

Synthesis of Conducting Poly[di-heteroaromatics] from Pyrrole, Indole, and Carbazole, and Their Mixed Hydroxamates, and Studies of Their Metal Complexes

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ABSTRACT: Compounds 1,1-di-(*N*-pyrrolyl)methane hydroxamic acid (**II**), 1,1-di-(*N*-indolyl)methane hydroxamic acid (**IV**), 1,1-di-(*N*-carbazolyl)methane hydroxamic acid (**VI**), 1-(*N*-pyrrolyl)-1-(*N*-carbazolyl)methane hydroxamic acid (**VIII**), and 1-(*N*-pyrrolyl)-1-(*N*-indolyl)-methane hydroxamic acid (**X**) were synthesized from their *N,N*-substituted ester group derivatives. They were chemically polymerized in the presence of oxidants such as ammonium persulfate and iron(III) perchlorate for hydroxamic acid and ester groups derivatives, respectively. The conductivity of these polymers was measured by a four-point probe method. The complexes of hydroxamic acid derivatives with

certain ions [such as Fe(III), Rh(III), Ir(III), Cr(III), Cu(II), and Ni(II)] were studied. Compounds **II**, **IV**, and **VI** and their ester group derivatives were successfully electropolymerized by a cyclic voltammetry method under the following conditions: 6×10^{-3} M of monomer, 0.1 M lithium perchlorate, 20 mL of acetonitrile, glassy carbon (GC) disk working electrode, and Ag/AgCl reference electrode and platinum wire counter electrode conditions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 63–71, 2003

Key words: conducting polymers; metal-polymer complexes; heteroatom-containing polymers

INTRODUCTION

The chemistry of hydroxamic acid was elucidated in 1869, when H. Lossen, working in W. Lossen's laboratory, isolated oxalohydroxamic acid from the reaction products of ethyl oxalate and hydroxylamine.¹ Extensive work has been carried out on the formation, reactions, and structures of hydroxamic acid-containing compounds (hydroxamates) in the ground state.

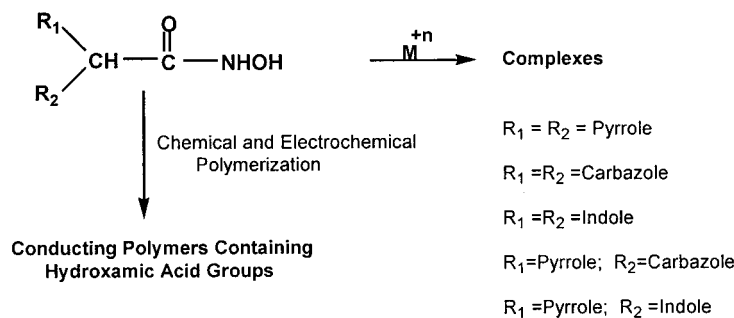
Hydroxamates are ubiquitous and are intimately associated with iron transport phenomena. The selectivity of this mechanism is critical because numerous other metal ions, which may not be essential or which may have a toxic effect on the organism, are present in the environment.² The single hydroxamic acid group behaves as typical bidentate donor towards various metal ions. Monohydroxamic acids have the form of octahedral complexes with a number of metal ions coordinating via two oxygen atoms of the deprotonated hydroxamic acid group. This structure has been proven, for example, in the X-ray studies of solid-state tris(benzohydroxamic acid) iron(III) dihydrate³ and tris(benzohydroxamic acid)chromium(III).⁴ Brown et al.⁵ also studied solid-state complexes of Fe(III), Co(II),

Cu(II), and Ni(II) with monohydroxamic acids. Hydroxamic acid is also known as constituent of growth factors, food additives, antibiotics, antibiotics antagonists, tumor inhibitors, antifungal agents, and cell division factor, several of which have been used as drugs.^{6–11}

Reports of the use of hydroxamic polymers as ion exchangers have appeared sporadically over the past 50 years.¹² Polymers are synthesized by either polymerization of vinyl monomers bearing hydroxamic acid groups^{13,14} or by converting functional groups in a polymer into hydroxamic acids.^{15,16} As in the case of conductance, other physical properties of these polymers are a strong function of the macromolecular structure of conducting polymers. Just as many attempts have been made to improve the electronic properties, so too has considerable effort gone into improving chemical and physical properties.¹⁷ One of these chemical properties is the ability to complex with certain metal ions.

