characterized by ^{1}H NMR spectroscopy. 5-Nitrofuroyl chloride was prepared by treatment of 5-nitrofuroic acid (Aldrich) with thionyl chloride under standard conditions.

Synthesis of the Di(2,2′-pyrrolyl)(2- or 4-nitro-1-phenyl)-methane. A solution of pyrrole (5 g) in acetic acid (20 mL) was cooled in an ice bath and treated by dropwise addition with the appropriate nitrobenzaldehyde (0.5 molar equiv) dissolved in a mixture of acetic acid and DMF (9:1, 50 mL). After completion of the addition (20 min), the mixture was stirred for a further 30 min with continued cooling in the ice bath and then at room temperature for an additional 2 h. The mixture was poured into ice–water (250 mL) with stirring and extracted with toluene (100 mL). The extract was filtered through Celite to remove the emulsion formed, and the organic layer was separated, washed with water (2 × 25 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to yield a crude solid product (3 g). A purity check of this material by TLC in toluene–ethyl acetate (9:1) indicated three main spots, the lower two probably due to higher molecular weight impurities (these lower spots were more intense with the 4-nitrophenyl isomer than the 2-nitro compound). Purification of the crude product was carried out by column chromatography with silica gel stationary phase and toluene as the eluent. The pure material was recovered from the first fraction.

The products were characterized by ^{1}H NMR, and mass spectrometry confirmed the products by recording a molecular ion peak for both.

2-Nitro Isomer (I). ^{1}H NMR ($CDCl_3$): δ 8.3–7.2 (m, 4 H, aromatic ring/heterocyclic ring protons), 6.9–6.6 (m, 2 H, pyrrole ring), and 6.4–5.7 (m, 5 H, CH, pyrrole ring).

4-Nitro Isomer (II). ^{1}H NMR ($CDCl_3$): δ 7.9 (d, 2 H), 7.1 (d, 2 H) (aromatic protons), 6.7–6.4 (m, 2 H), 6.0 (q, 2 H), 5.7 (m, 2 H, pyrrole protons), and 5.4 (s, 1 H, CH).

Electropolymerization. All the electrochemical polymerization reactions as well as the oxidation-state modification experiments were performed utilizing a cell configuration described previously,[31] which prevents the electrolyte solution from wetting the electrical contacts of the piezoelectric crystals. Deposition of polypyrrole on the gold-coated crystal surface was effected by the electropolymerization of a solution of pyrrole and tetrabutylammonium perchlorate (0.1 M) in acetonitrile. The solution was deoxygenated prior to the electrodeposition by bubbling nitrogen through for about 15 min. The copolymerization reactions of pyrrole with the appropriate nitroaromatic compounds were carried out under the same conditions as above, employing molar quantities (1 M) of the latter. A duration of 1 min per side at 1.0 V was uniformly used in all these experiments

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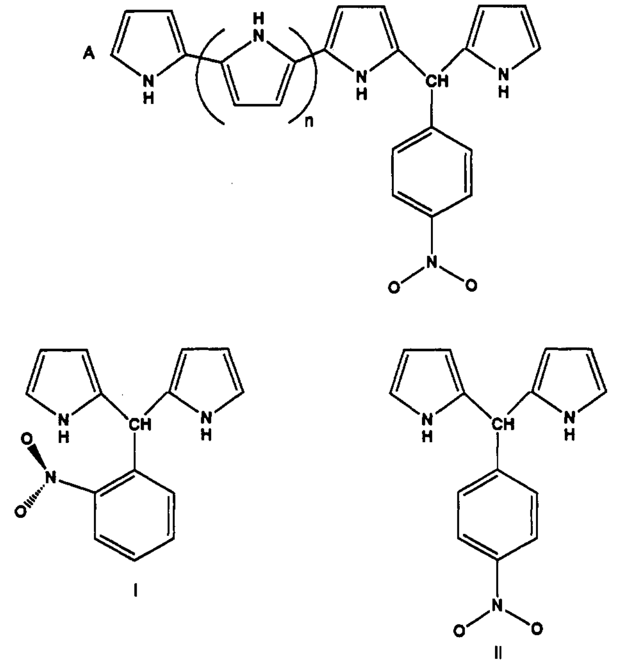

Figure 1. (A) Pyrrole/4-nitrotoluene copolymerization product proposed by Josowicz et al. *o*- (I) and *p*-nitrophenyl (II) monomers used to prepare analogs of A.

and produced a film of approximately 0.5-μm thickness as determined by SEM.

