Oxidation−Reduction Interactions between Electroactive Polymer Thin Films and Au(III) Ions in Acid Solutions

K. G. Neoh,* T. T. Young, N. T. Looi, and E. T. Kang

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

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Polyaniline (PAN) and polypyrrole (PPY) were coated on pristine and acrylic acid graft copolymerized low-density polyethylene (LDPE) films and exposed to chloroauric acid solutions. The reduction of Au(III) ions in solution was followed using ultraviolet−visible absorption spectroscopy. The structures of the PAN and PPY films after varying periods of immersion in the chloroauric acid solutions were analyzed using ultraviolet−visible absorption spectroscopy and X-ray photoelectron spectroscopy (XPS). In the process of reducing Au(III) to Au(0), the electroactive polymers underwent degradation, evidenced by a gradual decrease in electrical conductivity, ring substitution by chlorine, and a loss of material into solution. The degradation is due to the higher propensity of the polymers when existing in a higher oxidation state to undergo hydrolysis reactions to soluble products.

Introduction

It has been well established that polyaniline, $[-(C_6H_4-NH-C_6H_4-NH-)_y - (C_6H_4-N{=}C_6H_4{=}N-)_{1-y}]_x$, can exist in various intrinsic oxidation states ranging from leucoemeraldine (LM, $y = 1$) to pernigraniline (PNA, $y = 0$).[1] The polymer is usually synthesized in the 50% oxidized state, emeraldine (EM). Protonation of EM in the base form by acids occurs preferentially at the imine units[2,3] whereas the interaction of LM with 1 M acids can result in about 25% of the amine units being protonated in the absence of oxygen.[4] In the case of PNA, protonation is accompanied by a substantial decrease in the intrinsic oxidation state of the polymer and a 50% protonated polymer, similar to protonated EM is obtained.[5,6] This effect has been attributed to hydrolysis reaction occurring in the aqueous acid medium.[6] Polypyrrole (PPY) also exhibits similar protonation/deprotonation behavior and intrinsic oxidation states as polyaniline (PAN). The interaction of PAN and PPY with metal cations rather than H^+ has not been as extensively investigated. A comparative study has been carried out on the structural changes in LM and EM base upon treatment with $Cu(ClO_4)_2$ in acetonitrile.[7] In the case of LM, a nitrogenium ion structure analogous to that arising from the protonation of imine nitrogen in EM by a protonic acid is obtained and the complex is 3 orders of magnitude more conductive than the corresponding EM complex. It has been reported that the treatment of PPY perchlorate with Cu(II)-containing alkaline solution results in the formation of Cu−N bonds.[8] More recently, a study on polyaniline mixed with Li salts and cast from 1-methyl-2-pyrrolidinone solution found that pseudo-protonation of imine nitrogen by Li occurs to give rise to a structure of the type $Li-N^+$.[9]

In our recent work,[10,11] we have shown that PAN and PPY are capable of electroless precipitation of precious metals in elemental form from acid solutions. These experiments were carried out with these polymers either in the form of powders or free-standing films of ~10 μm thickness. The emphasis of our earlier work was to investigate how the rate and extent of the metal reduction are affected by the intrinsic redox states of the polymer and the effective surface area. We have shown that it is possible to obtain Au(0)/N mole ratio of substantially higher than 1 on the surface of the polymeric films. In the present work, we investigated how the electroactive polymer substrate is affected by the gold reduction process. Particular attention was paid to the possible degradation of the polymer since this is an important factor in the potential applications of this technique such as heavy metals recovery from waste streams or the coating of metals on insulating

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substrates. The experiments were carried out with thin films (<0.1 μm) on transparent substrates which permitted the use of ultraviolet (UV)−visible spectroscopy for the analysis of the bulk electronic structure to complement the X-ray photoelectron spectroscopy (XPS) analysis of the surface structure.

Experimental Section

Preparation of Thin Films. Low-density polyethylene (LDPE) films of dimensions 2 cm × 5 cm × 125 μm, obtained from Goodfellow Inc. of Cambridge, UK, were selected as the substrate for the coating of polyaniline (PAN) or polypyrrole (PPY). The coating process was either carried out on pristine LDPE or LDPE after graft copolymerization with acrylic acid (AAc) monomer. For coating on pristine LDPE, the LDPE films were cleaned by Soxhlet extraction with methanol for 6 h before the coating process. The PAN-coated films were prepared by suspending the LDPE films in a beaker containing 0.025 M $(NH_4)_2S_2O_8$ and 0.05 M aniline in 1 M $HClO_4$ for 2 h at 25 °C. After removal from the reaction mixture, the greenish transparent films were rinsed with 0.1 M $HClO_4$ and pumped dry under reduced pressure. In the case of PPY, a reaction mixture of 0.042 M $FeCl_3{\cdot}6H_2O$, 0.02 M pyrrole, and 0.015 M sodium salt of anthraquinone-2-sulfonic acid (AQSA) in deionized water was used. The coating procedure was identical with that of PAN except that deionized water was used to rinse the films. By visual inspection, the PPY coating appeared thicker than the PAN coating and had small clumps of bulk polymerized PPY adhering on the surface. The latter was easily removed using a jet of deionized water. The blackish transparent films were dried in the same manner as described earlier.

