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Modified Electrodes with Polymers Based on Aniline and Thiophene: Characterization and Possible Use as a Sensor

M. A. Pardo[1], C. Navarrete[2], A. Ramírez[1], N. P. Barrera[2], S. Shultz[3], M. A. del Valle[1], F. R. Díaz[4,]*

[1] Laboratorio de Electroquímica de Polímeros, LEP, Pontificia Universidad Católica de Chile, Av. V. Mackenna 4860, 7820436 Macul, Santiago, Chile.
[2] Laboratorio de Estructura de Proteínas de Membrana y Señalización, Departamento de Fisiología, Facultad de Ciencias Biológicas, Pontificia Universidad Católica de Chile, Av. L. B. O'Higgins 340, RM, Santiago, Chile.
[3] Department of Chemistry and Biochemistry, University of NotreDame, 140D McCourtney Hall, Notre Dame, IN 46556, USA
[4] Departamento de Química y Biología, Facultad de Ciencias Naturales, Universidad de Atacama, Copayapu 485, Copiapó, Chile.
[*]E-mail: mdvalle@uc.cl

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A systematic steel and platinum electrodes were modified *via* drop-coating with polymers based on aniline and thiophene or aniline and 3-alkylthiophene previously synthesized and reported by us. Having in mind the possible applications of these materials, electrochemical (cyclic voltammetry, CV, in different electrolytic solutions), morphological and RAMAN characterization of the electrode|polymer systems was accomplished, using platinum or stainless steel discs of 0.07 cm^2 geometric area as electrode substrates and poly[4-(2-thiophene)aniline], PTANI, poly [4-(3-methyl-2-thiophene)-aniline], PTANIr1, and poly [4-(3-hexyl-2-thiophene)-aniline], PTANIr2 polymer coatings. A suspension of the respective polymer in tetrahydrofuran was filtered and drops of the soluble fraction of each polymer was deposited on the electrode surface, allowing the solvent to evaporate between each drop, until the whole electrode surface was coated. *n*- and *p*-doping study was accomplished by CV in a $1.0 \cdot 10^{-3}$ mol L^{-1} NaF solution, using 0.05 mol L^{-1} $LiClO_4$ as supporting electrolyte. Thus, it was revealed that only the Pt|PTANI electrode displayed *p*-doping process, so it may be tried for anions removal or as an analytical sensor for this kind of species. Instead, PTANIr1 and PTANIr2 could be suggested as fluorescence sensors, while the absence of *p*- and *n*-doping processes of the PTANIr2 system on steel and platinum electrodes, makes it a good candidate for metallic corrosion inhibition, since it is highly stable towards potential changes without damaging the deposited polymeric film.

Keywords: modified electrodes; polyaniline; polythiophene; poly[4-(2-thiophen)-aniline]; poly[4-(3-metyl-2-tiophen)-aniline]; poly[4-(3-hexyl-2-tiophen)-aniline].

1. INTRODUCTION

Conducting polymers (CPs) are synthetic materials that conduct electricity such as those belonging to the polyarenes group, *e.g.* polyacetylene, and to polyaromatics: such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), etc. and derivatives thereof. PANI is one of the oldest known polymers; it was first synthesized by Letheby in 1862 by anodic oxidation of aniline in sulfuric acid,[1] and thanks to its electronic and optical properties is one of the most widely studied CPs.[2,3]

Conductive polymers are formed by a skeleton of conjugated π electrons that confer unusual electrochemical properties such as high current conductivity, low ionization potential and high electron affinity, giving the name of "synthetic metals", since due to the high overlapping degree between molecular orbitals of the polymer, the free movement of electrons through their molecular structure occurs. Furthermore, as result of their crystal packing, they also possess the ability to conduct electricity perpendicularly to the chains. This process takes place especially if they are in the doped state, presenting intra- and inter-molecular interactions.[4] Thus, CPs reach conductivities between 10^{-4} to 10^{-2} S cm^{-1}, due to the large number of states that can arise in the doped structure.[5] Usually, they have very low or no conductivity in its neutral state (undoped), the electronic conductivity being the result of charge transporters formation owing to doping with small ions, generated by the partial oxidation (*p*-doping) or reduction (*n*-doping) of the conjugate structure.[6,7]

