

# Preparation Electroactive Film of (*N*-pyrrolyl)1,1-Methane Dihydroxamic Acid and Its Derivative Containing Complexing Cavities Preformed by Entwining Ligands on Metallic Centers

Seyyed Hossein Hosseini

*Department of Chemistry, Faculty of Science, Islamic Azad University, Namaz Square, Sayad Shirazi Ave. Eslam-Shahr Branch, Tehran, Iran*

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**ABSTRACT:** The (*N*-pyrrolyl)1,1-methane dihydroxamic acid have been synthesized from its *N*-substituted ester group derivative, then chemically polymerized in the presence of oxidants such as ammonium persulphate and Iron (III) perchlorate for hydroxamic acid and ester groups derivatives, respectively. This compound and its ester group derivative was successfully electropolymerized by a cyclic voltammetry method. New functionalized polypyrrole films containing transition metal complexes have been prepared and studied. The strategy is based on the three-dimensional template effect of a metal center ( $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ) able to entwine two and three end functionalized chelating ligand before or after polymerization. The used ligand consists of a methyl dihydroxamic acid bearing one pyrrole nuclei. The rigidity of the polymer matrix is sufficient to allow demetalation of the template center (by  $\text{CN}^-$  or  $\text{SCN}^-$ ) without collapse of the three-dimensional structure. Such property is related to the expected complex

topology of the material prepared. The organic backbone certainly contains interlocking rings and various network substructures. The polymer matrix thus keeps a little memory of the templating metal used for building it. Fe(III) ion turned out to be the most convenient template during the polymer electrosynthesis and seemed to lead to the most structured network. The various complexes obtained using electrochemical synthesis method display electrochemical properties analogous to those of the corresponding catenate in solution. All complexes in low oxidation states are remarkably stabilized by the entwined and entangled system. The conductivity of these polymers and its metal complexes were measured using four-probe method. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 493–500, 2010

**Key words:** conducting polymer; hydroxamic acid; metal complexes; conductivity; chemical and electrochemical polymerization; polypyrrole

## INTRODUCTION

The electropolymerization of *N*-substituted pyrroles has attracted much interest as a route to the preparation of chemically modified electrodes.<sup>1–3</sup> Pyrrole groups have been attached to a range of amine ligands, and related compounds, and the feasibility of electrochemical oxidation of the pyrrole groups to give conducting polymer films investigated. The addition of one equivalent of hydrated metal salts, such as  $[\text{Zn}(\text{H}_2\text{O})_6][\text{ClO}_4]_2$ , is found to promote the electrochemical polymerization of the pyrrole-substituted amines in acetonitrile solution.<sup>4</sup> Electronic conducting polymers (ECP) are ideal candidates in such as molecular construction field and anion exchange.<sup>5,6</sup> First, their structure allows free interaction with ions and electrons, and second the synthe-

sis of such polymers is relatively easy since they are usually obtained as a film electrodeposited on the electrode surface.

The functionalization of ECP has turned out to be a powerful tool for the modification of electrode surfaces. This new approach to the immobilization of functional groups has moved from the inclusion of a suitable doping anion<sup>7–14</sup> toward the covalent grafting of a specific molecule to the ECP backbone through a spacer arm. Ferrocyanide,<sup>7</sup>  $\text{RuO}_4^{2-}$ ,<sup>8</sup> and sulfonated<sup>9</sup> and carboxylated porphyrins of cobalt,<sup>10</sup> iron, and manganese, as well as phthalocyanines of cobalt<sup>11</sup> and iron,<sup>12</sup> sulfonated dyes,<sup>13</sup> and heteropolyanions,<sup>14</sup> have been incorporated as dopants. To accomplish the covalent grafting, a suitable monomer is synthesized and subsequently electropolymerized.<sup>15–17</sup> Bidan et al.<sup>18</sup> prepared electroactive films of polypyrrole (PPy) containing complexing cavities preformed by entwining ligands on some of metallic centers.

In the preceding works,<sup>19</sup> we have prepared polyheteroaromatics from pyrrole, indole, and carbazole containing one hydroxamic acid group. This func-

Correspondence to: S. H. Hosseini (hosseini\_sh44@yahoo.com).

tional group N-substituted to zero, one, and two methylenic spacer to their compounds. Chemical and electrochemical polymerization samples of without spacer between ring and hydroxamic acid are neither sufficient growth nor high electrical conductivity. On the other hand, samples with one and two methylenic spacers have either sufficient growth or high conductivity. This phenomenon is for electron withdrawing and deactivating effects of hydroxamic acid to aromatic rings. We have studied complexation of polypyrrole with some of transition metals successfully. On continuing this work,<sup>20</sup> we increased reactivity and conductivity on the surface electrode with synthesis of poly(diheteroaromatics) such as pyrrole, indole, carbazole, and their mixed containing hydroxamic acid group. Although polymers grow on the surface electrode but complexation of properties decreased.