The graft copolymerization of LDPE with AAc monomer was carried out by first pretreating the precleaned LDPE film with O_3. The O_3 pretreatment was carried out in a Fisher Model 500 ozone generator with a pure O_2 input flow rate of 100 L h^{-1} and an O_3 production rate of 3 g h^{-1}. The pretreated films were immersed in 10 wt % aqueous AAc monomer solution which was thoroughly degassed and sealed off under a N_2 atmosphere. The thermally induced graft copolymerization was carried at 65 °C for 45 min, after which the film was removed from the viscous solution and washed thoroughly with water and pumped dry. The coating of PAN and PPY on the AAc polymer grafted LDPE films was carried out in a similar manner as that for the pristine films. The purpose of using AAc graft copolymerized LDPE as a substrate is 2-fold: to promote better adhesion between the electroactive polymers and the substrate and to have a source of immobilized anions (COO^- from the AAc graft) on the substrate.

Gold Reduction and Sample Characterization. The PAN and PPY films were immersed in 100 mg dm^{-3} chloroauric acid solution prepared from 1000 mg dm^{-3} of Au(III) in 0.5M HCl (supplied by BDH Chemicals). The Au(III) concentration in solution after various intervals was determined from the absorbance of the $AuCl_4^-$ band at 312 nm using a Shimadzu UV-3101 spectrophotometer. The films after varying periods of immersion in the chloroauric solution were also subjected to analysis by UV−visible absorption spectroscopy and XPS. The XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV). The surface elemental stoichiometries were determined from peak-area ratios, after correcting with experimentally determined sensitivity factors, and are accurate to within ±10%. To compensate for surface charging effects, all binding energies (BE) were referenced to the C(1s) neutral carbon peak at 284.6 eV. The electrical conductivities (σ) of the films were measured using the two-probe technique.

Results and Discussion

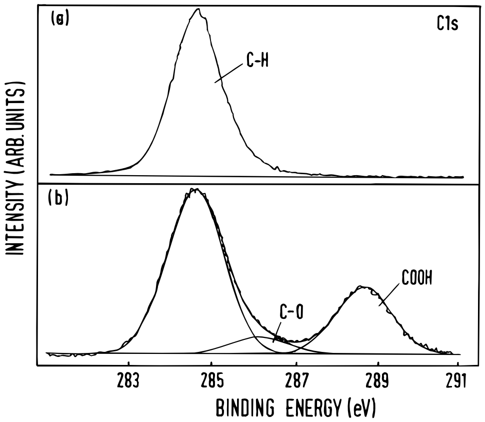

Figure 1. XPS C(1s) core-level spectra of (a) pristine LDPE, and (b) LDPE after graft copolymerization with acrylic acid.

Polyaniline on LDPE. The XPS Cls core-level spectra of the pristine LDPE film and the film after graft copolymerization with AAc are shown in Figure 1, a and b, respectively. The spectrum in Figure 1a shows a dominant peak at 284.6 eV attributable to neutral C which is consistent with the structure expected of LDPE which consists of $-CH_2-$ bonds. In Figure 1b, the spectral deconvolution was carried out by maintaining a constant line width (full width at half-maximum) for all the peak components. This procedure was followed for all the peak synthesis in this work. In Figure 1b, the second prominent peak at 288.8 eV is assigned to the carboxylic (O−*C*=O) groups of the graft-copolymerized AAc.[12] The density of grafting can be defined as the molar ratio of (O−C=O) groups to the $(-CH_2-CH_2-)$ groups of the LDPE substrate and is calculated from the following spectral area ratio:

$$\frac{\mathrm{AAc}}{\mathrm{LDPE}} = \frac{\text{peak area of (O—C=O)}}{[\text{total C(1s) area} - (\text{peak area of (O—C=O)} \times 3]/2}$$

The stoichiometric factors of 3 and 2 are introduced to account for the three carbons in each AAc unit and two carbons per repeating unit of the LDPE substrate, respectively. The molar ratio of the graft-copolymerized AAc unit per repeating unit of LDPE measured at a takeoff angle of 75° (with respect to the substrate surface) is 2.84. There is also a small amount of *C*−O formed in the process as indicated by the peak component at 286.2 eV.