Apart from the conductivity change, doping provides other interesting phenomena that can be used in various applications. The change in the electronic band structure is accompanied by the change of optical properties in the UV-Vis and IR regions. This is useful for the development of electro chromic devices and optical sensors.[8,9] For instance, electroluminescence of some CPs is employed in the fabrication of organic light emitting diodes, OLEDs, and photoluminescence can be used in fluorescence sensors.[10] Furthermore, ions incorporation to compensate charges during doping, allows them to be used in ion exchange membranes or ionselective sensors.[6,11]

Thorough characterization of these materials is therefore required, to decide its usefulness, as their various applications are *a priori* unpredictable. In this work, characterization of new polymers containing thiophene and aniline in their structure, whose synthesis has been recently reported,[12] is described. The research focuses on polymer modification of substrates such as platinum or steel, since it is on such kind of surfaces that these materials for use in the various abovementioned applications must be deposited.

2. EXPERIMENTAL

All reagents used in this work were used as received, except for inorganic salts that were previously oven dried at 120 °C.

Three polymers based on aniline and thiophene were employed to modify the surface of the working electrodes (AISI 316 stainless steel (SS) or platinum (Pt) discs of 0.07 cm^2 geometric area) namely, poly[4-(2-thiophene)-aniline], PTANI; poly[4-(3-methyl-2-thiophene)aniline], PTANIr1; and poly [4-(3-hexyl-2-thiophene)-aniline], PTANIr2, whose syntheses and classical characterizations have been described elsewhere.[12] Their structural formulas are depicted in Fig. 1.

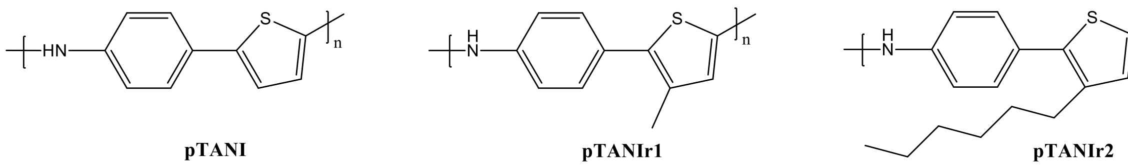

Figure 1. Studied polymers structural formulas.

A suspension of *ca*. 10 mg of the respective polymer in 1.0 mL of tetrahydrofuran was filtered through a 60 µm pore size filter and the soluble fraction reserved. Four 5 µL drops of the soluble fraction of each polymer was deposited on the electrode surface, allowing the solvent to evaporate between each drop, until the whole electrode surface was coated.

p- or *n*-doping were respectively achieved by partially oxidizing or reducing the polymer.

The voltammetric characterization was performed on a CH Instruments Model CHI750D potentiostat. All analyzes were conducted using an anchor-type three electrode, three compartment cell. An Ag|AgCl, KCl electrode was the reference electrode, while a platinum coil of large surface area was the counter electrode and the abovementioned discs the working electrode. As supporting electrolyte a pH 7.00 phosphate buffer (PBS), with a phosphate concentration of 0.05 mol L^{-1}, was used. Other solutions (NaF, NaCl, NaBr, KI, $NaNO_3$ and $NaNO_2$) were prepared in concentration $1.0 \cdot 10^{-3}$ mol L^{-1} in the same PBS solution. *n*- and *p*-doping study was accomplished in a $1.0 \cdot 10^{-3}$ mol L^{-1} NaF solution, using 0.05 mol L^{-1} $LiClO_4$ as supporting electrolyte.

3. RESULTS AND DISCUSSION

Firstly, the electrochemical behavior of modified electrodes was determined, in order to detect likely *p*- and/or *n*-doping processes of the resulting electrode|polymer systems.

Figure 2 shows the voltammetric response of platinum and steel modified electrodes in $1.0 \cdot 10^{-3}$ mol L^{-1} NaF solution, wherein it is clearly seen that all oxidation and reduction signals from steel and platinum are hindered in the same medium, corroborating that there was a complete modification of the evaluated surfaces.[13,14]

Moreover, by scanning the potential in the cathodic direction, to see if reduction processes occur, it was observed that none of the polymers exhibited *n*-doping under the evaluated conditions (Figs. 2a and 2b). However, scanning in the opposite direction, analyzing the possibility of oxidation, only the SS|PTANI system evidenced a small signal ascribed to *p*-doping at 0.74 V, the same as Pt|PTANI.

