

# Synthesis and Properties of Polymer Film Modified Electrodes to Detect Metal Ions

Bernabé L. Rivas,<sup>1</sup> S. Amalia Pooley,<sup>1</sup> Francisco Brovelli,<sup>1</sup> Eduardo Pereira,<sup>1</sup> Luis Basaez,<sup>1</sup> Felipe Osorio,<sup>1</sup> Jean-Claude Moutet,<sup>2</sup> Eric Saint-Aman<sup>2</sup>

<sup>1</sup>Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

<sup>2</sup>Laboratoire d'Electrochimie Organique et de Photochimie Redox, UMR CNRS 5630, ICMG-FR CNRS 2607, Université Joseph Fourier Grenoble 1, BP 53, 38041 Grenoble Cedex 9, France

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**ABSTRACT:** In order to obtain modified polymeric electrodes, polymers were synthesized that are insoluble in water but soluble in common organic solvents and contain different functional groups that are able to coordinate metal ions from low concentrations. Poly(acrylic acid-co-styrene), poly(acrylamide-co-4-vinyl pyridine), and poly(styrene-co-4-vinyl pyridine) were synthesized by radical polymerization. The copolymers were characterized by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, scanning electron microscopy, and thermal analysis. The molecular weight and molecular weight distribution

were determined by size exclusion chromatography. These complexing polymers were used in the preparation by spin coating of complexing chemically modified electrodes. The polymer film modified electrodes were then tested for the detection of metal ions using the chemical preconcentration and anodic stripping technique. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1192–1197, 2005

**Key words:** copolymers; polymer–metal complex; polymer film modified electrodes; stripping analysis

## INTRODUCTION

Contamination of the environment by trace metals represents a major problem currently. It results in an increasing demand for the determination of metal contaminants in environmental matrices.<sup>1</sup> Anodic stripping analysis has long been recognized as one of the most sensitive methods for the determination of trace metals, and it is very suitable for the task of on-site and *in situ* analysis.<sup>2</sup> The method was adapted for analysis with preconcentration by electrodeposition on a mercury electrode.<sup>3</sup> However, because of the toxicity of mercury, new alternative solid electrode materials are thus highly desired and different bare gold,<sup>4</sup> iridium,<sup>5</sup> bismuth-film coated,<sup>6</sup> or boron-doped diamond<sup>7</sup> electrodes have been used as possible alternatives to mercury.

One promising approach is the use of chemically modified electrodes (CMEs) which are capable of preconcentrating target analytes from dilute solutions.<sup>8</sup> The use of properly designed modified electrodes can add a new dimension to the preconcentration–voltammetric scheme, because electrostatic interactions, co-

valent bonding, or complexation can be used to trap and concentrate analytes on an electrode surface.<sup>8,9</sup> One main advantage of this approach is the ability of preconcentration at an open circuit, so that no addition of buffer or electrolyte is required in samples to be analyzed and preconcentration can be extended to analytes that cannot be electroreductively deposited. Moreover, chemical preconcentration by complexation can provide higher selectivity that is due to the selective coordination of a metal cation to a specific ligand.

Various ligands and surface manipulation strategies have been explored for the accumulation voltammetry of metal cations, including adsorbed and self-assembled monomolecular layers of ligands on gold electrodes,<sup>10,11</sup> composite electrode materials prepared by mixing ligands with carbon paste,<sup>12,13</sup> or complexing polymer films.<sup>14,15</sup> The use of functionalized polymers is an attractive approach because it yields large amounts of ligand at the electrode surface and hence allows large amounts of metal ions to be accumulated. One of the first striking examples of complexing polymer film modified electrodes deals with the analytical properties of poly(pyrrole-*N*-carbodithioate) synthesized by derivatizing NH groups of polypyrrole films with the dithiocarbamate ligand.<sup>16</sup> The ability of this electrode to uptake copper ions from an aqueous solution for subsequent cyclic voltammetry (CV) analysis indicated a detection limit of 1 ppm. An EDTA covalently bounded, polymer film modified electrode was fabricated by polymerization of 3',4'-diamino-

Correspondence to: B. L. Rivas (brivas@udec.cl).