The XPS C(ls) and N(1s) core-level spectra of the PAN-coated pristine LDPE are shown in Figure 2, a and b, respectively. The C(ls) spectrum shows that a small amount of oxidized C groups especially C−O is present. The N(1s) spectrum was deconvoluted using the following peak assignments: −N= component at 398.2 eV, −NH− component at 399.4 eV and N^+ at >400 eV.[3] The protonation level of the PAN as given by N^+/N was calculated to be 30% (Table 1). The N/C ratio calculated from the sensitivity corrected spectral area ratio is 0.09 which is substantially lower than the 1/6 ratio expected of PAN (Table 1). As a direct consequence of the short mean free path of the photoejected electrons in the energy range of interest in XPS, the sampling depth is typically limited to the top 10 nm of the material. Thus, the observation that N/C is lower than 1/6 may indicate

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Table 1. Surface Composition of PAN on Pristine and AAc Graft Copolymerized LDPE before and after Immersion in Chloroauric Acid

sample	immersion time (h)	−N=/N−	−NH/N	N^+/N	C^*/C^a	C−O/C	C=O/C	COO/C	Au/N	N/C
(I) PAN on Pristine LDPE	0	0	0.70	0.30	0.79	0.17	0.04	0	0	0.09
	1	0	0.71	0.29	0.74	0.18	0.05	0.03	0.07	0.10
	165	0	0.73	0.27	0.71	0.20	0.05	0.03	0.10	0.04
(II) PAN on Grafted LDPE	0	0	0.30	0.70	0.67	0.12	0	0.21	0	0.11
	1	0	0.71	0.29	0.65	0.16	0	0.19	0.03	0.10
	165	0	0.71	0.29	0.65	0.17	0	0.18	0.06	0.02

[a] C* refers to C bonded to H, C, or N.

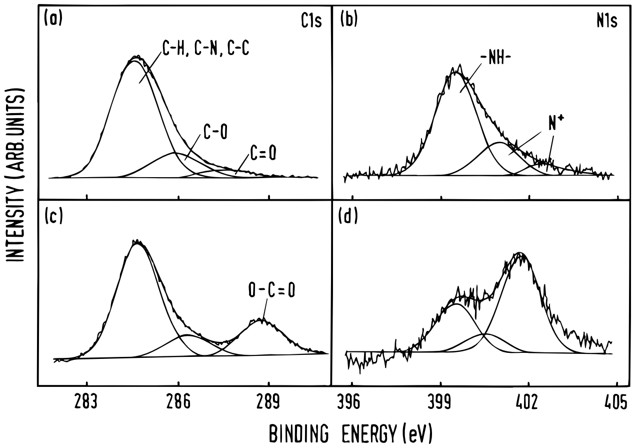

Figure 2. XPS C(1s) and N(1s) core-level spectra of (a and b) PAN coated on pristine LDPE, and (c and d) PAN coated on LDPE graft copolymerized with acrylic acid.

that the PAN layer is sufficiently thin such that the LDPE substrate contributes to the C(1s) signal. Alternatively, any holes present in the thin PAN layer would also allow the LDPE substrate to contribute to the C(1s) signal. With this possibility of substrate contribution the C(1s) signal in mind, the XPS compositions (with the exception of C) are normalized by the amount of N in the electroactive polymer. The C(1s) and N(1s) core-level spectra of PAN on AAc graft copolymerized LDPE are shown in Figure 2, c and d, respectively. It is obvious that with the PAN coating the intensity of the peak attributable to the *C*OO groups of the AAc-grafted LDPE substrate is decreased relative to the main peak at 284.6 eV (compare Figure 2c with Figure 1b). The line shape of the N(1s) spectrum in Figure 2d is significantly different from that in Figure 2b. The high protonation level (70%) achieved indicates that a substantial number of amine units are protonated in addition to the imine units. This phenomenon has been observed in PAN where there is a high concentration of anions.[13] In this case, the ClO_4^- anions from the synthesis medium and the immobilized COO^- anions can contribute to the protonation process.

The decrease in Au(III) concentration in the chloroauric acid solution due to reduction by the PAN-coated LDPE films is shown in Figure 3a. The results shown were obtained with 20 mL of 100 ppm chloroauric solution and 32 cm^2 of immersed film. The higher reduction rate achievable with PAN on the AAc graft copolymerized LDPE is probably due to the thicker PAN coating as indicated by the higher N/C ratio (Table 1) and the higher optical absorbance of the grafted LDPE films with PAN coating (see below). In either case, the rate after 20 h is minimal even though the Au(III) concentration has decreased by less than 50%. The UV−visible absorption spectra of PAN coated on pristine LDPE films after immersion in 0.5 M HCl and 0.5 M HCl containing 100 mg dm^{-3} Au(III) ions for varying periods of time are shown in Figure 4, a and b, respectively. The absorption spectrum of pristine PAN-coated LDPE (before treatment with HCl) is characteristic of that of fully protonated high molecular weight PAN with the absence of a well-defined absorption band at 320 nm (attributable to $\pi-\pi^*$ transition) and the presence of an absorption band at 400 nm (polaron band) and a long absorption tail extending into the infrared region (attributable to intrachain excitations).[14] After prolonged immersion in 0.5 M HCl, the intensity of the absorption spectrum shows a downward shift but its shape essentially remains the same. This change may be due to the exchange of anions, ClO_4^- anions in the as-synthesized PAN film being replaced by Cl^- anions from the HCl solution. This ion exchange process is confirmed by the XPS Cl(2p) core-level spectrum of the sample after 165 h immersion in HCl as shown in Figure 5a. The spectrum shows no peak component at 207 eV which would be indicative of ClO_4^- anions.[15] Instead, the Cl envelope shows the presence of $Cl(2p_{3/2})$ peak components at 197, 198.5, and 200 eV attributed to ionic chloride (Cl^-), chlorine species which have undergone partial charge transfer with the poly-