In the present work, we have prepared (*N*-pyrrolyl) 1,1-methane dihydroxamic acid that have a methylenic spacer with two ligand groups. This compound either increase conductivity, reactivity, or complexation properties. Polyhydroxamic acid film containing transition metal complexes have been prepared and studied in various pH.<sup>21</sup> Herein work, we have studied some of transition metal complexation such as Fe<sup>III</sup>, Cr<sup>III</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> with various potentials by used cyclic voltammetry (CV) method.

## EXPERIMENTAL

### Instrumentals and materials

Proton nuclear magnetic resonance (FT-<sup>1</sup>H NMR) spectra was recorded at 400 MHz on a Bruker WP 200 SY spectrometer. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and integration. FTIR spectra were recorded on a 8101M—Shimadzu, (*w*, wide; *sh*, sharp; *m*, middle; *s*, short). UV-visible spectra were obtained from filmed tin oxide glass electrodes by Perkin-Elmer Lambda 15 spectrophotometer and mass spectra with a Kratos MS80. GC-chromatogram was recorded on C-R4A SHIMADZU with the following conditions: Column = CBP-5, *L* = 25 m, ID = 0.33, Film thickness = 0.5 μm, Column Temp. = 35°C (hold 2 min) to 280°C (hold 7 min) (Rate = 15°C/min), Det. Temp. = FID 320°C, Inj. Temp. = 280°C (split, lilco, sample size 1 μL), Inlet Pre. = 0.8 atm, He. Cyclic voltammetry and electrochemical polymerization was carried out using a digital potentiostat/galvanostat DP8 (home made). Pyrrole (GPR) was dried with NaOH, fractionally distilled under reduced pressure from sodium or CaH<sub>2</sub>. Acetonitrile (Merck) was dried on silica gel, distilled on phosphoroxide and then on calcium hydride in the

presence of a nitrogen stream. All the other materials used in this work were purified commercial products, or were prepared by literature methods.

### Preparation of pyrrolyl potassium salt

Freshly distilled pyrrole (4.0 g, 0.06 mol) was diluted with about 100 mL of petroleum, which is boiled at about 110°C or xylene, that is, well above the melting point of potassium. Such a mixture was gently warmed, and metallic potassium (2 g, 0.05 mol) was gradually added in small, clean pieces. The addition of each piece of the metal caused brisk evolution of hydrogen, while potassium pyrrole separated out as a fine, nearly white precipitate. During the early stages of the preparation, the flask in which the operation took place required external cooling, but at the end temperature was raised so as to melt the potassium to secure complete action, hence the use petroleum (boiling point is about 110°C). When all metallic particles had disappeared, the pyrrole potassium salt was rapidly collected (using funnel plugged with asbestos), the precipitate was then well washed with light petroleum of low boiling point, and dried in under N<sub>2</sub> atmosphere. The slightly yellow powder so obtained must be carefully protected from moisture.

### Preparation of *N*-pyrrolyl diethyl malonate (I)

Diethylchloromalonate (9.73 g, 0.05 mol) in 20 mL anhydrous THF was added dropwise to the pyrrolyl potassium salt (5.25 g, 0.05 mol) suspended in 20 mL dry THF at 0°C. After 4 h, the mixture was added 50 mL water and 20 mL diethyl ether and then filtrated. Organic layer was separated and evaporated to give the crude C- and N-substituted compounds. *N*-pyrrolyl diethyl malonate was purified by alumina column chromatography appropriate solvents (petroleum ether/ethylacetate: 2/5), or by distillation under reduced pressure (yield 68%).

bp = 70–72°C/20 mmHg; UV (acetonitrile): λ<sub>max</sub> = 215 nm.

FTIR: 3140(m), 2995(s), 1750(sh), 1470(m), 1420(m), 1370(m), 1150(sh), 990(s), 780(s) cm<sup>-1</sup>. FT-<sup>1</sup>H NMR (CDCl<sub>3</sub>) = δ 6.8(d, 2H), 6.2(d, 2H), 4.8(s, 1H), 4.3(q, 2H), 1.3(t, 3H) ppm. Electron impact mass spectrum: *m/z* 225 as calc. for (I) (M<sup>+</sup>).

### Preparation of (*N*-pyrrolyl)1,1-methane dihydroxamic acid (II)

In a 250-mL three-necked flask, equipped with a dropping funnel, stirrer and thermometer, about 50 mL of methanol, 5.56 g (0.08 mol) hydroxylamine hydrochloride and 5 g (0.02 mol) of potassium hydroxide in 20 mL methanol were added (pH > 12).