Polymerizations involving the dipyrrolyl(nitrophenyl)methanes (I and II) were carried out in an analogous manner, except that concentrations of 0.7 g per 100 mL were utilized (i.e. the same mass/volume used in the pyrrole polymerizations), and the depositions were performed for 3 min.

Chemical Reduction of the Polypyrrole Films. The polypyrrole-coated crystals were suspended in a solution of acetic acid (30 mL, 1:1 aqueous) and treated with zinc dust in portions (10 × 10 mg) over a period of 2 h. The crystals were then washed thoroughly with distilled water and rinsed with acetone prior to XPS measurements.

N-Acylation/Arylation of the Polypyrrole Films. These derivatization reactions were carried out under conditions similar to those reported for pyrrole itself in literature,[32,33] with slight modifications. The polymer-coated crystals were treated with a solution of the appropriate derivatizing agent (4-nitrobenzoyl chloride, 5-nitro-2-furoyl chloride, or 2,4-dinitrofluorobenzene) in dichloromethane (2% w/v, 30 mL) and triethylamine (2 mL). The mixture was refluxed for 20 h, and the crystals were subjected to extraction with acetonitrile in a Soxhlet apparatus for 5 h.

RESULTS AND DISCUSSION

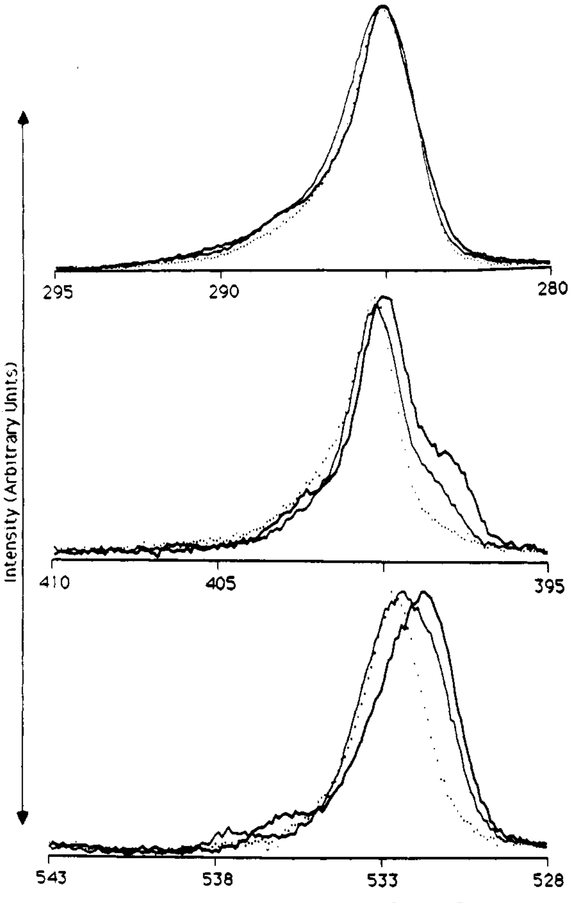

Figure 2. C(1s), N(1s), and O(1s) XPS, respectively, of polypyrrole in as-prepared (dots), neutral (thick line) and oxidized (thin line) states.

Table I. Relative Peak Intensities in C(1s) Region of Polypyrrole (±2%)

	peak positions		
state of polymer	285.0	286.5	288.0
as prepared	72	19	9
reduced at −1.5 V	77	16	7
oxidized at +1.0 V	62	25	13

XPS Analysis of Polypyrrole in Different Oxidation States. The high-resolution XP spectra of polypyrrole in various oxidation states are presented in Figure 2, and the data computed for the C(1s) region are included in Table I. In the N(1s) region, the neutral amino group exhibits a binding energy peak at 400 eV while the positive sites along the backbone in the oxidized polymer appear around 402.5 eV, the latter approximately corresponding to the extent of counteranion inclusion. These assignments are in agreement with those reported earlier.[34,35] This higher binding energy peak has also been assigned to either a quarternary nitrogen[36] or a Doniach–Sunjic type of surface electron excitation.[37] In the neutral form a third peak around 398.5 eV, which is usually accompanied on the higher binding energy side by a peak of similar intensity, is ascribable to a hydrogen bonded network with the pyrrolic nitrogens involved in electron donation and acceptance, as postulated by us earlier.[31]