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2,2',5',2'-terthiophene monomer, followed by reaction with EDTA.<sup>17</sup> Calibration plots were obtained with concentration ranges between  $5 \times 10^{-10}$  and  $1 \times 10^{-7}$  M for  $\text{Cu}^{2+}$  and between  $7.5 \times 10^{-10}$  and  $1 \times 10^{-7}$  M for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ . The detection limits for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  ions were determined to be about (6, 2, and  $5 \times 10^{-10}$  M, respectively.<sup>17</sup>

Another approach is based on embedding the complexing element inside a polymeric matrix. Thus, CMEs based on the anionic complexing ligand alizarin red S (dihydroanthraquinone sulfonate) into polypyrrole have been tested for the electroanalysis of Cu(I) and Cu(II) metal species ions. The sensitivity for determination of Cu(II) species was significantly better than that of Cu(I).<sup>18</sup> Another example concerns the determination of lead in the presence of copper by anodic stripping voltammetry on electrodes modified with 2,2'-bipyridyl in a polyaniline matrix. Lead stripping analysis is selective because of the formation of stronger complexes with Pb(II) than with Cu(II), which facilitates the separation of the former metal ions.<sup>19</sup> CMEs for  $\text{Hg}^{2+}$  determination have been synthesized by embedding the selective ligand Kryptofix-222 (4,7,13,16,21,24-hexaoxa-1,10 diazabicyclo[8,8,8] hexacocane) in Nafion films.<sup>20</sup> The host molecule is strongly retained inside the polymer film because of its high hydrophobicity, leading to increased stability and durability of the analytical device. Stable and highly sensitive CMEs for the determination of Cu(II) have also been prepared by the covalent attachment of poly(L-aspartic acid) on a gold surface. Detection limits of as low as 0.2 ppb have been achieved with this device.<sup>21</sup>

The aim of this article is to report preliminary results on novel complexing film modified electrodes prepared using a different approach. Complexing polymers, which were insoluble in water but soluble in organic solvents, were synthesized, characterized, and then used in the preparation by spin coating of complexing CMEs. The polymer film modified electrodes were then tested for the detection of metal ions using the chemical preconcentration and anodic stripping technique.

## EXPERIMENTAL

### Reagents

4-Vinyl pyridine (VP, 95% Aldrich, Milwaukee, WI), acrylic acid (AA, Merck, Stuttgart, Germany), and styrene (St, Merck) were purified by distillation. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Nitric acid suprapure (Merck), standard solutions of 1000 ppm (Merck) of each metal ion, and deionized water (Millipore) were acquired. All reagents were analytical grade, and the solvents were purified by the usual methods.

### Synthesis and characterization of polymers

The synthesis of the polymers was carried out by solution radical polymerization using AIBN as the initiator (0.1 mol %). Different feed mole ratios were utilized while keeping the total number of moles constant. The polymerization flask was kept under a nitrogen atmosphere at 70°C for 24 h. The polymer was precipitated in diethyl ether and dried under a vacuum until constant weight.

The polymers were characterized by FTIR and <sup>1</sup>H-NMR spectroscopy.

#### Poly(AA-co-st) [P(AA-co-st)]

##### *Solubility properties.*

P(AA-co-St) is soluble in dimethylsulfoxide (DMSO), dimethylformamide (DMF), MeOH, acetone, and tetrahydrofuran (THF) and insoluble in  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{H}_2\text{O}$ . FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3440 (O—H), 3030 ( $\text{Csp}_2$ —H), 2930 (C—H methyne), 1700 (C=O), 1450 (C—H methylene). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 12.0 (1H acid), 7.0 (5H aromatic), 3.5 (1H methyne), 2.5 (1H methyne), 1.9 (2H methylene).