After the mixture was cooled to 0°C, 4.5 g (0.02 mol) of *N*-pyrrolyl diethyl malonate dissolved in 50 mL of methanol (or diethyl ether) was added dropwise over a period of about 1 h. The temperature was maintained at 0°C for an additional 30 min, then mixture was stirred for 36 h at room temperature. Then crude solution was filtered and evaporated on a rotary evaporator. The resulting material was acidified by 20 mL (50 : 50) acetic acid and water, and then extracted by 100 mL diethyl ether in two stages. The (*N*-pyrrolyl)1,1-methane dihydroxamic acid (II) was purified by column chromatography with appropriate solvents (petroleum ether/chloroform/ethyl acetate(1 : 1 : 5), evaporation of the solvent afforded pure compound, or by distillation under reduced pressure. Therefore, we concentrated aqueous phase, then added ethanol and filtrated. The product (II) was purified by evaporation ethanol and then fractionation distillation under reduced pressure, too.

bp = 95–97°C/5 mmHg; UV (acetonitrile):  $\lambda_{\max}$  = 220 nm.

FTIR: 3744(s), 3649(m), 3198(w), 2995(s), 1674(w), 1556(m), 1420(m), 1375(m), 1234(s), 1149(sh), 1057(m), 983(s), 887(s), 688(s)  $\text{cm}^{-1}$ .

FT-<sup>1</sup>H NMR ( $\text{CDCl}_3$ ) = 6.6(d, 2H), 6.1(d, 2H), 4.3(s, 2H), 3.8(s, 2H), 2.6(s, 1H) ppm.

GC-chromatography = R.T = 8.9 (97.78%).

Electron impact mass spectrum:  $m/z$  199 as calc. for (II) ( $\text{M}^+$ ).

### Chemical polymerization of *N*-pyrrolyl diethyl malonate (I)

Chemical polymerization of compound I was carried out in a conventional reaction vessel. The bottom of the reaction vessel was covered with 25 mL  $\text{HClO}_4$  9.1M containing 8.1 g  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ . A definite amount of monomer was dissolved in 15 mL benzene and then floated on the surface of the aqueous solution in the vessel. After a period of time, the polymeric film was formed at the interface of the aqueous/organic solutions at room temperature under a  $\text{N}_2$  atmosphere. A polymeric film without air exposure was repeatedly washed with acetone at reflux conditions and then dried under vacuum for 2 h.

### Chemical polymerization of (*N*-pyrrolyl)1,1-methane dihydroxamic acid (II)

Chemical polymerization of (*N*-pyrrolyl)1,1-methane dihydroxamic acid (II) was carried out as the following procedure. A solution of compound II (0.057 mol) in 75 mL HCl (1M) was mixed with a solution of ammonium persulphate (3 g) in 50 mL HCl (1M). The mixture was cooled at 0–5°C. After a few minutes the color of solution changed and the pow-

dered polymer was formed. The mixture was filtered after 1 h and the powder washed with HCl (1M) and acetone. The polymer was dried in vacuum.

### Preparation of metal complexes with poly(II), poly[ $\text{M}(\text{L})_n$ ]

#### Preparation of poly[ $\text{Fe}(\text{L})_3$ ]

To prepare the polymer product of this material, 0.440 g of compound II (4.11 mmol) was added under  $\text{N}_2$  atmosphere into a solution of anhydrous  $\text{FeCl}_3$  (0.326 g, 2 mmol) in 50 mL THF containing 4 mL of pyridine. The mixture was stirred for 5 h at room temperature, and evaporated under reduced pressure to give a solid residue. The remains were washed several times with ether, and then dissolved in 100 mL dichloromethane, washed with water, the organic layer was separated and finally after evaporating the solvent gave the red color complex.

FTIR: 3501(w), 3350(s), 3010(m), 2990(m), 1610(sh), 1450(sh), 1408(s), 1050(sh), 990(m), 780(m)  $\text{cm}^{-1}$ . UV (acetonitrile):  $\lambda_{\max}$  = 209, 260, 340, and 420 nm.

#### Preparation of poly[ $\text{Cr}(\text{L})_3$ ]

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (6.4 g, 16 mmol) was dissolved in 30 mL water and stirred-magnetically. Then poly(II) (3.42 g, 32 mmol) dissolved in 150 mL of water was added, followed by a buffer solution of 0.1N of NaOAC-HOAC for attaining a fixed pH = 4.7. The final mixture was stirred 12 h at room temperature. After filtration, a solid precipitate (greenish blue) was obtained and recrystallized from THF.

FTIR: 3501(w), 3340(m), 3008(s), 2993(m), 1610(sh), 1450(sh), 1405(s), 1010(sh), 870(m)  $\text{cm}^{-1}$ .

