

# Synthesis and Properties of Styrene Copolymers. Preparation of Film-Modified Electrodes to Detect Pb<sup>2+</sup> 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> Jazmín Puentes,<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:** Organic solvent-soluble polymers containing different functional groups able to coordinate metal ions from low concentration were synthesized to build complexing polymer film modified electrodes. Poly(acetamide acrylic acid-co-styrene) and poly(itaconic acid-co-styrene) were synthesized by radical polymerization. The copolymers were characterized by Fourier transform infrared and <sup>1</sup>H NMR spectroscopy, electron scanning microscopy, and thermal analysis. The molecular weight and molecular weight distribution were determined by size exclusion chro-

matography. These complexing polymers have been used in the preparation of complexing modified electrodes (CME) by spin coating. The CME have been tested for the detection of metal ions using the chemical preconcentration-anodic stripping technique. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2380–2385, 2006

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

## INTRODUCTION

Growing concern about heavy metal contamination has generated an increasing demand to monitor trace metals in environmental matrices.<sup>1</sup> Anodic stripping analysis has long been recognized as one of the most sensitive methods for trace metal determination and is very suitable for on-site and in situ analysis.<sup>2</sup> The method was adapted for analysis with preconcentration by electrodeposition, and for many years, mercury was the choice of electrode material because of its very good properties (reproducibility and surface purity, high hydrogen overpotential).<sup>3</sup> Because of mercury's toxicity, alternative, less toxic solid electrode materials have been sought. Different electrodes from bare gold,<sup>4</sup> iridium,<sup>5</sup> bismuth-film coated<sup>6</sup> or boron-doped diamond<sup>7</sup> have been used as possible alternatives to mercury.

Another route is the use of chemically modified electrodes 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 since electrostatic interactions or complexation can be used to trap and concentrate metal ions onto an electrode surface.<sup>8,9</sup> One main advantage of this approach is the ability to preconcentrate at open circuit so that (i) the addition of any buffer or electrolyte to the sample to be analyzed is not required, and (ii) preconcentration can be extended to metal ions that cannot be electroreductively deposited. Moreover, chemical preconcentration by complexation can provide a higher selectivity because of 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>10–12</sup> composite electrode materials prepared by mixing ligands with carbon paste,<sup>13,14</sup> or complexing polymer films.<sup>15,16</sup>

The use of functionalized polymer electrode materials is an attractive approach, as they yield large amounts of ligand at the electrode surface and hence allow large amounts of metal ions to be accumulated.<sup>17</sup> The modification of electrode surfaces with complexing polymer films can be carried out in different ways. One of the first striking examples of complexing polymer film modified electrodes deals with the analytical properties of poly(pyrrole-*N*-car-

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

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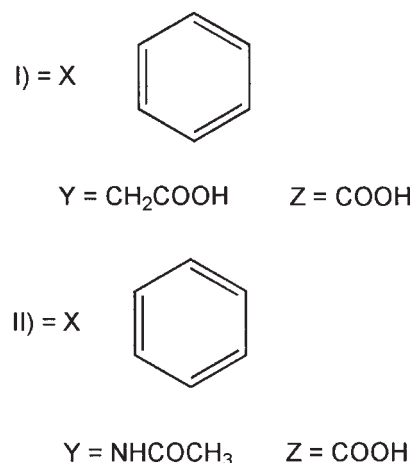
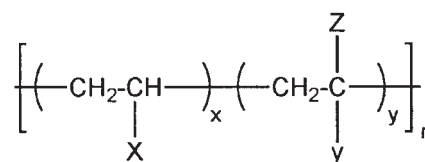
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bodithioate). It was synthesized by grafting dithiocarbamate ligands onto the NH groups of polypyrrole films previously coated on the electrode surface.<sup>18</sup> This electrode yielded a well-defined voltammetric response following the uptake of  $\text{Cu}^{2+}$  ions from a 1-ppm aqueous solution of the ion. Recently, an EDTA-covalently bounded polymer film modified electrode was fabricated by polymerization of the 3',4'-diamino-2,2',5',2'-terthiophene monomer, followed by chemical modification with EDTA.<sup>19,20</sup> The modified electrode was used for the selective electroanalysis of trace metals. The detection limits were below  $10^{-9}\text{M}$  for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$ , and between  $5 \times 10^{-8}$  and  $9 \times 10^{-8}\text{M}$  for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$ .<sup>20</sup>