#### Poly(acrylamide-co-VP) [P(AAm-co-VP)]

##### *Solubility properties.*

P(AAm-co-VP) (1.0:4.0) is soluble in DMSO and insoluble in MeOH, DMF, acetone,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ , THF,  $\text{CH}_2\text{Cl}_2$ , and  $\text{H}_2\text{O}$ . FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3430 (N—H), 2930 (C—H methyne), 1670 (C=O), 1600 ( $\text{Csp}_2$ —N), 1420 (C—H methylene). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.0–8.5 (4H heterocyclic), 3.6 (2H methyne), 1.0–2.0 (4H methylene).

#### Poly(st-co-VP) [p(St-co-VP)]

##### *Solubility properties.*

P(St-co-VP) (4.0:1.0, 1.0:1.0, and 1.0:4.0) is soluble in DMSO, MeOH,  $\text{CHCl}_3$ , DMF, and  $\text{CH}_2\text{Cl}_2$  and insoluble in  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ . FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3020 (C—H aromatic and heterocyclic), 2920 (C—H methylene), 1590 ( $\text{Csp}_2$ —H heterocyclic). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.0–8.5 (4H heterocyclic), 6.5 (5H aromatic), 3.2 (2H methyne), 1.0–2.0 (4H methylene).

To study the solubility, we used 1 mg of each dry copolymer with 1 mL of solvent. The solvents were water, acetone, dichloromethane, chloroform, methanol, DMSO, acetonitrile, and DMF.

### Electrochemical setup

The experimental methods employed to analyze the complexing properties of films were CV and square wave voltammetry (SWV).<sup>22–24</sup> In the CV experiments the potential was scanned between  $-0.9$  and  $-0.1$  V at a  $100 \text{ mV s}^{-1}$  scan rate. In the SWV experiments the

**TABLE I**  
Experimental Conditions and Results of Copolymerization Reactions

Copol. No.	Feed monomer ratio A/B (mol)	Copol. compos. A/B	Yield (%)	TDT <sub>10%</sub> (°C)	TDT <sub>50%</sub> (°C)
1 <sup>a</sup>	1.0 : 1.0	0.9 : 1.0	98	330	410
2 <sup>b</sup>	1.0 : 2.3	0.7 : 1.0	92	370	405
3 <sup>c</sup>	4.0 : 1.0	0.6 : 1.0	79	375	425
4 <sup>c</sup>	1.0 : 1.0	0.6 : 1.0	73	345	420

<sup>a</sup> A, acrylic acid; B, styrene.

<sup>b</sup> A, acrylamide; B, 4-vinyl pyridine.

<sup>c</sup> A, styrene; B, 4-vinyl pyridine.

potential was held at  $-0.9$  V for 40 s and scanned with 0.05-V amplitude and 60-Hz frequency. A polycrystalline platinum disk of  $0.2$  cm<sup>2</sup> geometric area was used as the working electrode. The reference electrode was an Ag/AgCl system. Its potential was 197 mV with respect to the normal hydrogen electrode. Platinum gauze was used as a counterelectrode and separated from the working compartment by fritted glass. Before each experiment, the working electrode was polished with alumina slurry (particle size =  $0.3$   $\mu$ m) and washed thoroughly with twice distilled water. The data were recorded in a BAS CV-50W system coupled to a PC computer. All electrolytic solutions were kept under nitrogen for 30 min before each experiment. The gas flux was inverted to keep an inert atmosphere while the electrochemical perturbation was applied.

### Modified electrode preparation

The modified electrodes were prepared by spin coating. The different polymers were spin coated from a solution of 1.3 mg of polymer in 1 mL of THF (deposited volume =  $10$   $\mu$ L, rotation rate = 500 rpm). Then, the spin-coated films were dried for 10 min in air and 1 min with hot air flux.