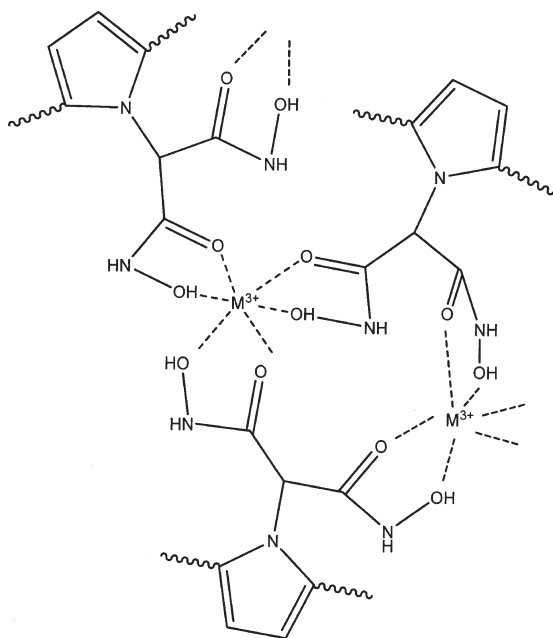
#### Preparation of poly[ $\text{Cu}(\text{L})_2$ ]

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.067 g, 0.4 mmol) was dissolved in 20 mL water, then poly(II) (0.059 g, 0.55 mmol) was added into it, and the pH = 4–5 with dilution with  $\text{H}_2\text{SO}_4$  was reached. The green color complex was obtained by washing with water and ether and then dried.

FTIR: 3490(m), 3360(m), 3010(s), 2990(s), 1620(sh), 1455(sh), 1420(m), 1010(sh), 880(m)  $\text{cm}^{-1}$ .

#### Preparation of poly[ $\text{Ni}(\text{L})_2$ ]

$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  (0.094 g, 0.4 mmol) dissolved in 10 mL water was added to the solution of poly(II) (0.059 g, 0.55 mmol) dissolved in 20 mL water. Diluted NaOH was added until fixed pH = 8.3. The blue precipitate was obtained, after washing with water and ether, the pure blue color complex was obtained.

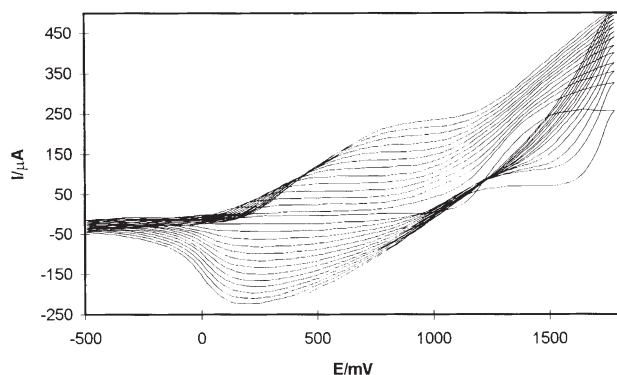


**Figure 1** Three dimensional coordination structure poly  $[M(L)_3]$ .

FTIR: 3650(sh), 3520(w), 3010(s), 2990(s), 1650(sh), 1470(sh), 1420(m), 1015(m), 880(m)  $\text{cm}^{-1}$ .

### Electrochemical polymerization

All electrochemical polymerizations of **I** and **II** compounds, were performed using a conventional three electrode system,  $6 \times 10^{-3} \text{M}$  of monomer, 0.1M  $\text{Bu}_4\text{NPF}_6$ , 20 mL acetonitrile, and employing GC disc working electrode, SCE reference electrode and a platinum wire as counter electrode. All solutions for electrochemical polymerization was freshly prepared using acetonitrile distilled from calcium hydride and stored over  $3^\circ\text{A}$  molecular sieves. Tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in 20 mL aceto-



**Figure 2** Cyclic voltammograms of *N*-pyrrolyl methane dicarboxylic acid  $6 \times 10^{-3} \text{M}$  in acetonitrile,  $\text{Bu}_4\text{NPF}_6$  0.1, GC disk electrode versus SCE, scan rate = 50 mV/s (15 cycles).

nitrile was bubbling dry oxygen free nitrogen for at least 20 min before each polymerization. Polymers were grown on GC disc electrode under potential scan in the range of  $-250$  to  $1250$  mV. The cyclic voltammetry of complexation poly(**II**) with  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  were performed by using lithium perchlorate ( $\text{LiClO}_4$ ) 0.1M as supporting electrolyte and  $\text{Ag}/\text{AgCl}$  as reference electrode with the same above conditions.