Another approach is based on embedding the complexing element inside a polymeric matrix. Thus, modified electrodes synthesized by trapping the anionic complexing ligand alizarin red S (dihydroanthraquinone sulfonate) into polypyrrole films during the polymerization have been tested toward the electroanalysis of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions. The determined sensitivity of  $\text{Cu}^{2+}$  species was significantly higher than that of  $\text{Cu}^+$ .<sup>21</sup> Another example concerns the determination of lead in the presence of copper by anodic stripping voltammetry on electrodes modified with 2,2'-bipyridyl simply doped in a polyaniline matrix. Lead stripping analysis was selective because of the formation of stronger complexes with  $\text{Pb}^{2+}$  than with  $\text{Cu}^{2+}$ , which facilitates the separation of the former metal ions.<sup>22</sup> Complexing modified electrodes (CMEs) for the determination of  $\text{Hg}^{2+}$  have been synthesized by embedding the selective ligand Kryptofix-222 (4,7,13,16,21,24-hexaoxa-1,10 diazabicyclo [8,8,8] hexacosane) in Nafion films.<sup>16</sup> The host molecule was strongly retained inside the polymer film because of its high hydrophobicity, leading to an increased stability and durability of the analytical device.

Recently, electrochemical sensors based on electrodes modified with entrapped ion-exchange polymers using the doping sol-gel methods have been developed. Poly(dimethyldiallylammonium chloride) or poly(vinyl sulfonic acid, sodium salt) has been used as anionic and cationic ion exchangers, respectively. Modified electrodes provide detection limits 2 and 3 orders of magnitude (for the cationic and anionic polymers, respectively) lower than those by analogous graphite electrodes. A good reproducibility of the analytical procedures developed was also obtained.<sup>23</sup>

A straightforward approach for the preparation of complexing polymer film modified electrodes is to produce polymer layers by spin-coating or dip-coating, using solutions of chemically synthesized chelating polymers. Following our previous result,<sup>17</sup> the aim of this article is to report results of novel complexing film-modified electrodes. For this purpose, complexing polymers poly(acetamide acrylic acid-co-acrylic



Scheme 1

acid) and poly(itaconic acid-co-styrene) (Scheme 1), which are soluble in organic solvents but insoluble in water, have been synthesized and characterized. CMEs of these polymers were prepared by spin-coating. The polymer film-modified electrodes have been tested for the detection of  $\text{Pb}^{2+}$  ion in aqueous media, using the chemical preconcentration-anodic stripping technique. The lead ion is of interest because of its environmental impact.

## EXPERIMENTAL

### Reagents

Styrene (Sty; Merck, Stuttgart, Germany), 2-acetamide acrylic acid (99%; Aldrich, Milwaukee, WI), and itaconic acid (99%; Aldrich) were purified by distillation and crystallization, respectively; 2,2'-azoisobutyronitrile (AIBN) was recrystallized from methanol. All reagents were of analytical grade. The solvents were purified by usual methods.

### Synthesis of the polymers and characterization

The synthesis of the polymers was carried out by solution radical polymerization using AIBN as initiator (0.1 mol %). Two different feed mol ratios were performed but keeping constant the total number of mol. The polymerization flask was kept under nitrogen atmosphere at  $70^\circ\text{C}$  for 24 h. Polymer was precipitated in diethyl ether and dried under vacuum until constant weight.

The polymers were characterized by FTIR and  $^1\text{H}$  NMR spectroscopies.

Poly(2-acetamide acrylic acid-*co*-styrene)

*Solubility properties:* Soluble in DMSO and MeOH, and insoluble in THF,  $(\text{CH}_3)_2\text{C}=\text{O}$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{H}_2\text{O}$ .

*FTIR* (KBr, in  $\text{cm}^{-1}$ ): 3407 ( $\nu$  N-H amide), 3025 ( $\nu$  Csp $_2$ -H), 2936 ( $\nu$  C—H methyne), 1657 ( $\nu$  C=O), 1440 ( $\nu$  C—H methylene).  $^1\text{H}$  NMR (DMSO- $d_6$ , in ppm): 12.0 (1H acid), 7.2 (5H aromatic), 2.9 (2H methylene of AAA), 2.6 (1H methyne of Sty), 1.9 (2H methylene).