The C(1s) spectra have been deconvoluted into three peaks around 285.0, 286.5, and 288.0 eV. While the former two have been assigned by earlier workers[34] to the α and β carbons of the pyrrole skeleton, it is conceivable that the resolution of the instrument will not be good enough to completely resolve these two species, if the conclusions drawn from the XPS studies on polythiophene are any indication.[38] In view of the fact that these polymers contain several types of structures which present various environments to functionalities (for example, the quinonoid regions over which the bipolarons are distributed in the oxidized form), peak overlap/broadening occurs making specific assignments difficult. Therefore, it is likely that the 285.0-eV peak includes both types of ring carbons. The second peak near 286.5 eV results from carbons subjected to electron abstraction caused by oxidation, in-

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teraction with counterions present, and from the formation of C–O (by the oxidation of the polymer) or C–Cl bonds (obtained by the electrophilic attack of chlorine initially present as perchlorate). The peak near 288 eV could result from carbonyl moieties (e.g. amides) produced by the oxidation of the polymer and residual acetonitrile, which is known to be retained even under vacuum conditions.[39] Both of the higher binding energy peaks have also been attributed to satellite[38] or shake-up[37] peaks.

In spite of the fact that specific assignments cannot be made to the C(1s) peaks observed, the data in Table I clearly shows that the oxidized form of the polymer exhibits enhancement in the relative intensities of the higher binding energy peaks. Such behavior has been noted previously,[38] although not quantitated. Thus, reduction over a duration of 10 min increases the abundance of the 285.0 eV peak by 5% while oxidation at +1.0 V for 10 min caused a 10% decrease. Furthermore, despite the fact that some changes in the spectra are permanent, such as the covalent attachment of chlorine upon oxidation, shifts between the 285.0-eV peak and the two higher ones are reversible and, therefore, indicative of the oxidation state of the polymer. Our studies also indicate that the polymer shows analogous increases in the higher binding energy peaks upon aging.

Assuming 25% perchlorate counteranion incorporation, the oxygen content of the as-prepared polymer is calculated to be 16%, and a value close to this figure is generally obtained (20 ± 3%). While the broad peaks usually observed in the O(1s) spectra make assignments difficult, the oxidized polymer has peaks at 532.5 ± 0.2 eV, attributable to the perchlorate oxygen, and 534 ± 0.5 eV due to organic oxygenated functionalities. However, although all the perchlorate has been removed consequent to neutralization, as evidenced by the absence of any chlorine in the spectrum, the oxygen content only decreases by about 5%. The more abundant O(1s) component moves down to 531.5 ± 0.2 eV and the other peak to 533 ± 0.5 eV. Some contribution from water in the solvent which can hydrogen bond to the pyrrole units can be expected. In a previous paper,[31] we have observed that the degree of solvation of polypyrrole is a function of its oxidation state. Upon electrochemical reoxidation, the two peaks shift back to the higher energy side by 1 eV, and the total relative oxygen content of the polymer goes back close to its initial value.

Copolymerization with Pyrrole. Two types of nitro aromatics were copolymerized in 10-fold molar excesses with pyrrole. One set comprised 2- and 4-nitrostyrenes and 2- and 4-nitrobenzaldehyde, which have either a reactive double bond or an aldehyde moiety capable of interacting with pyrrole through a nucleophilic addition mechanism. The second series consisted of nitrobenzenes with methyl and/or chloro substituents on the aromatic ring. With the former set, analysis of the N(1s) regions of the XP spectra revealed 10% incorporation of 4-nitrostyrene in the copolymerization product while no reaction was detected with the ortho isomer. In the case of the nitro aldehydes, the polymeric product consisted of equal amounts of the pyrrole and nitrophenyl moieties for the 4-nitro derivative, but only a 15% reaction was observed with the ortho isomer. A steric effect is thus obvious with both 2-nitro derivatives.

The nitro group was absent in the high-resolution N(1s) spectra of polymer films resulting from copolymerizations of pyrrole with 2- and 4-nitrotoluenes, 2-chloro-4-nitrotoluene, or 2,4-dichloronitrobenzene. However, the 60:25:15 distribution of the C(1s) components observed with these reagents indicates that the oxidation state of the resulting polymer is altered. This distribution is quite similar to that obtained from polypyrrole subjected to a +1.0-V potential (see Table I). The as-prepared copolymerization products contain about 30 mol % of perchlorate (computed from Cl(2p) vs N(1s) signal intensities), and the O(1s) region showed two peaks at 532.5 and 534.0 eV. Upon reduction to the neutral form, enhancement of the 285.0 eV C(1s) peak and a shift of the O(1s) peak to 531.5 eV were observed, characteristics exhibited by polypyrrole itself (see earlier discussion). A feature of note is that no covalently bound chlorine is detectable with these copolymerization products, while covalently bound chlorine is present in polypyrrole subjected to the extra oxidation step.