Carrying on with the study of *p*-doping of the three tested polymers, the response of modified electrodes in solutions of different halides, in order to determine whether the size of the anion has an effect on the oxidation process of the electrodes, was analyzed. The responses are exhibited in Fig. 3 where it is appreciated that in the case of platinum modified electrodes no significant response towards redox processes for any of the evaluated polymers are seen because, independently of the supporting electrolyte anion, no *p*-doping process would exist.

As for SS electrodes, both PTANI (Fig. 3d) and PTANIr1 (Fig. 3e) evidenced the response of the electrode holder, indicating that only a partial coating exists, due to the presence of phosphate in the SS|polymer interface, as detachment of the polymer occurs during the first voltammetric cycle when the characteristic protective oxide layer is formed.[13,15] Instead, the PTANIr2 film (Fig. 3f) remains coating the whole electrode surface and, as in the case of platinum, not current signals ascribable to polymer oxidation, with the resulting anion transport by the *p*-doping process, was observed.

These results are consistent with those reported in the literature concerning that aniline-based polymers have been used as steel anticorrosion agents, preventing oxidation processes occurring at the electrode surface of unmodified electrodes. [13, 15-18] As might be seen the three tested polymers would allow total Pt coating in a stable way, as happens with PTANIr2 on SS. Consequently, they may be projected as corrosion protection agents.

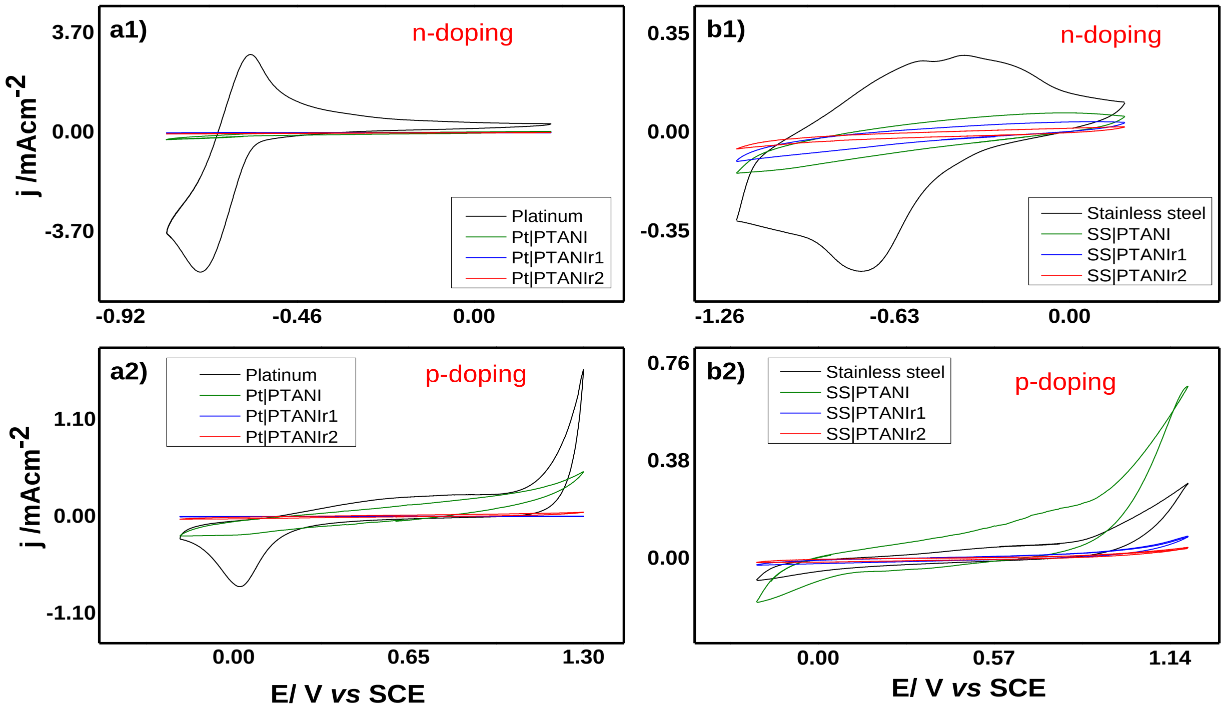

Figure 2. Voltammetric responses of platinum (Pt, serie a) and steel (SS, serie b) polymer modified electrodes in $1.0\cdot10^{-3}$ mol L^{-1} NaF + 0.05 mol L^{-1} $LiClO_4$ solution. ν = 0.1 V s^{-1}.