Poly(itaconic acid-*co*-styrene)

*Solubility properties:* Soluble in DMSO, THF, DMF, acetone, and MeOH, 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, in  $\text{cm}^{-1}$ ): 3028 ( $\nu$  Csp $^2$ —H), 2934 ( $\nu$  C—H methyne), 1709 ( $\nu$  C=O), 1447 ( $\nu$  C—H methylene).  $^1\text{H}$  NMR (MeOH- $d_4$  in ppm): 7.2 (5H aromatic), 3.6 (1H methyne), 2.2 (1H methylene), 1.9 (2H methylene).

### Electrochemical setup

Reagent-grade sodium acetate, acetic acid, and lead(II) acetate were obtained from Merck A.G. (Stuttgart, Germany). All reagents were used without further purification. Distilled water was obtained from a Barnstead water purification system (5 M $\Omega$  cm). Glassware were soaked in  $\text{KMnO}_4$ - $\text{H}_2\text{SO}_4$ , rinsed with a  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}_2$  solution, and carefully cleaned with distilled water before use to avoid contamination.

The experimental method to carry out the square wave voltammetry (SWV) has been previously described.<sup>24,25</sup> A carbon disc of 0.07-cm $^2$  geometric area was used as working electrode. The reference electrode was Ag/AgCl. The potential used was 197 mV with respect to the normal hydrogen electrode. Platinum gauze was used as counter electrode and placed in a compartment separated from the working electrode by fritted glass. Before each experiment, the working electrode was polished with alumina slurry (particle size 0.3  $\mu\text{m}$ ) and rinsed with abundant twice-distilled water. The data were recorded in a BAS CV-50W system coupled to a PC.

All solutions were kept under nitrogen for 20 min before each experiment. The gas flux was inverted to keep an inert atmosphere while the electrochemical perturbation was applied. All experiments were carried out at 25°C.

### Preparation of modified electrodes

The modified electrodes have been prepared by spin-coating. The different polymers were spin-coated from

a solution of 10 mg of polymer in 5 mL of methanol or THF. Exactly 10  $\mu\text{L}$  of the polymer solution were placed on the electrode surface, and the electrode was rotated at 500 rpm for 30 s. Then, the spin-coated films were dried 5 min in air and 4 min with hot air flux.

### Analytical procedure

Metal ion accumulation at the carbon-polymer modified electrode was carried out at open circuit by dipping the electrode for a given time (the accumulation time, typically 10 min) into 15 mL of a stirred buffered solution (pH 4.8) of metal salt at  $25 \pm 0.5^\circ\text{C}$ . The electrode was removed from the accumulation cell and washed thoroughly with purified water. It was then transferred to the electrochemical cell containing acetate buffer solution (pH 4.8). SWV experiments were conducted immediately under quiescent conditions. The accumulated metal ions were reduced at  $-0.6$  V for 40 s and the potential was scanned from the reduction potential to 0.2 V. SWV was applied with a 25-mV modulation amplitude, at 15-Hz frequency and 5-mV step potential.

### Measurements

FTIR and  $^1\text{H}$  NMR spectra were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI) and a Bruker AC 250 multinucleus spectrometer (Bruker Instruments, Billerica, MA), respectively. The thermal properties were studied under nitrogen atmosphere by a STA 625 thermal analyzer (Polymer Laboratories, Amherst, MA). The molecular weight and molecular weight distributions were determined by a HPLC (PerkinElmer) with refractive index detector and isocratic pump series 200; column for THF, poly(styrene-divinylbenzene), and GPC; and column for water PL-aquagel-0H (GFC). The surface of the polymer was coated with gold for 3 min to obtain a thickness of 150 Å, using an Edwards S 150 sputter coater. The electron micrographs were recorded on a scanning electron microscope (ETEC Corp., model ETEC Autoscan U-1 model).