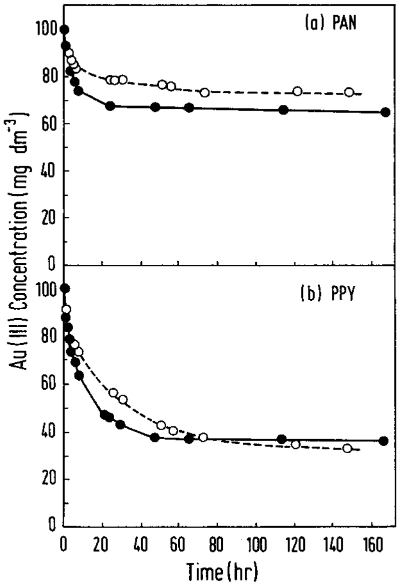

Figure 3. Rate of Au(III) reduction by (a) PAN, and (b) PPY. (○, pristine LDPE substrate; ●, grafted LDPE substrate).

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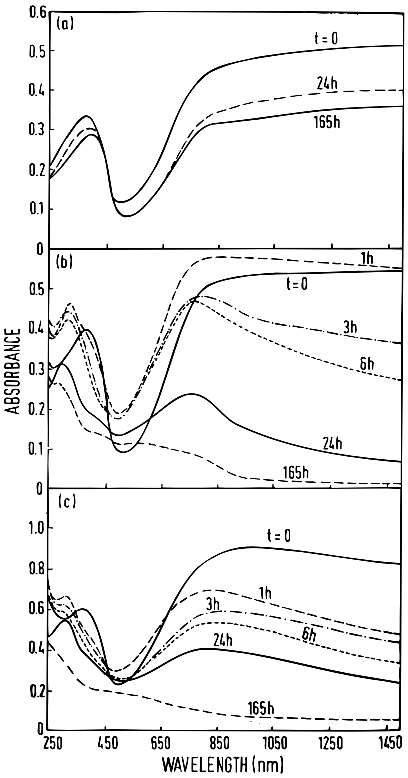

Figure 4. UV−visible absorption spectra of (a) PAN coated on LDPE after immersion in 0.5 M HCl, (b) PAN coated on LDPE after immersion in 0.5 M HCl containing 100 mg dm^{-3} Au(III), and (c) PAN coated on AAc-grafted LDPE film after immersion in 0.5 M HCl containing 100 mg dm^{-3} Au(III). Time on spectrum indicates period of immersion.

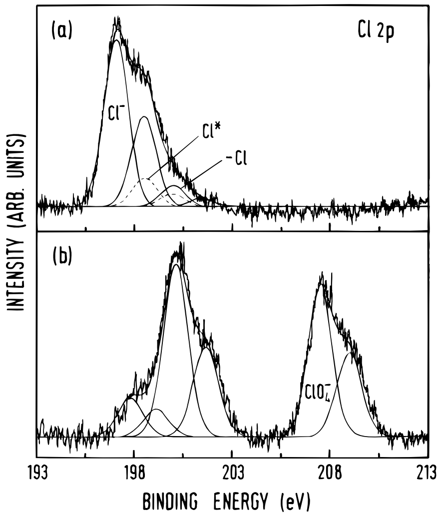

Figure 5. XPS Cl(2p) core-level spectra of PAN coated on LDPE after 165 h immersion in (a) 0.5 M HCl and (b) 0.5 M HCl containing 100 mg dm^{-3} Au(III).

mer (Cl*) and covalent chloride (−Cl), respectively.[16] The covalent chlorine accounts for less than 10% of the total chlorine (−Cl/N = 0.02).