The electrochemical synthesis of electrically conducting organic polymers, first described with polypyrroles,¹⁸ has proven important in allowing development of new polymeric materials with similar electrochemical and/or electrical properties. Using an electrochemical synthetic approach, semiconducting polymers have been obtained from a wide variety of monomers, including thiophene,¹⁹ furan,²⁰ carbazole,²¹ indole,²² and azulene.²³ The availability of

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Scheme 1

these various polymers presents a unique opportunity to investigate the effect of substituents on the overall properties of these materials. In particular, as has already been shown in a few isolated cases, simple substituents placed strategically on the monomer moiety allowed variations in the properties of various polymers. For example, polypyrrole films that are substituted with alkyl groups in the 1-position of pyrrole ring may electrooxidize polypyrrole anodically by ~ 800 mV. As a result, these films are more stable towards oxygen. However, 1-alkyl-substituted films are less electrically conducting than the parent polypyrrole, an effect attributed to steric constraints imparted by the bulky substituents. For example, polypyrrole has an electrical conductivity of $\sim 100 \text{ ohm}^{-1} \text{ cm}^{-1}$, whereas 1-methyl, 1-ethyl or 1-*n*-propyl polypyrroles have conductivities of the order $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.²⁴ Although these 1-substituents reduce the electrical conductivity of polypyrrole dramatically, the electron donor or acceptor substituents can improve the overall conductivity of other polymer films.²⁴

In our preceding work,²⁵ we synthesized heteroaromatics from pyrrole and carbazole, but the products could not be precipitated completely on a platinum electrode surface. In this work, therefore, di-heteroaromatics (such as, pyrrole, indole, and carbazole) and their mixtures containing ester and hydroxamic acid groups were synthesized (Scheme 1). These compounds could have good electrodeposition behavior on a glassy carbon (GC) electrode surface.

EXPERIMENTAL

Instruments and materials

Melting points were measured with a electrothermal 9100 melting point apparatus. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) and Fourier transform $^1\text{H-NMR}$ (FT- $^1\text{H-NMR}$) spectra were recorded at 200 and 400 MHz on a Bruker WP 200 SY spectrometer. The $^1\text{H-NMR}$ data are reported in the following order: chemical shift (ppm), spin multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet), and integration. Infrared (IR) spectra were measured on a

Cary recording spectrophotometer, Model 127, Infra-cord. Fourier transform infrared (FTIR) spectra were recorded on a 8101 M - Shimadzu. Ultraviolet-visible (UV-vis) spectra were obtained from films of tin oxide glass electrodes with a Perkin Elmer Lambda 15 spectrophotometer, and mass spectra were recorded with a Kratos MS80.

Pyrrole (GPR) was dried with NaOH and fractionally distilled under reduced pressure from sodium or CaH_2 . Carbazole (Aldrich) was purified by sublimation in a vacuum, followed by crystallization in acetic acid, washing in water, and drying ($\text{mp} = 246^\circ\text{C}$). Indole (Merck) was purified by crystallization from benzene and water or ethanol and water (1:10). Acetonitrile (Merck) was dried on silica gel and 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 methods published in the literature.