## RESULTS AND DISCUSSION

### UV spectrophotometry

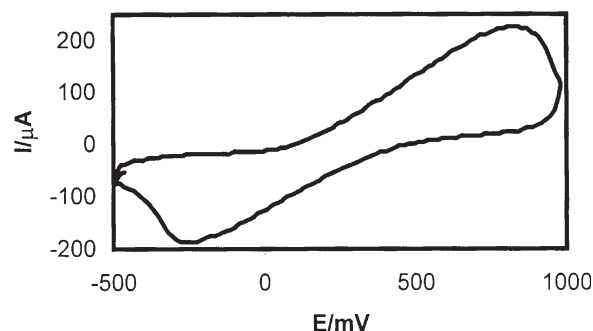
UV spectral results of compounds **I**, **II** show a shift to higher wavelengths for **II** because of increased density of electron intensity. On the other hand, comparison of UV spectra between the compounds **II** and **II-Fe** complex shows that the decrease of bond intensity corresponding to a  $n \rightarrow n^*$  transition of the oxygen atom of a carbonyl group is due to interaction with the metal. The increase of bond intensity corresponding to an  $n \rightarrow n^*$  transition of nitrogen atom is due to nonbonding interaction with the metal that is another confirmation for coordination of metal with an oxygen atoms.<sup>19</sup>

### Design of the ligand

As shown in Figure 1(a,b), two and three highly rigid coordinating fragments built on hydroxamic acid units could be held in an entwined geometry by  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$ . The pseudotetrahedral geometry of the precursor complex is such that after polymerization of the *N*-anchored pyrrole rings, a highly entangled network is obtained.

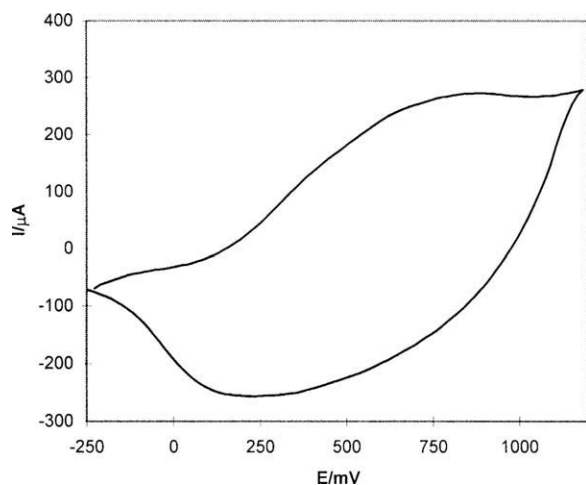
### Cyclic voltammetric behaviors

Oxidative electropolymerization of the various substituted pyrrole was carried out either by reported potential scanning or by electrolysis at a fixed potential by analogy with previously reported works.<sup>4,22</sup>



**Figure 3** Cyclic voltammogram of Poly(*N*-pyrrolyl diethyl malonate), Poly **I**, in acetonitrile,  $\text{Bu}_4\text{NPF}_6$  0.1, GC disk electrode versus SCE, scan rate = 50 mV/s.