It is noteworthy that in all voltammograms the response corresponding to the *n* cycle has been displayed, as successive voltammetric scans within the suitable potential window were conducted. It was shown that at the second cycle a stable profile is already reached, which is maintained up to at least 100 successive cycles, except in the abovementioned cases where the film detaches. Thus, when the profile stabilizes, the voltammetric scan is maintained for 100 cycles or more, which verifies the stability of these modified electrodes and warrants its usefulness in the proposed application.

Modified electrodes surface was firstly characterized by AFM. In Fig. 4 images of each of the modified surfaces prior to any electrochemical process are exhibited. The images clearly show that the substrate on which the sample is deposited significantly influences the morphology of the resulting film, showing significant differences between the deposits on steel and on platinum for the same polymer, *i.e*. it possesses morphology "memory" of the bulk electrode.

Similarly, as expected, the presence of the aliphatic chain provokes morphological changes of the evaluated films. In the case of SS (series), it was observed that a length increase of the aliphatic chain in the polymer backbone generated a film thickness increase, affording a more compact structure. Thus, in the case of a non-substituted polymer, *e.g*. PTANI, a low thickness porous film was obtained and, as the substituent on the thiophene ring is modified, for PTANIr2 a thicker and less porous film, with holes larger than before, was produced. This difference might be ascribed to a higher PTANIr2 polymer concentration because its solubility is greater than the other two.

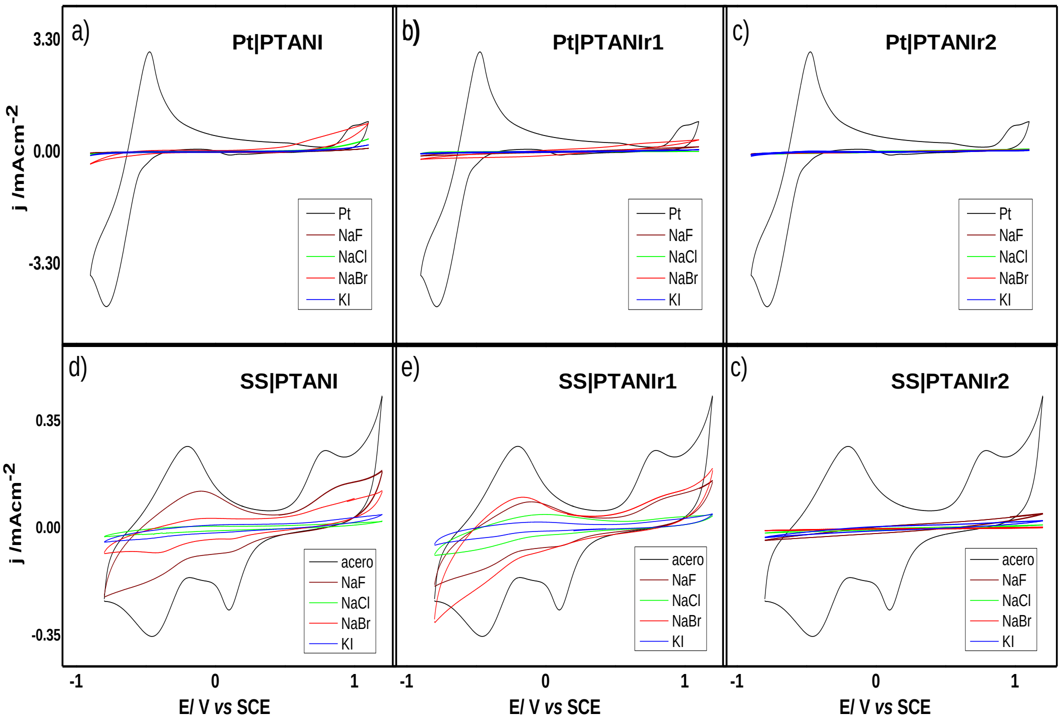

Figure 3. Cyclic voltammetry profiles of polymer modified electrodes in 1.0·10^{-3} mol·L^{-1} halide + PBS 0.05 mol L^{-1} solutions. ν = 0.1 V s^{-1}.