### Measurements

The pH was measured with a Hanna model HI 2023 pH meter. Metal ions were analyzed by a Unicam Solaar M5 series atomic absorption spectrophotometer. FTIR and NMR spectra were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI) and Bruker AC 250 multinucleus spectrometer (Bruker Instruments, Billerica, MA), respectively. The thermal properties were studied under a nitrogen atmosphere by a STA 625 thermal analyzer (Polymer Laboratories, Amherst, MA). The molecular weight and molecular weight distributions were determined by a Perkin-Elmer HPLC device with a refractive index detector; a series 200 isocratic pump; a column for THF, P(St-divinylbenzene), and gel permeation chromatography (GPC); and a column for water [PL-aquagel-OH, gel filtration chromatography (GFC)]. The micrographs were re-

corded on a scanning electron microscope (Autoscan 1, ETEC Corporation).

## RESULTS AND DISCUSSION

The metal ion binding capacity of pyridine and carboxylate groups is well known.<sup>25-31</sup> Therefore, there is interest to obtain polymers containing these ligand groups in order to synthesize supports to prepare modified electrodes that are able to detect metal ions with impact on the environment. The support polymeric materials were synthesized by solution radical polymerization by using AIBN as the initiator. The copolymerization yield ranged from 72 to 98%. These materials are insoluble in water and soluble in organic solvents like methanol, acetone, THF, and DMF (see Table I).

The copolymer composition was determined from the <sup>1</sup>H-NMR spectra by a comparison of the area of characteristic absorption signals of each monomer (see Table II). The copolymer near to an alternating composition is that it contains AA and AAm moieties, which is in agreement with the monomer reactivity ratios.

The thermal behavior demonstrated that those copolymers containing St and VP moieties have higher thermal stability due to the presence of the aromatic rings. Lower thermal stability corresponds to the copolymer containing carboxylic acid, which is probably attributable to the loss of CO<sub>2</sub> (see Table I).

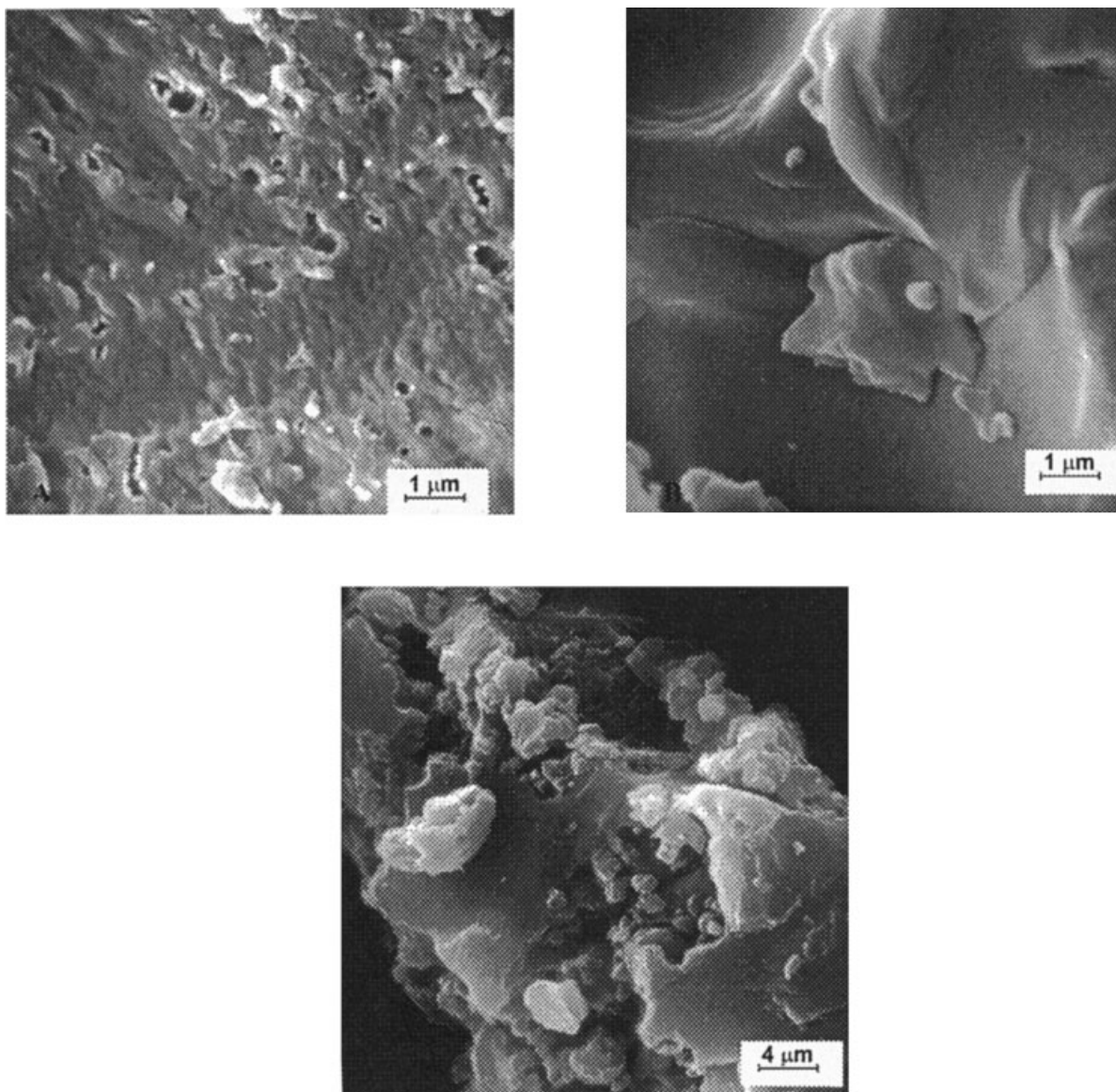
**TABLE II**  
Number-Average Molecular Weight, Molecular Weight Distribution (Weight-Average), and Polydispersity of Copolymers