Preparation of monomers

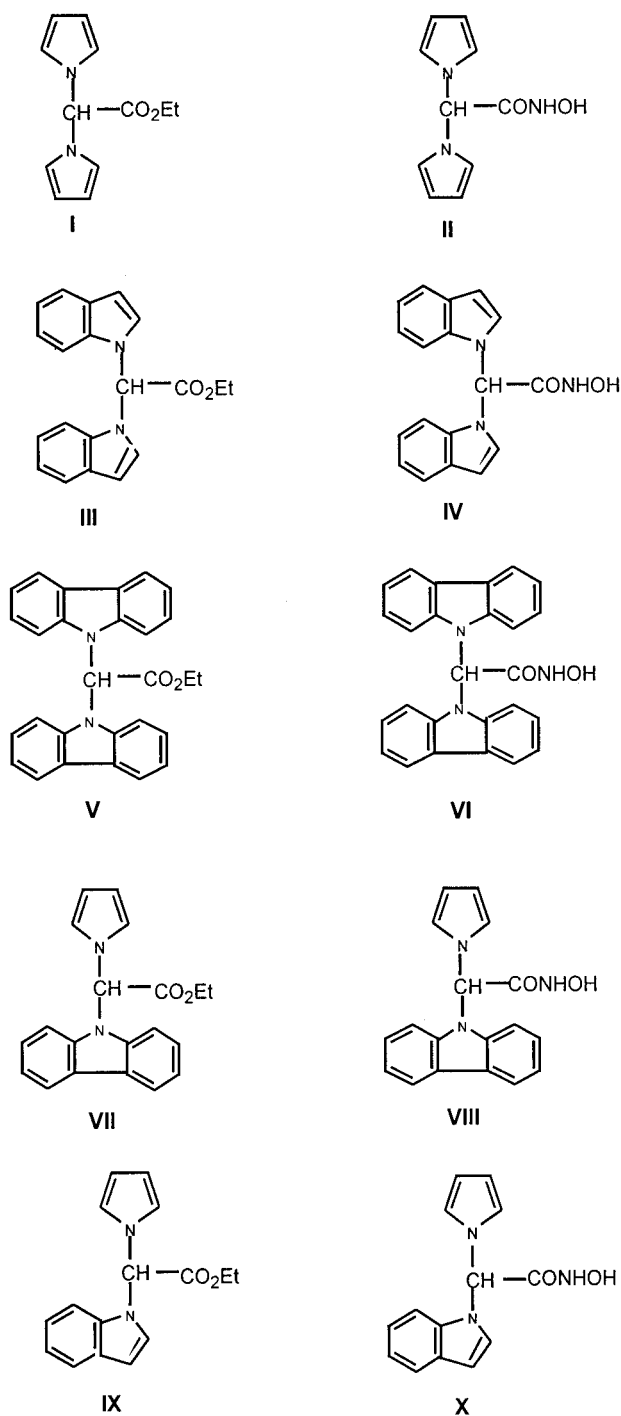
Monomer structure

The structures of the monomers synthesized in this study are shown in Scheme 2.

General synthesis of compounds I, III, and V

Potassium salts (0.05 M) of *N*-substituted I, III, and V^{26,27} were reacted with dichloroethyl acetate (0.025 M) in 50 mL of anhydrous tetrahydrofuran (THF) at 5°C . After 4 h, the mixture was filtered and water (50 mL) was added to the filtrate. The organic layer was then separated and evaporated to give the crude C- and N-substituted compounds. These compounds were purified by alumina column chromatography (using appropriate solvents; e.g., petroleum ether/ethylacetate/methanol, 1:5:15) or by distillation under reduced pressure.

1,1-Di-(N-pyrrolyl)ethyl acetate (I). Compound I was found to have the following characteristics: boiling point (bp) = $88\text{--}90^\circ\text{C}/20 \text{ mmHg}$; UV (CH_3CN): λ_{max}



Scheme 2

= 215 nm; FTIR: 3020, 2960, 1720, 1400, 1100, 1000 cm^{-1} ; $^1\text{H-NMR}$ (CCl_4) δ 6.71 (s,4H), 5.8 (s,4H), 5.3 (s,1H), 4.3 (q, 2H), 1.4 (t,3H) ppm.

ANAL. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ (218.26): C, 66.04%; H, 6.46%; N, 12.84%; O, 14.66%. Found: C, 66.45%; H, 6.81%; N, 13.20%; O, 14.65.

1,1-Di-(N-indolyl)ethyl acetate (III). Compound III was found to have the following characteristics: melting point (mp) = 184–185°C; UV (CH_3CN): λ_{max} = 220,

271.3, 277.1, and 287.4 nm; FTIR: 2990, 1700, 1300–1400, 1200, 1090, and 700 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 6–8 (m,12H), 5.7 (s,1H), 4.3 (q, 2H), and 1.35 (t, 3H) ppm.

ANAL. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2$ (318.38): C, 75.45%; H, 5.70%; N, 8.80%; O, 10.05%. Found: C, 76.21%; H, 6.41%; N, 9.36%; O, 10.06%.