These results are consistent with what is verified from the voltammetric response, since on steel electrodes the response of bold electrode was evidenced, corroborating that only a partial coating of the surface occurred. By contrast, in the case of Pt, the three polymers show a total surface coating, although some morphological differences are evident, ascribed to monomer structure and therefore to the solubility of the respective polymer. The Pt|PTANI surface corresponds to a thin, porous film that uniformly covers the entire surface; in the case of Pt|PTANIr1 a polymer with globular arrangement, forming rougher structures than before, was observed. Finally, as for Pt|PTANIr2, a completely different growth was found, with the presence of a smooth, compact and homogeneous film, on which small globular structures are formed.

To corroborate the results obtained by atomic force microscopy, AFM, and scanning electron microscopy, SEM surface images of each of the studied polymer-modified Pt electrodes were obtained, disregarding those from SS as it was found that the film easily detached.

SEM images in Fig. 5 show that the PTANI film is uniform and partially porous. On the other hand, PTANIr1 produces a more heterogeneous film, consistent with previously observed data. As for PTANIr2, a very smooth film that provides a total electrode coating was attained, in agreement with the AFM results and also with the voltammetric responses, in which a modification was already evidenced as a result of the total coating of the Pt electrode surface with these polymers.

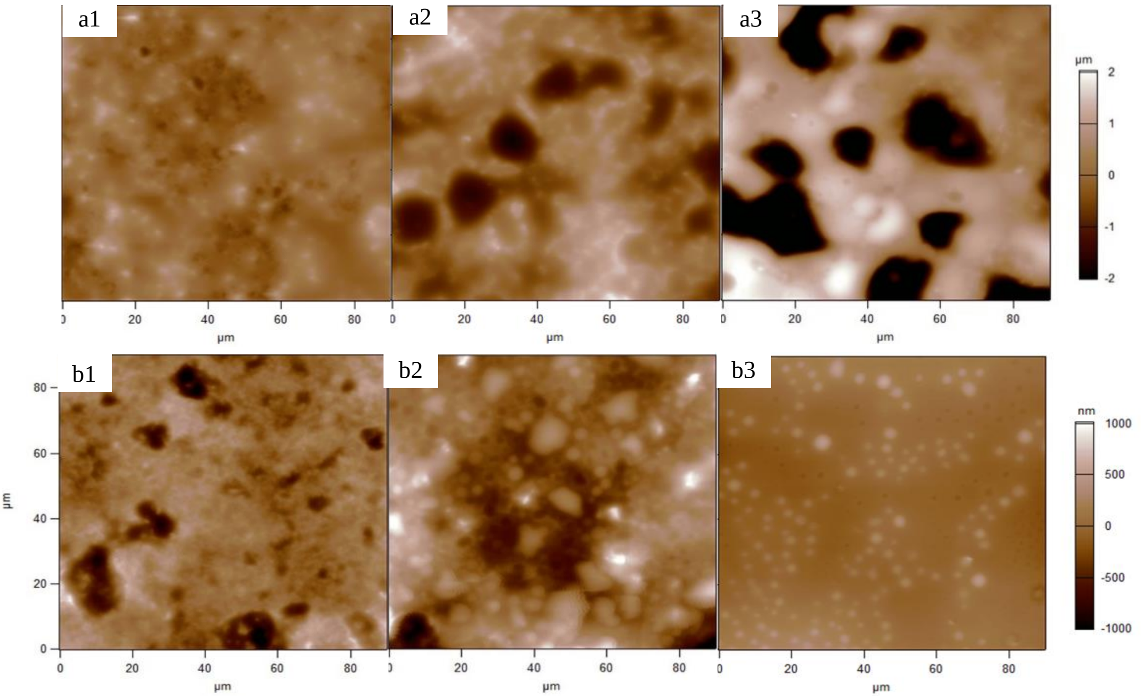

Figure 4. AFM images of SS (serie a) and Pt (serie b) electrodes modified with polymer: a1) SS|PTANI; a2) SS|PTANIr1; a3) SS|PTANIr2; b1) Pt|PTANI; b2) Pt|PTANIr1; b3) Pt|PTANIr2.