Copol. No.	$M_n$	$M_w$	Polydispersity
1	14,720	21,350	1.45
2 <sup>a</sup>	—	—	—
3	12,390	27,940	1.86
4	6,450	9,850	1.53

The measurements were carried out in THF at 20°C.

<sup>a</sup> The measurement was not carried out because the polymer was insoluble in THF and H<sub>2</sub>O.





**Figure 1** Scanning electron micrographs of copolymers (a) P(AA-co-St), (b) P(AA-co-VP), and (c) P(AAm-co-VP).

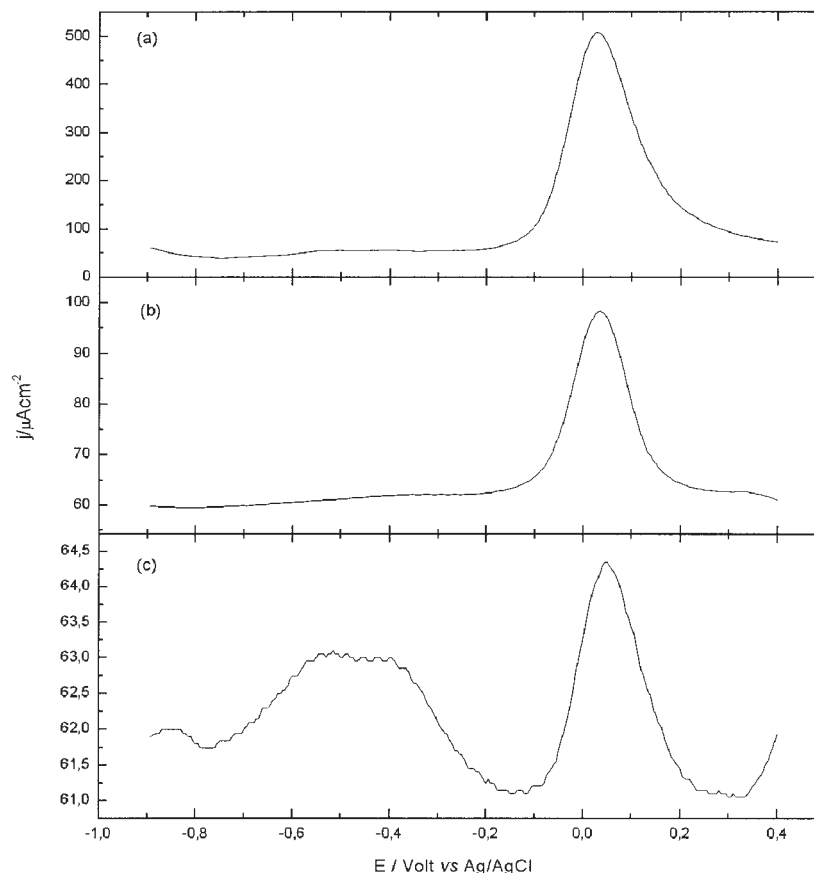
The molecular weight, molecular weight distribution, and polydispersity were determined by size exclusion chromatography. The number-average molecular weight values were lower than 15,000 and increased with the higher content of the St count. The polydispersity ranged from 1.45 to 1.86, which is in agreement with a radical polymerization in which terminating reactions are present (see Table II).