In the presence of Au(III) ions, the UV−visible absorption spectrum obtained after a 3 h immersion period is substantially changed from the original spectrum (Figure 4b). The $\pi-\pi^*$ transition band at 320 nm is now clearly discernible, the 400 nm band has disappeared, and the intraband free carrier excitation has decreased significantly as shown by the decrease in the intensity of the long absorption tail. A new feature, the absorption band at 780 nm, is indicative of interchain charge effects. Earlier studies[14,17] on the electronic structure of PAN have shown that the intensity of the intrachain feature will decrease with the decrease in molecular weight and the level of protonation due to the need for long uninterrrupted chains and the decrease in the number of free carriers. After 24 h in the chloroauric acid solution, the shape of the spectrum is essentially similar to that after 3 h immersion but the intensity has decreased drastically. This suggests a gradual loss in PAN. This is supported by the gradual reduction in the N/C ratio of the films (Table 1) which indicates that there is an increasing contribution of the LDPE substrate to the XPS signal. After 165 h immersion, the thinning of the PAN film is very evident upon visual inspection. The reasons for the loss of PAN are postulated as follows: The pristine PAN coating is in an oxidation state (70% −NH− and 30% N^+) somewhat lower than EM. In 0.5 M HCl solution, all the imine nitrogens can be expected to remain protonated. When Au(III) ions are present, the PAN undergoes oxidation while the Au(III) ions are reduced to elemental gold. It is possible that the PAN is oxidized to either the nigraniline (25% −NH−) or fully oxidized pernigraniline (0% −NH−) state. However, PAN in these oxidation states existing in the acidic medium is prone to degradation by hydrolysis reactions, due to the presence of $-HN^+{=}C_6H_4{=}N^+H-$ groups.[18,19] A major soluble degradation product resulting from the hydrolysis of oxidized PAN has been identified to be *p*-benzoquinone.[20] This process reduces the chain length of the polymer and will continue until the excess oxidized repeat units are removed to restore the EM state. In the EM (or lower) oxidation state, the resonance between the oxidized and reduced repeat units (polaronic form) eliminates the presence of $-HN^+{=}C_6H_4{=}N^+H-$ groups. Concomitant with the hydrolysis reactions, the PAN becomes susceptible to ring substitution by chlorine from the chloroauric acid. Evidence of this process is clearly shown when the Cl(2p) of the PAN film after 165 h immersion in the chloroauric acid solution (Figure 5b) is compared with that of PAN after an equivalent time in HCl (Figure 5a). In Figure 5b, the −Cl component accounts for about 50% of the total chlorine. The anions in this PAN film are mainly the ClO_4^- anions from the PAN synthesis process ($ClO_4^-/N = 0.24$) rather than Cl^- from the chloroauric acid solution. The X-ray satellite lines from the ClO_4^- peak in the 207 eV region as well as a small amount of Cl* contribute to the envelope in the 198 eV region. The propensity of PAN of higher oxidation state than EM to react with HCl to give ring chlorination has also been mentioned in an earlier publication.[5]

The presence of elemental Au on the polymer surface is confirmed by the XPS analysis of the substrate. The Au(4f) core-level spectra of the PAN-coated LDPE after

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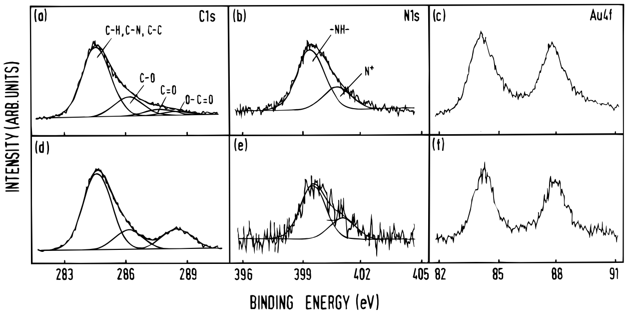

Figure 6. XPS C(1s), N(1s), and Au(4f) core-level spectra of (a, b, c) PAN coated on LDPE after 165 h immersion in chloroauric solution, and (d, e, f) PAN coated on grafted LDPE after 165 h immersion in chloroauric solution.

immersion in the Au(III) solution reveal the presence of a predominant single Au species with an Au(4f$_{7/2}$) BE at about 83.8 eV, characteristic of Au(0).[21] The C(1s), N(1s), and Au(4f) core-level spectra of the PAN-coated LDPE after 165 h are shown in Figure 6a−c, respectively. Comparing Figures 6a,b with Figure 2a,b, it can be seen that the chemical states of the C and N species are not drastically different. The proportions of the different C and N species are given in Table 1. Essentially, as the time of immersion in the chloroauric acid increases, there is a slight increase in the −NH− content and a corresponding decrease in N$^+$. All the −N= units remain protonated. There is also a slight increase in the proportion of oxidized C species. Thus, even though hydrolysis reactions have reduced the amount of PAN on the substrate, the distribution of N species in the remaining PAN is not drastically different from that in the pristine PAN. Therefore, when thick (free standing, ∼10 μm thickness) PAN films were used in our earlier work,[10] the reduction of Au(III) to Au(0) can be sustained and a significantly higher Au(0)/N ratio can be obtained.