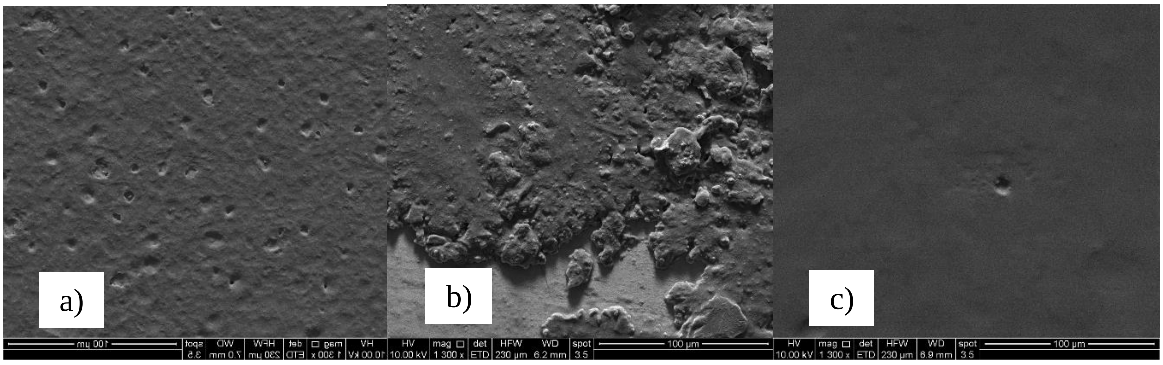

Figure 5. SEM images of Pt electrodes modified with a) Pt|PTANI; b) Pt|PTANIr1; c) Pt|PTANIr2.

In summary, it was corroborated that the hexyl substituent warrants improved PTANIr2 solubility, whereby the coating is greater, because the solution is more concentrated, having a greater amount of soluble fraction. Thus, AFM images, on both SS and Pt, show more homogeneous and compact surfaces, resulting in the total absence of oxidation current indicating that, of the three studied polymers, this would be the more suitable to prevent corrosion to both Pt and SS.

Finally, searching for other possible uses of these deposits, Raman spectroscopy studies were accomplished. In Fig. 6 RAMAN spectra of the monomers and their respective polymers are shown, besides Pt and SS electrodes modified with the latter.

Firstly, it was observed that the addition of an alkyl derivative in the thiophene ring has a significant effect on RAMAN signals namely, as the chain length increases an increase in the fluorescence of the system takes place, making that PTANIr1 and PTANIr2 RAMAN vibration signals cannot be appreciated (Figs. 6b and 6c, respectively).