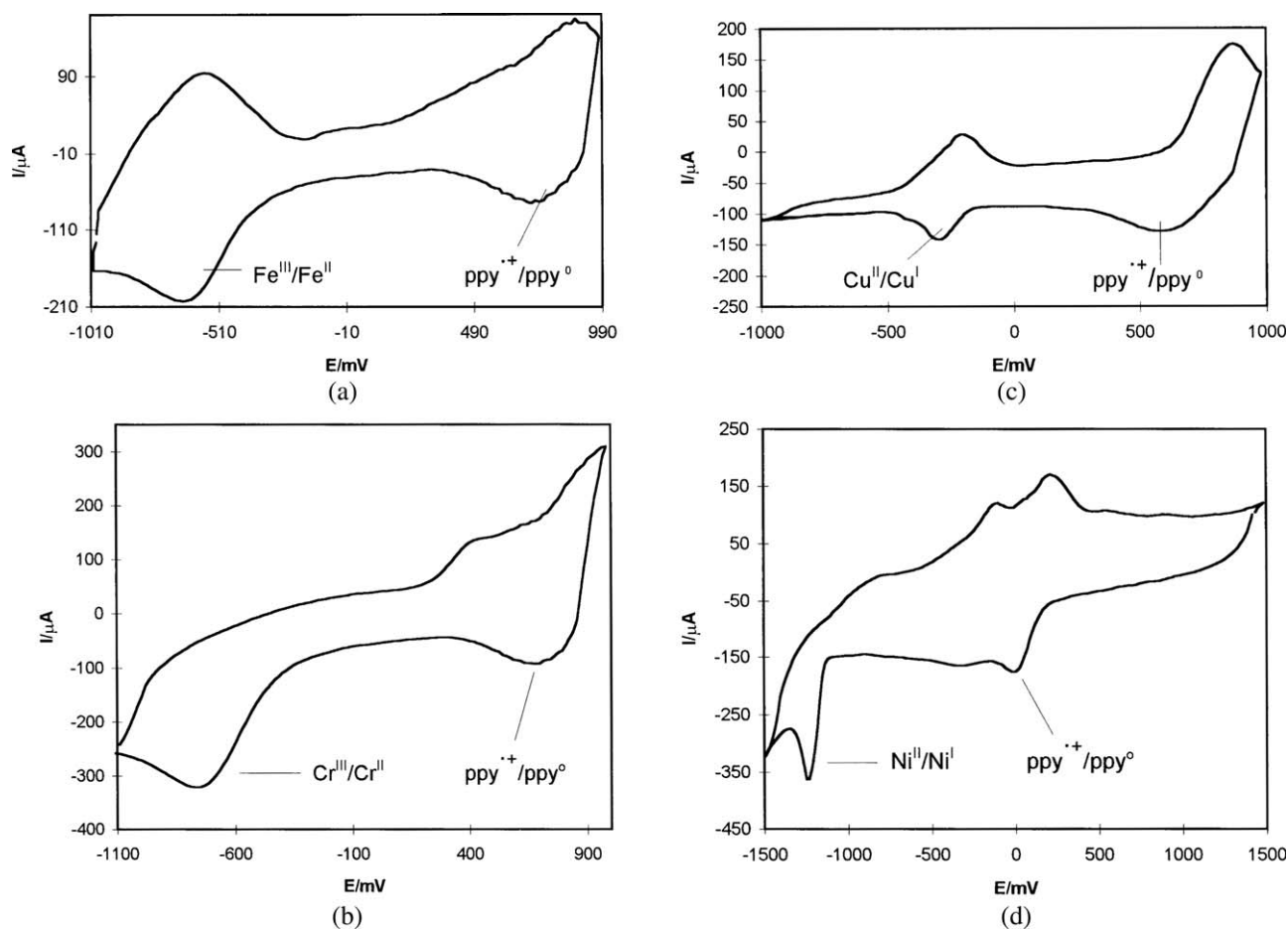




**Figure 4** Cyclic voltammogram of Poly(*N*-pyrrolyl methane dicarbohydroxamic acid), Poly II, in acetonitrile,  $\text{Bu}_4\text{NPF}_6$  0.1M, GC disk electrode versus SCE, scan rate = 50 mV/s.

The species resulting from oxidation of the precursor monomers polymerized and led to a film deposited on the electrode. This process could easily be followed visually (appearance of a colored deposit coating the electrode surface). The strategy favors the formation of immobilizes cavities ready for complexing any transition metal species provided the geometrical agreement between the coordination site and the metal is good enough, since the polymer matrix is built around the complexing metal during the electropolymerization process. In addition, formation of the film was monitored by CV.

These monomers electropolymerized by a cyclic voltammetry method in acetonitrile, with  $\text{Bu}_4\text{NPF}_6$  0.1M, GC disk working electrode and SCE reference electrode. Poly(II) obtained by electropolymerization was precipitated completely on an electrode surface. But poly(I) cannot be precipitated completely on an electrode surface. We know heteroaromatics contain-



**Figure 5** Cyclic voltammogram of (a) poly([Fe(*N*-pyrrolyl methane dicarbohydroxamic acid)<sub>3</sub>]), Poly(II-Fe<sup>III</sup>), (b) poly([Cr(*N*-pyrrolyl methane dicarbohydroxamic acid)<sub>3</sub>]), Poly(II-Cr<sup>III</sup>), (c) poly([Cu(*N*-pyrrolyl methane dicarbohydroxamic acid)<sub>2</sub>]), Poly(II-Cu<sup>II</sup>), and (d) poly([Ni(*N*-pyrrolyl methane dicarbohydroxamic acid)<sub>2</sub>]), Poly(II-Ni<sup>II</sup>), films on glassy carbon electrode (diameter 3 mm) in acetonitrile versus Ag/AgCl,  $\text{LiClO}_4$  0.1M, scan rate = 50 mV/s.