The hydrolysis reactions reduces the chain length of the PAN and hence the extent of effective conjugation. This is evident from the UV−visible absorption spectra within the first few hours of treatment (Figure 4b). This effect is also manifested in the rapid decrease in the electrical conductivity of the film (Figure 7). Within the first 3 h of treatment, the electrical conductivity has decreased by over 2 orders of magnitude, consistent with the change in the electronic structure which results in the diminishing of intrachain excitations and the predominance of interchain effects. After 90 h in the chloroauric acid solution, the σ has decreased by more than 6 orders of magnitude. In contrast, after immersion in 0.5 M HCl for 165 h, σ decreases by only an order of magnitude.

The use of AAc graft copolymerized LDPE substrate gives rise to a thicker PAN coating than that achieved with pristine LDPE, as can be seen from the higher absorbance of the coated film before immersion in the gold solution (compare $t = 0$ curves in Figure 4, b and c). The absorption spectrum of the PAN coated on the grafted LDPE after 1 h immersion in the chloroauric acid solution shows a higher extent of change than that observed with PAN coated on pristine LDPE (Figure 4c). The XPS results show that the distribution of N species

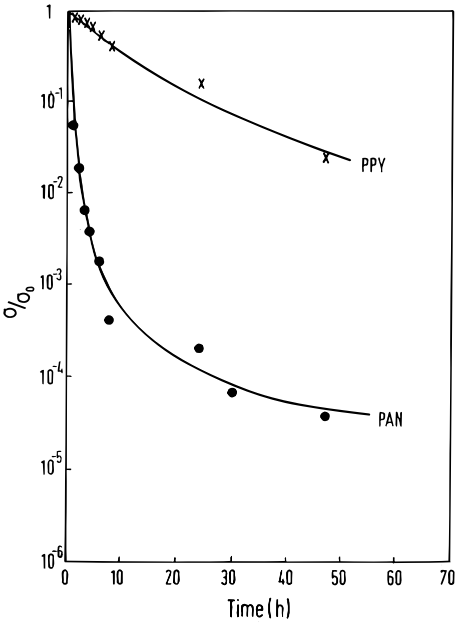

Figure 7. Normalized electrical conductivity of PAN and PPY coated on LDPE after various periods of immersion in chloroauric acid solution. (σ_0 is the electrical conductivity before immersion in the chloroauric acid solution.)

in the former is now identical with that of the latter; i.e., the high N$^+$/N ratio due to the protonation of −NH− units is no longer observed. The trends observed with the PAN coated on grafted LDPE are similar to those discussed above for the PAN coated on pristine LDPE. The XPS results of the samples after 1 and 165 h immersion are again remarkably similar (Table 1). Although the Au(III) concentration in solution has decreased to a lower level (Figure 3a) with the grafted substrate, the Au/N on the substrate surface (Table 1) shows a smaller value, probably due to the thicker PAN coating.

Polypyrrole on LDPE. The decrease in Au(III) concentration in the chloroauric acid solution due to reduction by PPY-coated on pristine and AAc-grafted LDPE films is shown in Figure 3b. A higher initial rate of reduction is achieved with PPY coated on AAc graft copolymerized LDPE but the Au(III) concentration eventually reaches an asymptotic value that is similar for both types of films. The PPY films exhibit higher optical absorbance than the PAN films. However, the N/C ratio of the PPY-coated substrates after correction for the C in the AQSA dopant (using the $-SO_3^-$/N ratio, Table 2) is still less than the value expected of PPY (0.25). The C(1s) and N(1s) spectra of pristine PPY coated on LDPE are given in Figure 8a,b. The N(1s) spectrum in Figure 8b shows a small peak component at 397.7 eV attributable to the −N= units, while the dominant peak at 399.7 eV is attributed to the −NH− units.[22,23] The high-BE tail is assigned to the N$^+$ species. The presence of a small amount of −N= units is probably due to a small extent of deprotonation of the film by water during the rinsing process after the coating of the PPY film on the substrate. In the pristine film, the anions are mostly AQSA anions, and the

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Table 2. Surface Composition of PPY on Pristine and AAc Graft Copolymerized LDPE before and after Immersion in Chloroauric Acid

sample	immersion time (h)	$-N{=}/N$	$-NH-/N$	N^+/N	C^*/C^a	$C-O/C$	$C{=}O/C$	COO/C	Au/N	$(N/C)^b$	$-SO_3^-/N$	Cl^-/N	Cl/N
(I) PPY on pristine LDPE	0	0.05	0.69	0.26	0.76	0.16	0.08	0	0	0.17	0.23	0	0
	1	0	0.71	0.29	0.70	0.20	0.10	0	0.10	0.15	0.16	0.13	0.27
	165	0	0.79	0.21	0.66	0.22	0.12	0	0.12	0.09	0.08	0.04	0.45
(II) PPY on grafted LDPE	0	0	0.68	0.32	0.73	0.18	0.09	0	0	0.19	0.26	0	0
	1	0	0.68	0.32	0.66	0.21	0.09	0.04	0.05	0.17	0.15	0.11	0.20
	165	0	0.78	0.22	0.57	0.29	0.08	0.06	0.07	0.10	0.06	0.07	0.33

[a] C* refers to C bonded to H, C, or N. [b] (N/C)** refers to N/C after correction for C in the AQSA anions.