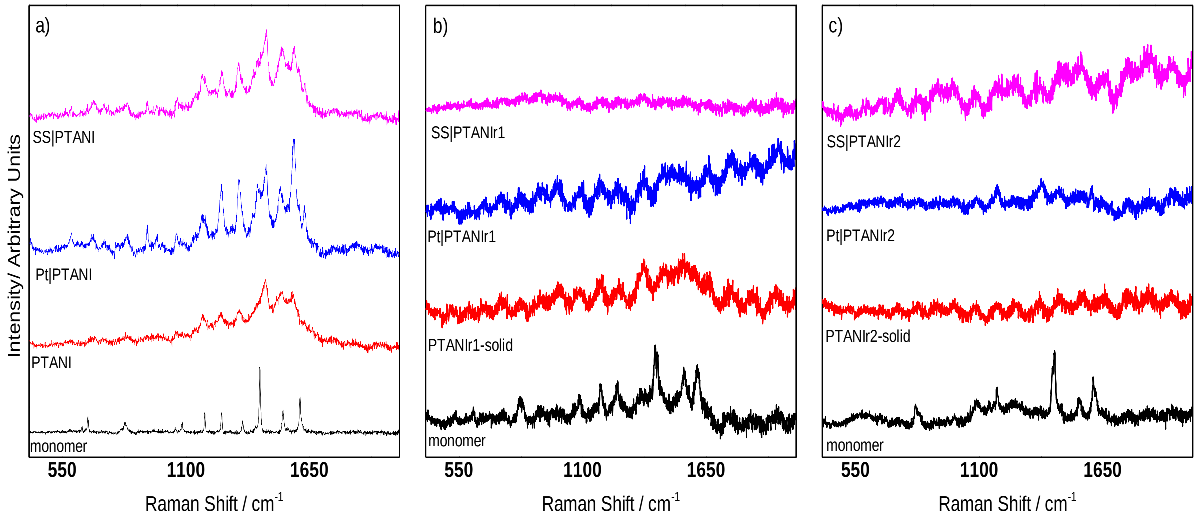

Figure 6. Synthesized polymers Raman spectra. Monomer, polymer, Pt and SS electrodes modified with: a) PTANI, b) PTANIr1, c) PTANIr2 comparison.

On the other hand, PTANI exhibits, as compared with its respective monomer, widening of all bands associated with conjugation increase of the system as well as an increase of vibrational modes existing in the structure. A complete assignment of the signals is found in Table 1.

It is very important to emphasize the effect of the metal on which the polymer is deposited, since the appearance of the 1625 cm^{-1} band, related to the formation of quinoid structures of the thiophene rings in the deposits on platinum, is clear evidence that the polymer is more oxidized owing to its contact with Pt. These results agree with those reported by Bazzaoui *et al.*,[19] who corroborated that polythiophene is in a more oxidized state on Pt than on easily oxidizable metals.

As for deposition on SS, it was observed that the signals are the same as for the partially oxidized polymer obtained by the chemical synthesis and the thiophene quinoid band is not evident on this material.

When results of RAMAN studies are compared with the obtained voltammograms, it can be said that, at least for the case of PTANI, increased oxidation of the polymer ocurred. This fact was associated to the interaction between S atoms of the polymer and the Pt surface, which would confer greater stability towards potential changes,[20] which is reflected by the lack of coating detachment. Conversely, on SS this oxidation does not take place and, as such, film loss was observed from the very first voltammetric cycle.

Unfortunately, the increase in fluorescence based on PTANIr2 and PTANIr1 systems, ascribable to substituents effect, precludes a detailed analysis in such cases. However, this phenomenon opens up the possibility that these materials can be tested as fluorescence sensors (study beyond the scope of this work, but to be dealt with in another forthcoming research).

Thus, it was demonstrated that PTANI was not very suitable for any desired applications, although its *p*-doping could be tested to analyze or remove anions. Instead, both PTANIr1 and PTANIr2, based on their fluorescence, may be useful as sensors; in addition, PTANIr2 would project especially to prevent corrosion.

Table 1. Assignment of Raman bands (in cm^{-1}) of the produced final films deposited on Pt or SS electrodes.

Polymer	Pt|PTANI	SS|PTANI	Assignment [19, 21-25]
1172	1169	1169	-C-H stretching in quinoid ring (aniline)
1257	1257	1256	-C-N stretching
1336	1332	1332	$-C-N^+$ stretching (polaron state)
1447	1461	1457	$-C_\alpha=C_\beta-$ stretching
1520	1516	1526	$-C_{\alpha'}=C_{\beta'}-$ stretching and N-H flexion
1571	1576	1579	Aniline quinoid structure
	1625		Thiophene quinoid structure

4. CONCLUSIONS

Electrodes modified with a conductive polymer layer and subsequent characterization enables assessing the prospective applications of these materials for various uses. In the case of the three polymers studied herein, it was verified that the Pt|PTANI system presents very stable *p*-doping processes under the evaluated working conditions as result of its higher degree of oxidation, ascribed to polymer-platinum interactions. This allows proposing it as anions amperometric sensor or for the removal of such species.

On the other hand, the large amount of fluorescence evidenced in the Raman analysis, points out that both PTANIr1 and PTANIr2 could be put forward as fluorescence sensors.

Finally, the observed lack of *p*- and *n*-doping processes of the PTANIr2 system on steel and platinum electrodes, makes it a good candidate for the inhibition of metallic corrosion, since it is highly stable to potential changes, showing no damage of the deposited polymer coating.

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