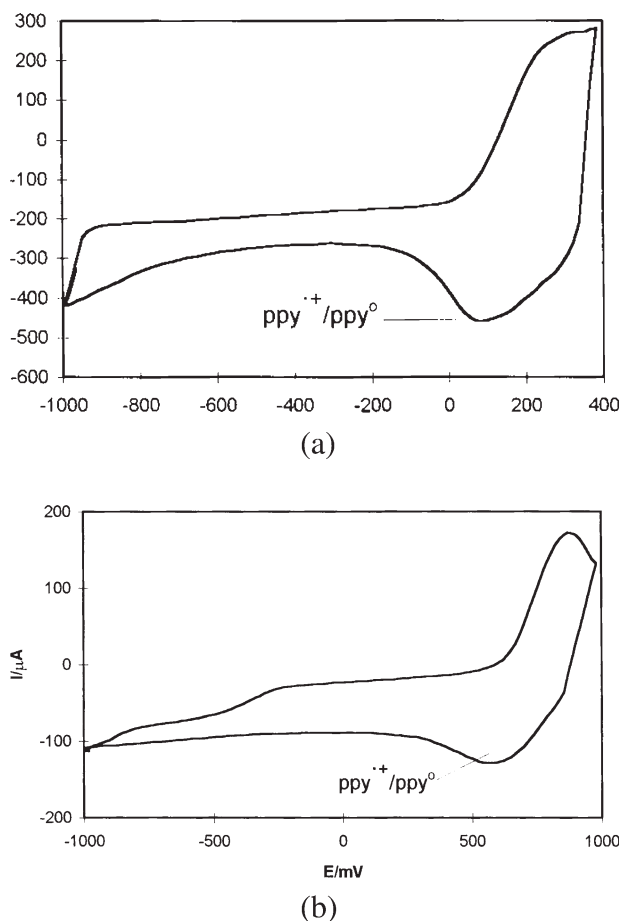
ing *N*-substituted withdrawing electron groups, would be deactivated. Figure 2 show the cyclic voltammogram of compound II and Figures 3 and 4 show the cyclic voltammograms of their blank poly(I) and (II).

The modified electrodes so obtained could be washed, dried and stored in air for some time. The cyclic voltammetry of complex of poly(II) with Fe<sup>III</sup>, Cr<sup>III</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> were performed, using LiClO<sub>4</sub> 0.1M as supporting electrolyte and Ag/AgCl reference electrode as described previously. The cyclic voltammetry studies were performed on poly([Fe(L)<sub>3</sub>]), poly([Cr(L)<sub>3</sub>]), poly([Cu(L)<sub>2</sub>]), and poly([Ni(L)<sub>2</sub>]) and are shown in Figures 5(a,b).

In each case, the resulting polymers have similar CVs. On the four metal complexes, Fe and Cu complexes are the most effective, giving smooth adherent polymer films on the electrode and shown symmetric voltammograms. These films are initially green, but turn red on washing with acetonitrile. All complexes stable under electrochemistry conditions. Oxidation potentials of complexes higher than poly(II), (moiety PPy), but for poly [Ni(L)<sub>2</sub>] it is similar. Therefore, electrochemistry behavior is better and passed more currently. Herein we used LiClO<sub>4</sub> instead Bu<sub>4</sub>NClO<sub>4</sub>, because it electrochemically behavior is better. In our future research, we will study the effect of variation of carrier electrolytes on the CV of complexes.

#### Demetalation of poly([M-(L)<sub>2</sub>]) and poly([M-(L)<sub>3</sub>])

The rigidity of the polymer matrix is sufficient to allow demetalation of the template center (by CN<sup>-</sup> or SCN<sup>-</sup>) without collapse of the three-dimensional structure. Such property is related to the expected complex topology of the material prepared. In our approach, one end-functionalized with two chelating fragments are coordinated to a potentially easily removable transition metal prior to electropolymerization, so as to entwine the complexing moieties. The obtained material in this way must be highly entangled in nature, this characteristic being kept even after demetalation. Bidan et al.<sup>22</sup> demetalated polypyrrole containing phenanthroline derivatives by action of cyanide ions by simply dipping the polymer films into an acetonitrile-water-potassium cyanide solution. In the same method, using potassium thiocyanate instead of cyanide, demetalation of various polymeric films built around Fe<sup>III</sup> complexes can be performed. Figure 6(a,b) illustrates the electrochemical behavior of poly(II) films before complexation with Fe<sup>III</sup> and after treatment with the releasing agent. After demetalation, the electroactivity of the polymeric matrix is nearly like to *N*-alkyl polypyrrole films. But demetalation show a history



**Figure 6** Electrochemical behaviors of poly(*N*-pyrrolyl methane dicarbohydroxamic acid), poly(II), (a) before complexation and (b) after demetalation on glassy carbon electrode (diameter 3 mm) in acetonitrile versus Ag/AgCl, LiClO<sub>4</sub> 0.1M, scan rate = 50 mV/s.

effect and higher oxidation potential poly(II) illustrated in Figure 6(b).