1,1-Di-(n-carbazolyl)ethyl acetate (V). Compound V was found to have the following characteristics: mp = 214–215°C; UV (CH_3CN): λ_{max} = 208 and 227 nm; FTIR: 3110, 2995, 1720, 1500, 1450, 1300–1200, and 1100–1000 cm^{-1} ; FT- $^1\text{H-NMR}$ (CDCl_3): δ 7–8 (m, 16H), 4.9 (s, 1H), 4.2 (q, 2H), and 1.1 (t, 3H) ppm.

ANAL. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2$ (418.50): C, 80.36%; H, 5.30%; N, 6.69%; and O, 7.65%. Found: C, 80.86%; H, 5.73%; N, 7.2%; and O, 7.65.

General synthesis of compounds VII and IX

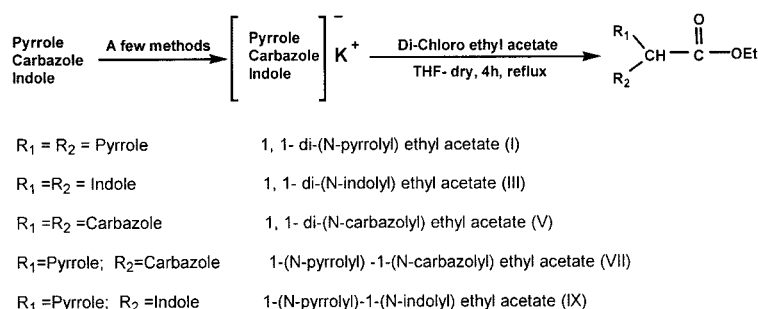
N-Carbazole or *N*-indole potassium salt (0.05 M) were suspended in 100 mL of dry THF. Then, a solution of dichloroethyl acetate (0.05 M) in 50 mL of ether was added in a dropwise manner into this suspension at 0°C over a period of 0.5 h. The mixture was then stirred for 1 h at room temperature. During the following 0.5 h, *N*-pyrrole potassium salt (0.05 M) in 20 mL of dry THF was added to the mixture in a dropwise manner at –5°C. The mixture was again stirred for 1 h at room temperature. Then, 200 mL of water was added to the mixture, the mixture was stirred for 1 h, and then the water was extracted by treatment with 3×50 mL of diethyl ether. The evaporation of solvent gives crude material that is purified by column chromatography with appropriate solvents (petroleum ether/ethyl acetate, 2:10; Scheme 3).

1-(*N*-pyrrolyl)-1-(*N*-carbazolyl)ethyl acetate (VII) Compound VII was found to have the following characteristics: mp = 168–170°C; UV (CH_3CN): λ_{max} = 205, 228, 250, and 289 nm; FTIR: 3010, 2990, 1725, 1550, 1470, 1430, 1320, 1190, and 1100 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 6–8 (m, 12H), 5.2 (s, 1H), 4.2 (q, 2H), and 1.3 (t, 3H) ppm.

ANAL. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2$ (318.38): C, 75.45%; H, 5.70%; N, 8.80%; and O, 10.05%. Found: C, 76.25%, H, 6.31%, N, 9.41%, and O, 10.07%.

1-(*N*-pyrrolyl)-1-(*N*-indolyl)ethyl acetate (IX) Compound IX was found to have the following characteristics: mp = 158–159°C; UV (CH_3CN): λ_{max} = 210, 268, 275, and 282 nm; FTIR : 3010, 2995, 1720, 1300–1400, 1190, 1100, and 700 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 6–8 (m,10H), 5.8 (s, 1H), 4.2 (q, 2H), and 1.3 (t, 3H) ppm.

ANAL. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ (268.32) C, 71.62%; H, 6.01%; N, 10.44%; and O, 11.93%. Found: C, 72.37%; H, 6.66%; N, 10.90%; and O, 11.95%.