## RESULTS AND DISCUSSION

The metal ion binding capacity of the carboxylate groups is well known,<sup>26–32</sup> and consequently, it is interesting to obtain polymers containing these ligand groups to synthesize supports for preparing modified electrodes able to detect metal ion with environmental impact. The support polymer materials containing a hydrophobic unit such as styrene, and a hydrophilic unit such as itaconic acid and acetamide acrylic acid were synthesized by solution radical polymerization by using AIBN as initiator (see Scheme 1). The copolymerization yields were higher than 50%. These ma-

TABLE I  
Experimental Conditions and Results of the Copolymerization Reactions

| Copolymer sample no. | Feed monomer ratio (A:B; mol) | Copol. compos. (A:B) | TDT <sup>a</sup> <sub>10%</sub> (°C) | TDT <sup>b</sup> <sub>50%</sub> (°C) | Surface (by SEM) |
|----------------------|-------------------------------|----------------------|--------------------------------------|--------------------------------------|------------------|
| I-1 <sup>c</sup>     | 1.0:1.0                       | 0.8:1.0              | 206                                  | 366                                  | Rough            |
| I-2 <sup>c</sup>     | 1.0:3.0                       | 0.4:1.0              | 214                                  | 400                                  | Smooth           |
| II-1 <sup>d</sup>    | 1.0:1.0                       | 1.0:0.9              | 211                                  | 399                                  | Pierced smooth   |
| II-2 <sup>d</sup>    | 1.0:2.0                       | 1.0:0.5              | 185                                  | 235                                  | Pierced smooth   |

<sup>a</sup> Temperature at which 10% of weight was lost.

<sup>b</sup> Temperature at which 50% of weight was lost.

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

<sup>d</sup> A, itaconic acid; B, styrene.

materials are insoluble in water and soluble in organic solvents such as methanol and DMF.

The copolymer composition was determined from the <sup>1</sup>H NMR spectra by comparison of the area of characteristic absorption signals of each monomer (see Table I). The copolymer close to an alternating composition is the one that contains itaconic acid and acetamide acrylic acid moieties, which is in agreement with the monomer reactivity ratios.

The thermal behavior demonstrated that the copolymer containing styrene and acetamide acrylic acid with an excess of styrene shows a higher thermal stability because of the presence of the aromatic ring. The copolymer containing a higher content of carboxylic acid moieties displays a lower thermal stability, probably due to the loss of CO<sub>2</sub> (see Table I).

The molecular weight, molecular weight distribution, and polydispersity were determined by size exclusion chromatography (SEC) only for the P(IA-co-Sty) system. The other copolymers are insoluble in common solvents used in SEC.  $M_n$  values were higher than 3500 and lower than 10,000. The polydispersity was 1.35 and 1.45 for P(IA-co-Sty) system, which is in

agreement with a radical polymerization wherein the terminating reactions are occurring. Copolymers morphology was studied by scanning electron microscopy. In general, the surface was flat, rough, and porous. Figure 1 shows the micrographs corresponding to the copolymers 1 and 3.

The complexing properties of poly(AAA-co-Sty) and poly(IA-co-Sty) film electrodes toward metal ions were studied using the chemical preconcentration and anodic stripping method.<sup>17,33</sup> The modified electrode was immersed into a buffered solution containing lead ions to obtain the chemical accumulation of the cation in the film through complexation between the metal ions and the carboxylic acid groups. After the preconcentration step, the modified electrode was transferred into a blank solution of sodium acetate/acetic acid buffer, where the complexed metal ions were reduced to lead metal before recording the lead stripping current.

Figure 2(a) shows the square wave voltammogram recorded using a carbon electrode modified with a P(IA-co-Sty) film, after accumulation of Pb<sup>2+</sup> ions. In this case, we observed a sharp peak of stripping cor-