The morphology of the copolymer was studied by scanning electron microscopy. In general, the surface was flat, rough, and porous. Figure 1 shows the micrographs corresponding to copolymers 1, 3, and 4.

Through electrochemical techniques like CV and SWV, the complexing properties of the film modified electrodes were investigated at pH 5.5 in aqueous solutions containing  $10^{-3}$  M  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ .

Figure 2(a) shows the SWV response of the P(AAm-co-VP) film in the presence of  $\text{Cu}^{2+}$ . The modified

electrode was contacted with an aqueous solution of metal ions during 10 min at 25°C, then reduced at  $-0.9$  V for 40 s to reduce copper ions and to precipitate copper metal in the polymer film. Under these conditions, an anodic peak corresponding to Cu stripping was observed around 0.05 V. The stability of the stripping peaks was investigated by performing repetitive scans with the same modified electrode. The second scan was performed 1 min after the first one. One important feature is that the stripping peak decreases in intensity as the stripping cycles are repeated. This indicates that the stability of the complex is low. Moreover, the intensity of the peak depends on the thickness of the film: decreasing the film thickness decreases the stripping peak current. This may be attributed to the lower amount of available complexing sites in thinner films. It is not possible to discount that this film is protonated at pH 5, which involves an electro-



**Figure 2** Square wave voltammetry curves of different films performed in solution containing  $10^{-3}$  M  $\text{Cu}^{2+}$  ions in 0.1M  $\text{KNO}_3$ ; (a) P(AAm-co-VP), (b) P(AA-co-St), and (c) P(St-co-VP). After an accumulation time of 10 min, the potential was held at  $-0.9$  V for 40 s and scanned with 0.05-V amplitude and 60-Hz frequency.

static repulsion between the positively charged species.

Figure 2(b) shows the response of the P(AA-co-St) film. The intensity of the current for the stripping peak is significantly lower than for P(AAm-co-VP), but the shape is more symmetrical.