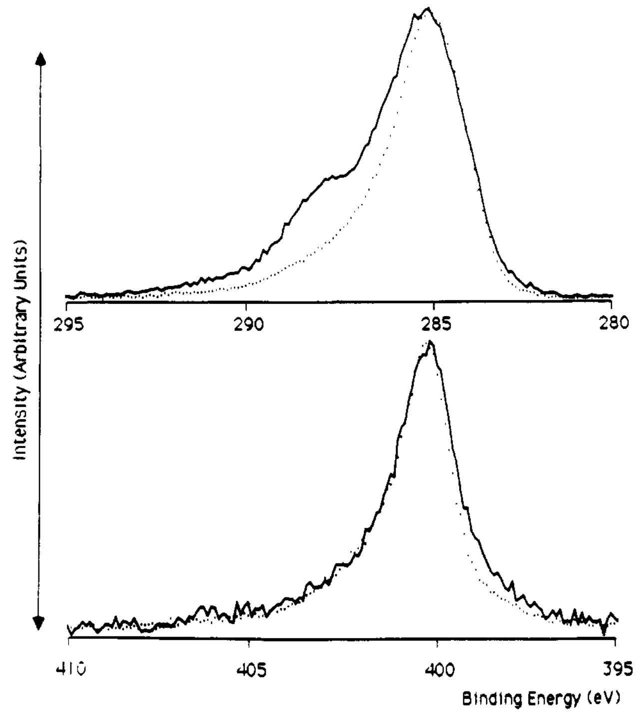

Figure 3. C(1s) and N(1s) XPS of as-prepared polypyrrole (dots) and pyrrole/4-nitrotoluene copolymer (line).

When copolymerization of pyrrole was performed with either 4-nitrophenol or 4-chloro-2-nitrotoluene, no such oxidative effect was observed. The behavior of the latter compound could be due to steric factors. The former perhaps reacts with the pyrrole skeleton through a weak acid–base interaction rather than through the nitro moiety.

As it has been postulated that nitrotoluenes become covalently attached to polypyrrole,[21] copolymerizations with furan and 3-methylthiophene were performed in order to ascertain whether these nitro aromatics become incorporated into non-nitrogenous polymer skeletons through reactions involving the nitro group. However, only 1–3% of nitrogen was observed in the spectra of the products, and this was determined to be from the solvent, acetonitrile, as equal amounts were also found in plain polyfuran and poly(3-methylthiophene) samples. The chemical shifts are also consistent with this interpretation. The low affinity of the nitrotoluenes toward polypyrrole was verified by soaking the polymer in a 4-nitrotoluene/acetonitrile solution overnight and examining the sample with XPS. The absence of a nitro signal indicates that any adsorption that does occur cannot survive ultra-high vacuum conditions. The rapid loss (over 30 min) of nitrotoluenes deposited on polypyrrole-coated 9-MHz gold piezoelectric crystals under atmospheric conditions further supports the low level of interaction between the compounds and polypyrrole.

The formation of polypyrrole with a higher degree of oxidation during the copolymerization of pyrrole with nitro

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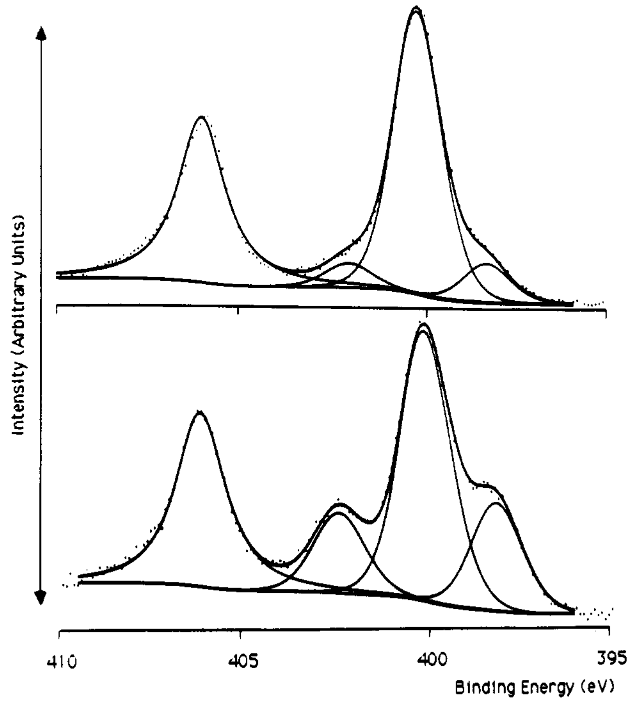