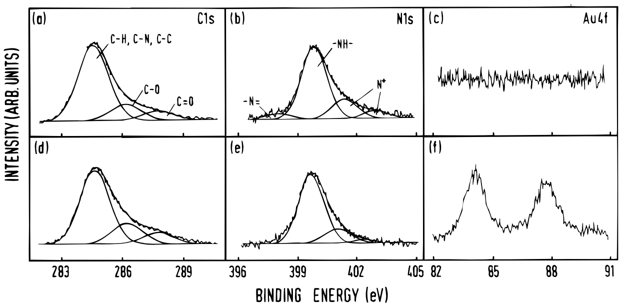

Figure 8. XPS C(1s), N(1s), and Au(4f) core-level spectra of (a, b, c) pristine PPY coated on LDPE, and (c, d, e) PPY coated on LDPE after 165 h immersion in chloroauric acid solution.

$-SO_3^-/N$ ratio calculated from the areas of the N(1s) envelope and the $-SO_3^-$ peak component at 167 eV[24] in the S(2p) core-level spectrum is close to the N^+/N ratio (Table 2). The Cl(2p) core-level spectrum shows no substantial amounts of either Cl^- anions (peak component at ~197 eV[3]) or covalently bonded Cl (peak component at ~200 eV[3]).

The UV−visible absorption spectra of the PPY-coated LDPE films after immersion in 0.5 M HCl and 0.5 M HCl containing 100 mg dm^{-3} Au(III) ions for varying periods of time are shown in Figure 9, a and b, respectively. The absorption spectrum of the pristine film is characterized by absorption bands at 330 and 470 nm and a high-intensity tail extending into the near-IR region. The first absorption band is attributed to the AQSA dopant while the second absorption band and the absorption tail are characteristics of doped and highly conductive PPY.[25,26] After 165 h in 0.5 M HCl, the 330 nm absorption band has decreased in intensity due to the replacement of AQSA anions by Cl^- anions. This is confirmed by the XPS results which show that the $-SO_3^-/N$ ratio has dropped from 0.23 to 0.18 while the Cl^-/N has increased from 0 to 0.09. The absorption band at 470 nm and the high-intensity tail remain essentially unchanged, suggesting that the PPY has not undergone significant degradation. In contrast, in the presence of 100 mg dm^{-3} of Au(III) ions, the 470 nm absorption band has almost disappeared after 1 h immersion. Prolonging the period of immersion shifts the absorption curve downward. By 165 h, the absorption spectrum is rather featureless. The XPS, C(1s), N(1s), and Au(4f) core-level spectra of the film after 165 h immersion are shown in Figure 8d−f. The C(1s) core-level spectrum is more skewed toward the high-BE side suggesting the formation of oxidation products. The increase in C−O, C=O species is observed even for a 1 h immersion period (Table 2). The oxidation state of the PPY as indicated by the proportion of −NH− species and the protonation level as indicated by the N^+/N ratio have obviously decreased. The presence of Au(0) is again confirmed by the $Au(4f_{7/2})$ peak component at a BE of 83.8 eV. The process of gold reduction by PPY is akin to that discussed earlier for PAN. The reduction of Au(III) ions results in the PPY attaining an oxidation state higher than 25% (i.e., less than 75% −NH− units).[27] The protonation of the PPY is ensured in the acid medium but a level beyond 30% was not indicated by the XPS results. Hydrolysis reactions, similar to those proposed for PAN,[20] must have limited the extent of protonation and caused the dissolution of some PPY. A possible degradation product is soluble maleimide which has been detected in the degradation of PPY in oxidizing $FeCl_3$ solution.[28]