#### Polymerization and conductivity

Poly(I) and poly(II) were prepared at room temperature by contact between an aqueous solution of HClO<sub>4</sub> 9.1M containing Fe(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O and ammonium persulfate in aqueous solution of HCl (1M) under N<sub>2</sub> atmosphere, respectively. Therefore, we have calculated electrical conductivities of its complexes that poly [Fe(L)<sub>3</sub>] is better. Conductivities of complexes decreased for less coplanary main chain polymer. Four-probe electrical conductivity data were measured on compressed (6 ton/cm<sup>2</sup>) pellets of the polymers (Table I).

#### Stability to electrochemical cycling

The studies of the electrochemical polymer response were performed on poly([Fe(L)<sub>3</sub>]), poly([Cr(L)<sub>3</sub>]),

TABLE I  
Conductivity of Poly(I) and Poly(II) and Metallic Complexes of Poly(II)

Polymer	Oxidant	Conductivity (S/cm)	Physical properties
Polypyrrole	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	1 × 10 <sup>-2</sup>	Black, smooth, slightly flexible, strong
Poly(I)	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	3.3 × 10 <sup>-5</sup>	Black, smooth, most flexible, strong
Poly(II)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , HCl	9.2 × 10 <sup>-4</sup>	Green, smooth, most flexible, strong
Poly[Fe(L) <sub>3</sub> ]	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , HCl	3.2 × 10 <sup>-4</sup>	Red, smooth, strong
Poly[Cr(L) <sub>3</sub> ]	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , HCl	1.5 × 10 <sup>-5</sup>	Greenish blue, strong
Poly[Ni(L) <sub>2</sub> ]	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , HCl	6.5 × 10 <sup>-5</sup>	Blue, slightly smooth, strong
Poly[Cu(L) <sub>2</sub> ]	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , HCl	4.5 × 10 <sup>-5</sup>	Green, smooth, strong

poly([Cu(L)<sub>2</sub>]), and poly([Ni(L)<sub>2</sub>]) by cycling the corresponding modified electrode in the electroactivity range of the polymeric matrix activity at 50 mV/s. During the electrooxidative polymerization process, protons are liberated from pyrrole. Since the metal free polymers described in the present work contain basic sites (hydroxamic acid oxygen atoms), the protons generated in the course of film growth can be trapped in the material. It is therefore necessary to perform a careful neutralization by dipping the film in a basic solution prior to further studies. The poly([Cr(L)<sub>3</sub>]) shows a lesser stability than polypyrrole itself, in accordance with the observed stability of other N-substituted pyrroles.

### Thermal properties

Thermal properties of poly(II) can also be noted from the oxidative degradation curves through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies. The representative TGA and DSC curve is shown in Figure 7. The methods of interpreting TGA results are numerous and also do not exactly follow the standard previous pattern. Five percentage loss of temperature or on the temperature inflection of the downward slope, or by the first detectable break in the curve is observed. The initial decomposition temperature, the tempera-

ture at 5% weight loss (PDT), and the maximum polymer decomposition temperature (PDT<sub>max</sub>) ranged from 200 to 300°C. The residual weights (γ<sub>c</sub>) of the polymers were reported at 600°C. This polymer was stable in N<sub>2</sub> up to temperature presented.

### CONCLUSIONS

In continuation of the preceding work, we have synthesized a new heteroaromatic compound containing two hydroxamic acid groups. The monomer (II) grows on the surface of electrode and makes sufficient electrical conductivity. The modified electrode can be complexed with some of transition metals in different potentials. The produced complexes are demetalated by simple dipping in thiocyanate or cyanide solution. The prepared modified electrode seems to be used for detection, separation, and measurement some of transition metals in different environments successfully. The electrical conductivity decreases by the steric bulk complexation, because coplanarity in geometry is decreased. This can be improved with increasing length of the spacer arm between the pyrrole and the hydroxamic acid ligand, which is consistent with our previous findings.<sup>19</sup> So this effect is decreased by spacer arm for complexes, and if there are longer arms, the electrical conductivity will be improved.

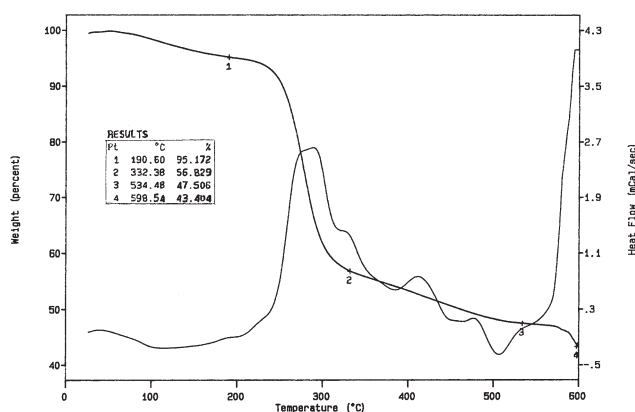


Figure 7 STA (DSC and TGA) thermograms of poly(II).

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