Figure 4. N(1s) spectrum of poly(bis(2,2′-pyrrolyl)(4-nitro-1-phenyl)methane) as-prepared (top) and after reduction at −1.5 V (bottom).

aromatics may be attributed to either an increase in the polarity of the electrochemical reaction medium caused by the polar nitro compounds or an interaction between the nitro group and pyrrole (or its oligomers), in a manner analogous to that proposed for *N*-methylphenothiazine.[40] By complexing with pyrrole, the *N*-methylphenothiazine dication produces a species with a lower ionization potential than free pyrrole, and hence the polymerization is catalyzed. Although the nitrotoluene copolymerization reactions show no evidence of catalysis or incorporation of nitro compounds, a weak complex may form in solution and produce a polarization of pyrrole which will alter the ionization of the monomer or the growing oligomers.

Polymerization of Dipyrrolyl(nitrophenyl)methanes. In order to study the characteristics of a product structurally similar to that proposed by Josowicz et al.,[21] pyrrole was reacted with 2- and 4-nitrobenzaldehydes to furnish the dipyrrolyl(nitrophenyl)methanes (DPMs, see Figure 1). The polymers obtained from these DPMs possess spectral characteristics quite similar to polypyrrole, although they do not appear to achieve as high an oxidation level. The lower oxidation level can be inferred from a much lower level of anion incorporation, the perchlorate contribution being only 5% relative to the pyrrole nitrogens. The nitrogen spectra (Figure 4) clearly show nitro N(1s) binding energy peaks with intensities comprising up to 40% of the total intensity of the N(1s) region. The value appears to be higher than that expected from this structure (two pyrrolylimino moieties per nitro group) and may be the result of an enrichment of the nitro group at the surface, contributions from shake-up peaks overlapping the nitro region or the inclusion of some higher molecular weight products in the polymerization solution. Both isomeric polymers show larger enhancements on the lower binding energy side of the amino peaks (near 398 eV) than seen with polypyrrole. This may be an indication of hydrogen bonding between the oxygen of the nitro groups and the amino protons.

The C(1s) spectra of the two isomeric polymers are comprised of a relatively larger 285.0-eV component (about 78% for the as-prepared polymers) which arises from the additional carbons from the phenyl ring. While the relative intensities of the carbon peaks still change upon oxidation and reduction, the changes are only about half as large as those seen with polypyrrole. Likewise, the O(1s) spectra show a shift to lower binding energies upon reduction, which is reversible with subsequent oxidation, but it is not as pronounced as that observed with polypyrrole. The ortho isomer is particularly insensitive to oxidation and reduction and only shows shifts of a few tenths of an eV. These polymers obviously contain stable nitro oxygens which moderate the extent of changes observed in total oxygen content with oxidation and reduction.

The stability of the nitro group in the above polymers to electrochemical reducing conditions can be monitored through the N(1s) spectra. While it has been reported that reduction of a nitro group at the 3-position of pyrrole to an amino functionality requires a reducing potential of more than −2.0 V[25] (with respect to the Ag/AgCl reference electrode), the application of lower potentials to these polymers does cause some reduction, possibly to a nitroso, which is detected by a decrease in the intensity of the peak at 406 eV. Reductions at −1.5 V decrease the amount of surface nitro groups present, but this effect appears to be limited. A 10-min reduction at this potential lowers the nitro component by about 5% in the N(1s) spectrum but does not result in lowering the nitro component to less than 25% of the total nitrogen content (about 30% less than the initial value) even after several reduction cycles. The reduction also produces large enhancements on both sides of the 400-eV peak, a result of hydrogen bonding.

Lowering the nitro content to 15–20% (50% of the original level) could be observed by the application of a potential of −2.5 V. After 10 min, this higher negative potential causes severe degradation as evidenced by much broader peaks and a loss in resolution of the components. While reduction potentials of −1.5 V or lower increase the 285.0-eV component in the C(1s) spectrum with respect to the 286.5- and 288-eV components for polypyrrole and these DPM polymers, the −2.5-V potential produces carbon species with greater contributions from the higher oxidation states. This suggests that the polymers undergo some type of reaction with reagents in solution.