An examination of the Cl(2p) core-level spectra of the films after immersion in chloroauric acid reveals that the Cl^-/N ratio first increases as Cl^- anions replace the AQSA anions in the films and then decreases as the PPY degrades. On the other hand, the −Cl/N (covalently bonded Cl/N as given by the difference between the total Cl/N and Cl^-/N ratios in Table 2) increases. The −Cl/N ratio of 0.41 is much higher than that obtained after immersion in 0.5 M HCl in the absence of Au(III) for a similar period of time (−Cl/N = 0.02). This shows that the PPY ring has become more susceptible to substitution by Cl from the chloroauric acid, similar to the process observed with PAN. The N^+/N ratio after 165 h immersion is substantially higher than the $(Cl^- + -SO_3^-)/N$ ratio. Thus the "excess N^+" are not associated with the Cl or AQSA anions but probably resulted from the replacement of the anions by oxygen-containing species.[29] A comparison of the PAN and PPY results (Tables 1 and 2, respectively) shows that PPY is more susceptible to reactions with O_2. From the above results, it can be expected that the σ of PPY would also decrease as the period of immersion increases. This is indeed the case as can be seen from Figure 7. However, it may be surprising that the decrease in σ of PPY is not as drastic as that observed with PAN. It has also been observed that the σ of PPY does not change as much as that of PAN when these polymers are converted from the doped state to the undoped state or vice versa. The resulting change in σ of PPY[22,30] is

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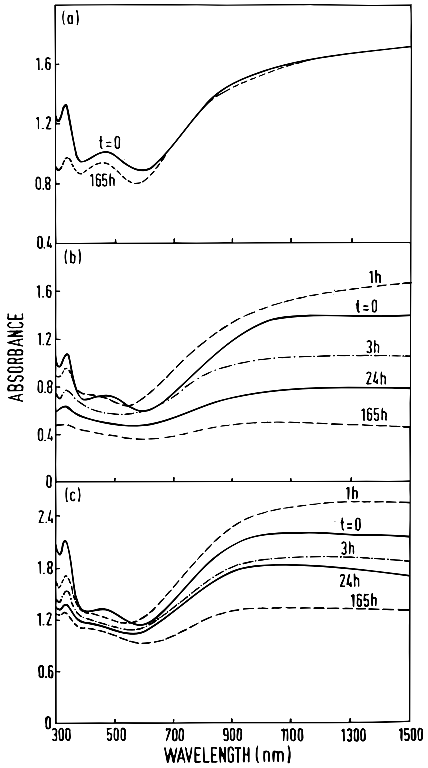

Figure 9. UV−visible absorption spectra of (a) PPY coated on LDPE after immersion in 0.5 M HCl, (b) PPY coated on LDPE after immersion in 0.5 M HCl containing 100 mg dm^{-3} Au(III), and (c) PPY coated on AAc graft copolymerized LDPE after immersion in 0.5 M HCl containing 100 mg dm^{-3} Au(III). Time on spectrum indicates period of immersion.

of the order of 10^3−10^4 whereas PAN undergoes a 10^{10} change in σ.

The use of AAc graft copolymerized LDPE as a substrate instead of pristine LDPE results in a thicker PPY, as evident from the higher intensity of the UV−visible absorption spectrum in Figure 9c. The C(1s) core-level spectrum of PPY coated on the AAc graft copolymerized LDPE is fairly similar to Figure 8a and shows no discernible *C*OO peak component (Table 2), unlike the corresponding PAN coating (Table 1). The N^+ species are mainly balanced by the AQSA anions. The rapid ion exchange of Cl^- and AQSA anions and the ring substitution by Cl are also evident within the first hour of immersion in chloroauric acid (Table 2). In addition, COO groups are now evident in the C(1s) spectrum. By analogy with the results obtained from PPY coated on pristine LDPE, COO groups are not expected to result from the PPY backbone. Hence, the COO groups are probably those from the grafted AAc polymer. Both the UV−visible absorption spectra in Figure 9c (showing a decrease in absorbance) and the XPS results in Table 2 (decrease in N/C) indicate that the PPY coating on the AAc graft copolymerized LDPE undergoes a similar thinning process as the PPY coating on pristine LDPE. The XPS results also show an increase in the proportion of oxidized C species arising from the oxidation of the PPY rings and the increasing degree of exposure of the AAc polymer graft. Thus the mechanisms of PPY degradation are similar in the two cases.

Conclusion

In the present work, the interactions between thin films of polyaniline and polypyrrole with Au(III) ions in acidic solution have been elucidated through UV−visible absorption spectroscopy and XPS. The reduction of Au(III) to Au(0) results in the electroactive polymers attaining a higher oxidation state which undergo degradation by hydrolysis reactions. As the products of degradation are soluble, this process results in a gradual thinning of the electroactive polymer films. In the process of reducing the Au(III) ions, the polyaniline and polypyrrole rings also become more susceptible to substitution reactions with chlorine. In the case of polyaniline, even after the remaining material has undergone a substantial degree of degradation, the distribution of N species remains similar to that of the pristine polymer. For polypyrrole, the rings are more prone to oxidation resulting in oxidized C species and a decrease in protonation level. The use of acrylic acid graft copolymerized LDPE as substrate instead of pristine LDPE results in thicker coatings of electroactive polymer films and the availability of immobilized COO^- anions. However, the degradation processes for polyaniline and polypyrrole coated on either pristine LDPE or acrylic acid graft copolymerized LDPE appear similar.

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