Scheme 3

General synthesis of compounds **II**, **IV**, **VI**, **VIII**, and **X**

A typical procedure for hydroxamic acid monomers (**II**, **IV**, **VI**, **VIII**, and **X**) is described here. About 50 mL of methanol, 5.56 g (0.08 M) of hydroxylamine hydrochloride, and 5 g (0.02 M) of potassium hydroxide in 20 mL methanol (pH > 12) were added to a 250-mL three-necked flask that was equipped with a dropping funnel, stirrer, and thermometer. After the mixture was cooled to 0°C, compounds (0.02 M) containing ester groups (**I**, **III**, **V**, **VII**, **IX**) dissolved in 50 mL of methanol (or diethyl ether) were added in a drop-wise manner over a period of ~1 h. The temperature was maintained at 0°C for an additional 30 min, and then the mixture was stirred for 36 h at room temperature. Next, the mixture was filtered, and the moisture was evaporated on a rotary evaporator. The resulting material was acidified with 20 mL of 50:50 acetic acid and water, and then extracted by treatment with 2 × 50 mL of ethyl acetate. These compounds were purified by column chromatography with appropriate solvents (petroleum ether/chloroform/ethyl acetate, 1:2:10). Evaporation of the solvent or by distillation under reduced pressure afforded pure compounds, (Scheme 4).

1,1-Di-(N-pyrrolyl)methane hydroxamic acid (II) Compound **II** was found to have the following characteristics: bp = 79–80 °C/2 mmHg; UV (CH₃CN): λ_{max} = 220 nm; FTIR: 3350–3000, 2995, 1690, 1410, 1250, and 1050 cm⁻¹; FT-¹H-NMR (d₆-DMSO): δ 6.52 (s, 4H),

5.7 (s, 4H), 4.0 (s, 1H), 1.5 (d, 2H) ppm; FT-¹³C-NMR (d₆-DMSO): δ 162.4, 117.2, 106.9, 30.8, and 23.59 ppm; electron-impact mass spectrometry (EIMS) *m/z*: M⁺ 205.

ANAL. Calcd for C₁₀H₁₁N₃O₂ (205.22): C, 58.53%; H, 5.40%; N, 20.48%; and O, 15.59%. Found: C, 58.96, H, 5.89, N, 20.93, and O, 15.60.

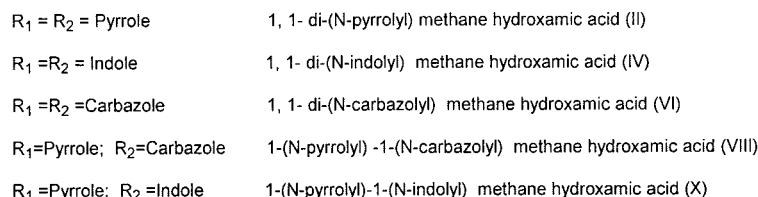
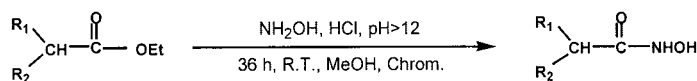
1,1-Di-(N-indolyl)methane hydroxamic acid (IV) Compound **IV** was found to have the following characteristics: mp = 166–167°C; UV (CH₃CN): λ_{max} = 219, 270, 276, and 285 nm; FTIR: 3500–3100, 2995, 1690, 1490, 1250, 1050, and 990 cm⁻¹; FT-¹H-NMR (d₆-DMSO): δ 6–7.5 (m, 12H), 3.5, 4.5 (b,s,2H), and 1.7 (d, 2H) ppm; EIMS *m/z*: M⁺ 305.

ANAL. Calcd for C₁₈H₁₅N₃O₂ (305.34): C, 70.81%; H, 4.95%; N, 13.75%; and O, 10.48%. Found: C, 71.29%; H, 5.43%; N, 14.43%; and O, 10.50%.

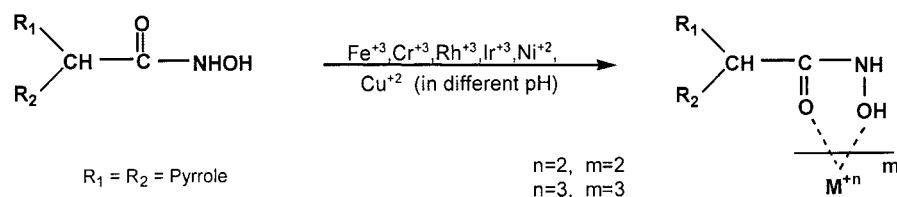
1,1-Di-(N-carbazolyl)methane hydroxamic acid (VI) Compound **VI** was found to have the following characteristics: mp = 198–200°C; UV (CH₃CN): λ_{max} = 210, 230, and 254 nm; FTIR: 3227–3010, 2937, 1717, 1562, 1416, 1279, and 1020 cm⁻¹; EIMS *m/z* M⁺ 405.