The effect of aging appears to be as significant as the application of reduction potentials. The nitro component decreases by about 10% of the total N(1s) signal over a period of a few months and then remains essentially stable for up to 1 year. This phenomenon also appears to be limited to eliminating the surface nitro groups to no less than 15% of the N(1s) signal, similar to the −2.5-V reduction. The relative areas of the higher binding energy components in the C(1s) spectra increase with respect to the 285-eV peak by about 10% for the para isomer and 5% for the ortho. To reduce the nitro group to insignificant levels typically requires a chemical reduction with zinc in aqueous acetic acid. The loss of the nitro signal from aging is at least partially ascribable to a restructuring of the polymer surface to reduce the interfacial energy while it is in contact with a nonpolar environment, viz. air. However, upon either oxidation or reduction after standing for several months, an increase of the nitro signal is normally obtained. A typical set of results from a series of oxidation and reduction potentials for the 4-isomer is presented in Table II, but similar behavior is also observed for the ortho case. The nitro signal appears to be stable to initial oxidation but decreases by one-fourth upon reduction and then by about one-third after standing for 1

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Table II. Stability of Surface Nitro Groups for a Poly(*p*-trimer) Sample

conditions	% nitro of N(1s) region (±3%)	fwhm of nitro signal (eV)	fwhm of amino signal (eV)
as prepared	40	1.51	1.53
oxidized at +1.0 V[a]	40	1.62	1.62
reduced at −1.5 V[a]	30	1.74	1.68
two oxidations at +1.0 V[a]	31	1.51	1.76
2 months after oxidations	18	1.54	1.72
12 months after oxidations	16	1.36	1.68
reduced at −1.5 V[a]	23	1.66	1.77
oxidized at +1.0 V[a]	26	1.55	1.81

[a] Oxidations/Reductions performed for 10 min.

year. The partial regeneration of the surface nitro groups seems to be possible upon either oxidation or reduction and is most likely the result of restructuring induced in a polar electrolytic environment.

Reduction and aging both decrease the amount of the nitro signal measured but the values in Table II show a difference in the width of the nitro peaks resulting from the two sets of conditions. The reduction usually causes a broadening of the nitro peak, although it is reversible with oxidation, while aging normally produces only small, random changes in the widths of the peaks. As with the N(1s) spectrum of the neutral polypyrrole, this phenomenon is related to the strong hydrogen-bonding capabilities of the pyrrole units. In the neutral state, many pyrrole units in the DPMs hydrogen bond to the highly electronegative nitro group, producing a new environment for some of the moieties, which is manifested in a broader peak. The aging effect arises predominantly from surface reorientation and is partially reversed when it is subjected to the polarizing conditions of either oxidation or reduction with only minor changes in the oxidation level of the polymer such that hydrogen-bonding capabilities remain about the same. The broadening of the amino signals are independent of the electrochemical conditions although there does appear to be a general increase in fwhm values with time which probably results from greater irreversible oxidation of the polymer.

Derivatization of Polypyrrole through Reactions Involving the Amino Groups. The third method utilized to functionalize polypyrrole was through the reaction of the thin film polymers with 4-nitrobenzoyl chloride, 2,4-dinitrofluorobenzene, and 5-nitro-2-furoyl chloride. The synthetic routes are depicted in Figure 5, and the yields of the reactions under various conditions are presented in Table III. The reaction with 4-nitrobenzoyl chloride proceeds faster at elevated temperatures, and the yields could be higher than those presented, given appropriate conditions. Doubling the reflux time to ca. 40 h with 4-nitrobenzoyl chloride allows the reaction to proceed to 70%. Reaction of neutral polypyrrole with all the reagents was more facile than with the oxidized form due to its greater nucleophilic character. The dicationic bipolaron segments in the polymer must limit the available regions where the S_N2 reactions may occur. Better yields are obtained from polymers which have been reduced with zinc than those which are electrochemically reduced.

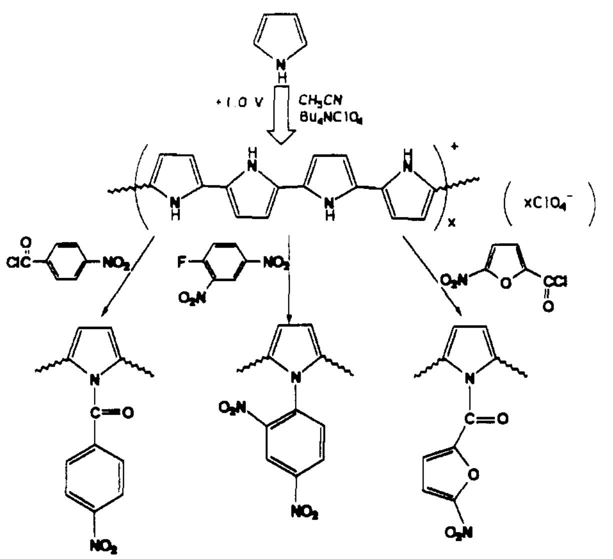

Figure 5. Reaction schemes used for the derivatization of polypyrrole.