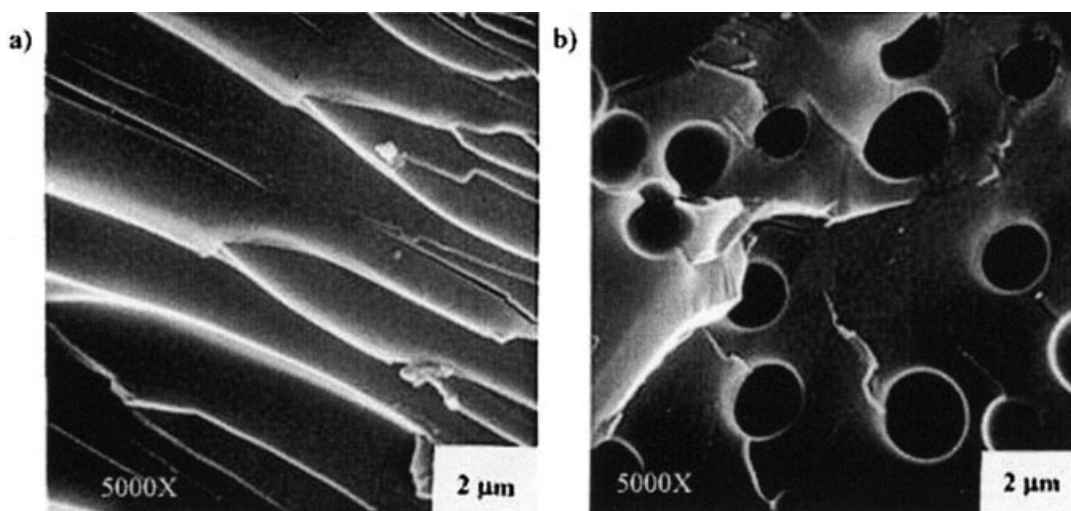
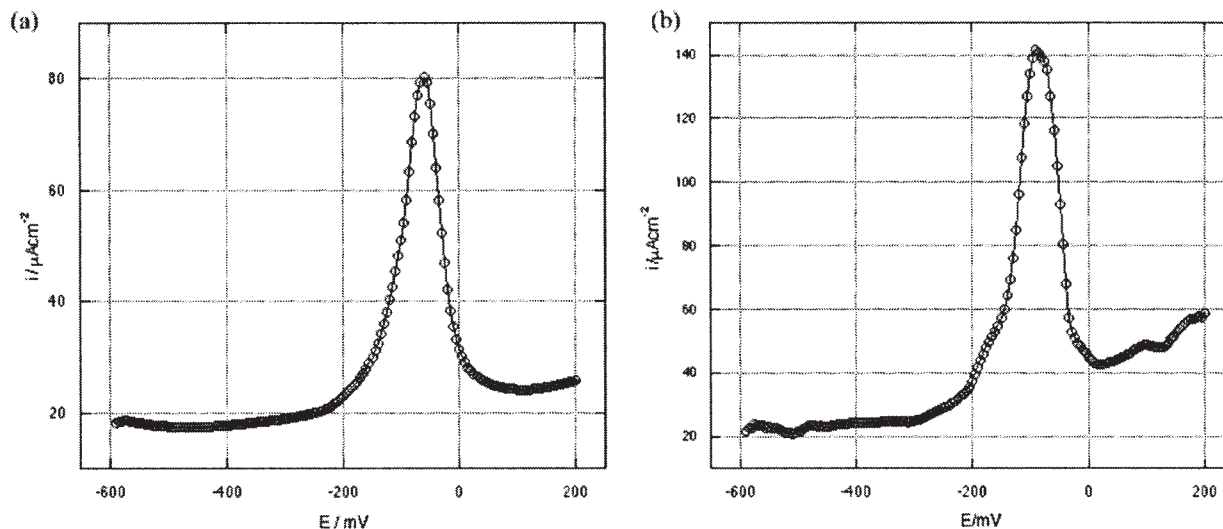


Figure 1 Scanning electron micrographs of the copolymers (a) poly(AAA-co-Sty) and (b) poly(IA-co-Sty).





**Figure 2** Square wave voltammograms recorded using a carbon-polymer modified electrode in 0.1M acetate buffer (pH 4.8) after an accumulation time of 10 min in acetate buffer containing  $10^{-3}M$   $Pb^{2+}$  ions; deposition of metal was at  $-0.6$  V for 40 s. (a) P(IA-co-Sty) and (b) P(AAA-co-Sty).

responding to the oxidation of lead at approximately  $-50$  mV. One important aspect is that this peak decreases in intensity as the stripping cycles are repeated, which would indicate that the stability of the complex is not very high. Figure 2(b) shows the response of the modified electrode with P(AAA-co-Sty) film in the presence of  $Pb^{2+}$ . The intensity of the stripping peak is very close to the other polymer. In both electrodes the complexing properties are attributed to the higher complexing capacity of the carboxylate groups.