ANAL. Calcd for C₂₆H₁₉N₃O₂ (405.46): C, 77.02%; H, 4.72%; N, 10.36%; O, 7.92%. Found: C, 77.63%; H, 5.21%; N, 10.91%; and O, 7.95%.

1-(N-pyrrolyl)-1-(N-carbazolyl)methane hydroxamic acid (VIII) Compound **VIII** was found to have the following characteristics: mp = 149–150°C; UV (CH₃CN): λ_{max} = 210, 220, 230, and 250 nm; FTIR: 3300–3000,



Scheme 4



Scheme 5

2960, 1690, 1600, 1420, 1300, and 1060 cm^{-1} ; EIMS m/z M^+ 305.

ANAL. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_2$ (305.34): C, 70.81%; H, 4.95%; N, 13.75%; and O, 10.48%. Found: C, 71.65%; H, 5.30%; N, 14.22%; and O, 10.49%.

1-(N-pyrrolyl)-1-(N-indolyl) methane hydroxamic acid (X) Compound **X** was found to have the following characteristics: mp = 128–130°C; UV (CH_3CN): λ_{max} = 210, 272, 276, and 286 nm; FTIR: 3350–3000, 2995, 1695, 1300–1400, 1190, and 700 cm^{-1} ; FT- $^1\text{H-NMR}$ (d_6 -DMSO): δ 6–7.5 (m, 10H), 3.9 (s, 1H), 1.8 (d, 2H) ppm; EIMS m/z M^+ 255.

ANAL. Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ (255.28): C, 65.87%; H, 5.13%; N, 16.46%; and O, 12.54%. Found: C, 66.28%; H, 5.33%; N, 17.01%; and O, 12.54%.

Preparation of metal complexes with compound **II**

The preparation of metal complexes with **II** is depicted in Scheme 5.

$M = \text{Fe}$ Compound **II** (0.440 g, 4.11 mM) was added under N_2 atmosphere to a solution of anhydrous FeCl_3 (0.191 g, 1.17 mM) in 50 mL of THF containing a 4 mL of pyridine. The mixture was stirred for 5 h at room temperature, and the liquid was evaporated under reduced pressure to give a solid residue. The remains were washed several times with ether, then dissolved in 100 mL of dichloromethane, and washed with water again. The organic layer was separated and finally, after evaporating the solvent, gave a red color complex; FTIR: 3425, 3002, 2992, 1579, 1412, and 1043 cm^{-1} ; UV (CH_3CN): λ_{max} = 206, 254, and 327 nm.

$M = \text{Rh}$ Compound **II** (3.75 g, 0.035 M) was dissolved in 10 mL of ethanol. Then, the solution was added to a solution of RhCl_3 (2.094 g, 0.01 M) and sodium acetate (2 g) dissolved in 45 mL of water. The mixture was heated for 10 min, until boiling, and then cooled. The resultant precipitate that was separated was an orange color complex, which was recrystallized with ethanol; FTIR: 3452, 3076, 2995, 1593, 1531, 1445, 1068, and 885 cm^{-1} ; UV (CH_3CN): λ_{max} = 208.9 (intensity 1.4), 261.2 (intensity 2.2), and 340 (intensity 0.3) nm.

$M = \text{Ir}$ (NH_4) $_3\text{IrCl}_6$ (4.591 g, 0.01 M) and sodium acetate (0.9 g) were dissolved in 10 mL of water. The ethanol was added until a gel precipitate was obtained, and then the solution of **II** (3.21 g, 0.03 M) in 10 mL of ethanol was added. The mixture was heated at

50°C for 2 h, cooled, and stirred for 3 days at room temperature. The crude material was purified by silica gel column chromatography with appropriate solvents (benzene/petroleum ether, 50:50). This red color complex was recrystallized in dichloromethane/ethanol; FTIR: 3420, 3050, 2992, 1601, 1420, and 1050 cm^{-1} ; UV (CH_3CN): λ_{max} = 210.1 (intensity 1.9), 266.1 (intensity 3.1), and 349.1 (intensity 0.8) nm.