Table III. Reaction Yields with Polypyrrole

polymer state	reactant	reaction temp, °C	% completion
neutral	4-nitrobenzoyl chloride	22	43
oxidized	4-nitrobenzoyl chloride	22	24
neutral	4-nitrobenzoyl chloride	40	69
oxidized	4-nitrobenzoyl chloride	40	56
neutral	2,4-dinitrofluorobenzene	40	28
oxidized	2,4-dinitrofluorobenzene	40	24
neutral	5-nitro-2-furoyl chloride	40	40
oxidized	5-nitro-2-furoyl chloride	40	38

Table IV. Stability of Surface Nitro Groups of Polypyrrole Reacted with *p*-Nitrobenzoyl Chloride

conditions	% nitro of N(1s) region (±3%)	fwhm of nitro signal (eV)	fwhm of amino signal (eV)
after reaction of zinc-reduced polypyrrole	33	1.45	1.91
1 min at −1.5 V	19	1.51	1.85
+15 min at −1.5 V	10	1.57	1.79
19 months later	—[a]		1.84

[a] A 4% signal at 406 eV did appear, but upon inspection of C(1s) and O(1s) regions, it was determined to be a shake-up peak.

Of the three reagents studied, the reaction with 4-nitrobenzoyl chloride was the most facile. The resulting functionalized polymer surface appears to be composed of the calculated amount of carbon (72%), but the oxygen content is high (17%) and the nitrogen is low (11%) [assuming a 50% reaction, the calculated values are carbon 71%, oxygen 14% and nitrogen 14%]. The increased oxygen level results from adsorbed water or oxidation of the polymer. The oxygen level is seen to increase to about 25% over several months, and this is probably due to oxidation of the polymer. Similar to the parent polypyrrole, the O(1s) spectrum is deconvoluted into two peaks at 531.7 and 533.0 eV which shift to higher binding energy upon oxidation to 532.4 and 534.0 eV. However, the regular shifts in the C(1s) components are no longer observed with oxidation and reduction. The shifts appear to be more random, and in fact there is a tendency for some reductions to actually decrease the 285-eV component, which indicates a much greater sensitivity to experimental conditions than is observed with the underivatized polymer.

Table IV lists the relative abundance of the nitro group for a typical sample subjected to some reducing potentials and aging. This derivative is more electrochemically-labile than the poly-DPMs, although repeated reductions seem to be limited to decreasing the nitro level to 5%. In this case, though, the reduction does not produce the broader nitro peaks recorded with the poly-DPMs; the nitro peak tended to broaden with age, but no obvious reversal of peak widths was observed upon oxidation of the reduced polymers. Aging of the samples seems to bring about complete elimination of the nitro groups from the surface.

Table V. Stability of Surface Nitro Groups of Polypyrrole Reacted with 5-Nitro-2-furanoyl Chloride

conditions	% nitro of N(1s) region (±3%)	fwhm of nitro signal (eV)	fwhm of amino signal (eV)
after reaction of electrochemically-reduced polypyrrole	30	1.75	2.11
1 min at −1.5 V	5	1.51	1.87
+5 min at −1.5 V			1.73

Table VI. Stability of Surface Nitro Groups of Polypyrrole Reacted with 2,4-Dinitrofluorobenzene

conditions	% nitro of N(1s) region (±3%)	fwhm of nitro signal (eV)	fwhm of amino signal (eV)
after reaction of electrochemically-reduced polypyrrole	31	1.96	1.92
3.75 min at −1.5 V	23	2.18	1.86
+3.75 min at −1.5 V	17	2.30	1.96
+15 min at −1.5 V	17	2.75	1.86