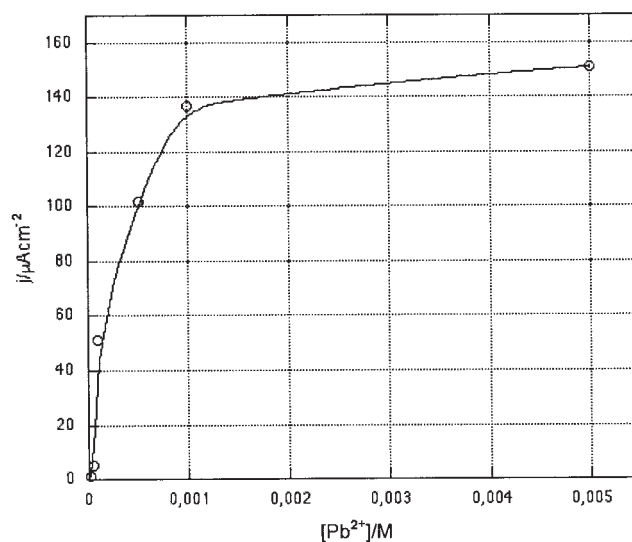
The variations in peak current with the metal ion concentration in the accumulation solution are shown in Figures 3 and 4. Calibration plots were obtained for poly(IA-co-Sty) (see Fig. 3) and poly(AAA-co-Sty) (see Fig. 4) in the concentration range from  $10^{-5}$  to  $5 \times 10^{-3}M$  of  $Pb^{2+}$ .

Poly(IA-co-Sty) film-modified electrodes provide better results for the determination of the lead ion than do electrodes with poly(AAA-co-Sty). These results indicate that the sensing behavior depends on the complexing properties of the carboxylic acid moieties. It is suggested that the interactions between polymeric complexing sites and metal ion are increased by a favored orientation of the carboxylate moieties. Nevertheless, no data exist in the literature with respect to the complexing properties of these copolymers.

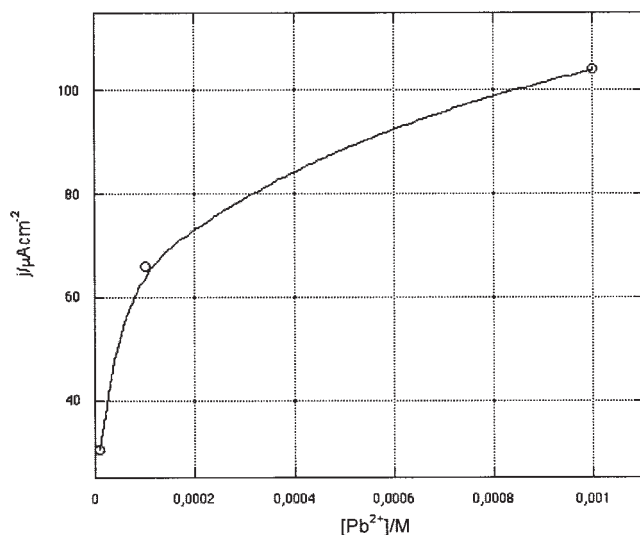
It has been shown that carbon electrodes modified by poly(AAA-co-Sty) and poly(IA-co-Sty) can be used for electroanalytical sensing of metal cations. The feasibility of this approach has been demonstrated by chemical preconcentration and anodic stripping analysis of  $Pb^{2+}$  ions. The major advantage of this approach is that the synthesis of the complexing electrode material is performed using a very simple and

reproducible one-step procedure, leading to stable, easy-to-manipulate polymer film-modified electrodes.

In addition, four copolymers were obtained by solution radical polymerization. They are insoluble in water but soluble in some organic solvents. The polymerization yield ranged from 50 to 70%, the molecular weight ranged from 3500 to 10,000  $g\ mol^{-1}$ , and the polydispersity values are in agreement with a radical polymerization. Modified electrodes prepared by spin-coating using organic solution of these copolymers have been studied using SWV techniques in aqueous solutions containing  $Pb^{2+}$  ions. The best results in terms of metal analysis by anodic stripping



**Figure 3** SWV peak currents versus concentration of  $Pb^{2+}$  ions in the accumulation solution with carbon-P(IA-co-Sty)-modified electrode.



**Figure 4** SWV peak currents versus concentration of  $Pb^{2+}$  ions in the accumulation solution with carbon-P(AAA-co-Sty)-modified electrode.

voltammetry were found for the polymer film prepared from P(IA-co-Sty).