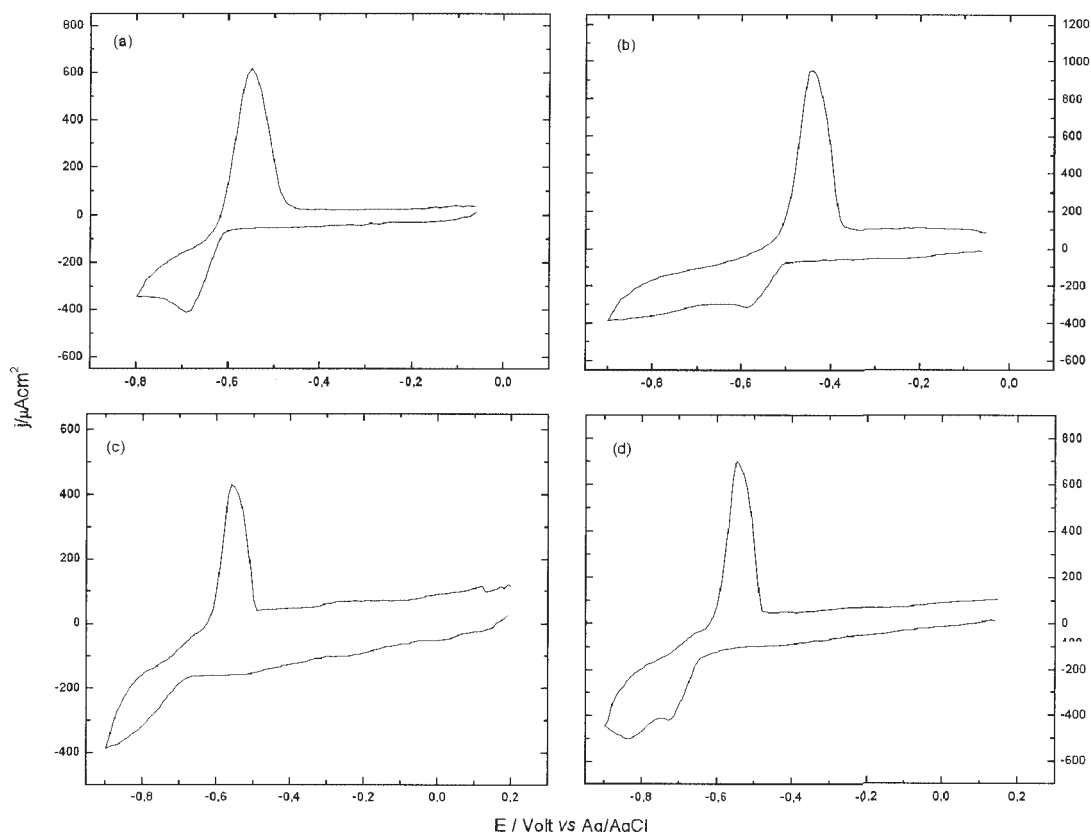
Figure 2(c) shows the response of the P(St-co-VP) film. The intensity of the peak is very similar to that found with P(AA-co-VP) films under the same conditions. This observation suggests that there is competition between the polymer functional groups. At the investigated pH, the pyridine groups are basically protonated and the carboxylic groups are in their carboxylate form. This means that the cationic species are under the effect of two opposite forces. Thus, the carboxylate groups attract the metal ion species and the pyridine groups repel it.

Stripping analysis of  $\text{Pb}^{2+}$  on different polymer films was investigated by CV (see Fig. 3). The best results were found for the films prepared from P(AA-co-St). Figure 3(a) shows a reduction peak of the Pb ions around  $-0.7$  V and in the reverse scan an oxidation peak at  $-0.575$  V, corresponding to Pb ion stripping. By comparing the results obtained using copolymers of different compositions, we found that for

P(St-co-VP) [see Fig. 3(b–d)], as the content of St increases, the moiety increases the stripping peak of the metal. This may be associated with the separation between pyridine groups as they are protonated, allowing a higher interaction between the metal ion and the aromatic ring. The shape and position of voltammetric peaks are the same in the naked and modified electrode, wherever the current intensities in the naked ones are major.

## CONCLUSION

In summary, five copolymers insoluble in water but soluble in some organic solvents by solution radical polymerization were obtained. The yield varied from 73 to 98%. The molecular weight was low ( $<15,000$  g  $\text{mol}^{-1}$ ) and the polydispersity values are in agreement with radical polymerization. Modified electrodes prepared by spin coating using organic solutions of these copolymers were studied by CV and SWV techniques in aqueous solutions containing copper and lead ions. The best results in terms of metal analysis by anodic stripping voltammetry were found for the film prepared from P(AA-co-St) with respect to the detection of  $\text{Pb}^{2+}$  ions.



**Figure 3** Cyclic voltammograms profiles of different films performed in solution containing  $10^{-3}$  M  $\text{Pb}^{2+}$  ions in 0.1M  $\text{KNO}_3$ : (a) P(AA-co-St), (b) 4 : 1 P(St-co-VP), (c) 1 : 1 P(St-co-VP), and (d) 1 : 4 P(St-co-VP). The potential was switched between  $-0.9$  and  $-0.1$  V at a  $100 \text{ mV s}^{-1}$  scan rate.

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