Reaction of oxidized polypyrrole with subsequent Soxhlet washing with acetonitrile yields a product in the neutral state. Therefore, regardless of the state of the starting polypyrrole, the modified polymer requires an additional oxidation step in order to synthesize the cationic polymer backbone. Application of a +1.0-V potential in an acetonitrile solution containing tetrabutylammonium perchlorate has a similar effect to that observed with polypyrrole itself; the level of chlorine increases to near 35% of the nitrogen level (or about 50% of the pyrrolic amines, very similar to the value obtained with polypyrrole) which is approximately evenly divided between perchlorate counteranions and the covalently-incorporated form. The neutral form of the modified polypyrrole was the one predominantly studied, and a major difference in the distribution of the anionic components was observed for this material compared to the other polymers thus far. While the other polymers were able to form hydrogen-bonded networks that were detected by large enhancements on both sides of the amino signal at 400 eV, this is not seen after reaction with nitrobenzoyl chloride. While some combinations of reductions and standing for periods of time did cause large enhancements, the 400-eV peak is generally more prominent in the spectrum (80% of the amino region versus 65% for polypyrrole itself), and this was most likely the result of steric factors from the attached nitrobenzoyl substituent preventing hydrogen bond interactions.

The next most reactive species was 5-nitro-2-furoyl chloride. The values from Table V indicate the much greater sensitivity of the nitro group to reduction; complete elimination of the nitro group is observed within 10 min at −1.5 V. While no conclusions can be drawn from the breadth of the nitro signal since it is eliminated so easily, the fwhm of the amino components decreases somewhat, indicating a more uniform environment within the polymer. However, a major difference with this more labile derivative is observed upon oxidation. While the nitro groups of all the polymers discussed so far are stable to oxidation, 10 min at +1.0 V decreases the nitro signal by about 50% in the spectrum of the 5-nitrofuroyl derivative, and further oxidation is seen to essentially eliminate the nitro signal entirely.

The third reagent utilized was 2,4-dinitrofluorobenzene, and while only about 50% as much reacted with the surface compared to the other two compounds, similar levels of nitro groups are present as this molecule obviously contains two nitro substituents. While some of the reduced yield may be attributed to the different nucleophile involved in this case, part of the reason for this behavior may be from steric hindrance resulting from the additional functionality. Reduction of this surface does decrease the nitro signal, but typically by no more than about two-thirds. This is similar to the stability exhibited by the 4-nitrophenyl derivative (see Table VI). However, an additional artefact of the electrochemical reductions is the broadening of the nitro signal. Subsequent reductions increase the peak width in the example shown from 1.96 to 2.75 eV, and this is probably also due to hydrogen bonding between the nitro groups and amino moieties. This may infuse some stability to the nitro groups and be a factor in their resistance to further reduction. There does not appear to be any correlation to the width of the amino components.

This derivatized product also shows susceptibility to oxidizing potentials. Applying a potential of +1.0 V for 10 min also eliminates about 50% of the nitro signal. These last two derivatizing agents both show a loss of the nitro group upon oxidation, but as nitro groups are normally stable to oxidizing potentials, this loss must be a result of elimination of the whole derivatized segments. Although the two species are covalently attached through different bonds, one an amide and the other a nitrogen–aryl carbon linkage, both molecules are lost at approximately the same rate. Therefore, the lability of certain species bound to polypyrrole through the nitrogen atom must arise from a property within the attached-species, and this characteristic will need to be further examined in future work.

CONCLUSIONS

The current study demonstrates that X-ray photoelectron spectroscopy can serve to distinguish between various oxidation states of polypyrrole. In addition, this technique can provide information on structural features such as inter/intramolecular hydrogen bonding and degree of surface modification, besides enabling one to follow the effects of aging and behavior of unique functionalities under different electrochemical conditions.

The results also indicate that nitro-functionalized polypyrrole surfaces could be generated either by copolymerization of pyrrole with reactive molecules like nitrobenzaldehydes or nitroethenylbenzenes (styrenes) or by derivatization of a preformed polypyrrole with nitro aromatic acid chlorides or halodinitrobenzenes through the neutral imino moieties of the polymer. A strong steric effect is observed with copolymerizations involving *o*-nitro aromatics which retards the functionalization process severely. The stability of the nitro group in *N*-(nitroaroyl)- and *N*-(nitroaryl)polypyrroles has also been shown to be dependent upon the electrochemical conditions. A third route for nitro functionalization consists of the electropolymerization of dipyrrolyl(nitroaryl)methanes, which could be synthesized by treating pyrrole with nitrobenzaldehydes. The polymers thus obtained show a limited degree of reduction under electrochemical conditions as well as aging effects.

An interesting feature in the present study is the production of a polypyrrole with a higher oxidation state when pyrrole is electropolymerized in the presence of nitrotoluenes and nitrohalobenzenes. Subsequent oxidations and reductions follow the trend noted for polypyrrole formed in the absence of any coreagents.

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