## References

- Wang, J.; Lu, J.; Luo, D.; Wang, J.; Jiang, M.; Tian, B. *Anal Chem* 1997, 69, 2640.
- Wang, J.; Tian, B.; Wang, J.; Lu, J.; Olsen, C.; Yarnitzky, C.; Olsen, K.; Hammerstrom, D.; Bennett, W. *Anal Chim Acta* 1999, 385, 429.
- Achterberg, E. P.; Braungardt, C. *Anal Chim Acta* 1999, 400, 381.
- Wang, J.; Foster, N.; Armalis, S.; Larson, D.; Zirino, A.; Olsen, K. *Anal Chim Acta* 1995, 310, 223.
- Wang, J.; Lu, J.; Luo, D.; Hocevar, B.; Farias, P. M. *Anal Chem* 2000, 72, 3218.
- Nolan, M. A.; Kounaves, S. P. *Anal Chem* 1999, 71, 3567.
- Tsai, Y.-C.; Coles, B. A.; Holt, K.; Foord, J. S.; Marken, F.; Compton, R. G. *Electroanalysis* 2001, 13, 831.
- Arrigan, D. W. M. *Analyst* 1994, 119, 1953.
- Wang, J. In *Electroanalytical Chemistry*; Bard, M. A., Ed.; Marcel Dekker: New York, 1998; Vol. 16, p 1.
- Steinberg, S.; Rubinstein, I. *Langmuir* 1992, 8, 1183.
- Turyan, I.; Mandler, D. *Anal Chem* 1994, 66, 58.
- Yang, W.; Gooding, J. J.; Hibbert, D. B. *Analyst* 2001, 126, 1573.
- Baldwin, I. P.; Christensen, J. K.; Kryger, L. *Anal Chem* 1986, 58, 1790.
- Etienne, M.; Bessiere, J.; Walcarius, A. *Sens Actuators B* 2001, 76, 531.
- Guadalupe, A. R.; Abruna, H. *Anal Chem* 1985, 57, 142.
- Turyan, I.; Atiya, M.; Mandler, D. *Electroanalysis* 2001, 13, 653.
- Rivas, B. L.; Pooley, S. A.; Brovelli, F.; Pereira, E.; Basaez, L.; Osorio, F.; J.-Moutet, C.; Aman, E. S. *J Appl Polym Sci* 2005, 98, 1192.
- O'Riordan, D. M. T.; Wallace, G. G. *Anal Chem* 1986, 66, 128.
- Rahman, M. A.; Won, M.-S.; Shim, Y.-B. *Anal Chem* 2003, 75, 1123.
- Rahman, M. A.; Park, D. S.; Won, M.-S.; Park, S.-M.; Shim, Y.-B. *Electroanalysis* 2004, 16, 1366.
- Shiu, K. K.; Chan, O.-Y. *J Electroanal Chem* 1995, 388, 45.
- Wagner, K.; Strojek, W. J.; Koziel, K. *Anal Chim Acta* 2001, 447, 11.
- Gutiérrez, J. A. R.; Domínguez, M. D. P.; Macías, J. M. P. *Anal Chim Acta* 2004, 524, 339.
- Brovelli, F.; del Valle, M. A.; Díaz, F. R.; Bernède, C. J. *Bol Soc Chil Quim* 2001, 46, 319.
- Córdova, R.; del Valle, M. A.; Gómez, H.; Schrebler, R. J. *Electroanal Chem* 1994, 377, 75.
- Rivas, B. L.; Maturana, H. A.; Pereira, E. *Angew Makromol Chem* 1995, 230, 89.
- Rivas, B. L.; Maturana, H. A.; Ocampo, X.; Peric, I. M. *J Appl Polym Sci* 1995, 58, 2201.
- Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. *J Polym Sci Part A: Polym Chem* 1997, 35, 2461.
- Rivas, B. L.; Moreno-Villoslada, I. *Polym Bull* 1997, 34, 656.
- Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2001, 22, 418.
- Rivas, B. L.; Pooley, S. A.; Luna, M. *J Appl Polym Sci* 2002, 83, 2556.
- Rivas, B. L.; Pereira, E. D.; Moreno-Villoslada, I. *Prog Polym Sci* 2003, 28, 173.
- Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1984; Chapter 10.