$M = \text{Cr}$ $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.2 g, 8 mM) was dissolved in 30 mL of water and stirred magnetically. Then, **II** (3.42 g, 32 mM) dissolved in 150 mL of water was added, followed by 0.1 N NaOAC-HOAC to attain a fixed pH = 4.7. The final mixture was stirred for 12 h at room temperature. After filtration, a solid precipitate was obtained and recrystallized from THF; FTIR: 3440, 3010, 2990, 1588, 1435, and 1018 cm^{-1} .

$M = \text{Cu}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.042 g, 0.25 mM) was dissolved in 20 mL of water, and then **II** (0.059 g, 0.55 mM) was added. The pH was adjusted to 4–5 by dilution with H_2SO_4 . A green color complex was obtained by washing with water and ether and then drying; FTIR: 3390, 3010, 1608, 1402, 1018, and 860 cm^{-1} .

$M = \text{Ni}$ $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (0.059 g, 0.25 mM) dissolved in 10 mL of water was added to the solution of **II** (0.059 g, 0.55 mM) dissolved in 20 mL water. Diluted NaOH was added until pH remained fixed at 8.3. The resultant blue precipitate was washed with water and ether to yield the pure blue color complex; FTIR: 3643, 3579, 3006, 2993, 1620, 1400, 1017, and 870 cm^{-1} .

Polymers: general procedure

Chemical polymerization

Chemical polymerization of di-heteroaromatics from pyrrole, indole, carbazole, and their mixed containing ester groups was carried out in a conventional reaction vessel. The bottom of the reaction vessel was covered with 25 mL of HClO_4 (9.1 M) containing 8.1 g of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$. A definite amount of monomer was dissolved in 15 mL of 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 and organic solutions at room temperature under a 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.

TABLE I
Conductivity (δ) of Poly[di-(*N*-substituted) Pyrrole, Carbazole, and Indole and their Mixtures Containing Esters Groups Measured by the Four-Point Probe Method

Polymer	Oxidant	δ ($S \cdot cm^{-1}$)
Polypyrrole	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	1×10^{-2}
Polycarbazole	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	5×10^{-4}
Polyindole	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	3×10^{-4}
Poly (I)	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	5.4×10^{-3}
Poly (III)	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	4.6×10^{-5}
Poly (V)	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	2.4×10^{-4}
Poly (VII)	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	6.5×10^{-3}
Poly (IX)	Fe(ClO ₄) ₃ • 9H ₂ O in HClO ₄ (9.1 M)	5.2×10^{-4}

Chemical polymerization of di-heteroaromatics from pyrrole, indole, and carbazole and of their mixtures containing hydroxamic acid groups is described as follows. To a solution of di-heteroaromatics containing hydroxamic acid groups (0.057 M) in 75 mL of HCl (1 M) was dropped a solution of ammonium persulfate (3 g) in 50 mL of HCl (1 M). The mixture was cooled at 0–5°C. After a few minutes, the color of solution changed and the powdered polymer was formed. The mixture was filtered, and the powder was washed with HCl (1 M) and acetone. The polymer was dried in vacuum.

Electrochemical polymerization

All electrochemical polymerizations of ester and hydroxamic acid group compounds were performed using a conventional three-electrode system with a Ag/AgCl reference electrode (0.01 mol L⁻¹), platinum wire counter electrode, and GC disk working electrode. All solutions for electrochemical polymeriza-

TABLE II
Conductivity (δ) of Poly[di-(*N*-substituted) Pyrrole, Carbazole, and Indole, and Mixtures Containing Hydroxamic Acid Groups Measured by the Four-Point Probe Method

Polymer	Oxidant	Before doping δ ($s \text{ cm}^{-1}$)	After doping δ ($S \text{ cm}^{-1}$)
Poly (II)	(NH ₄) ₂ S ₂ O ₈ HCl (1 M)	3.6×10^{-4}	4.2×10^{-3}
Poly (IV)	—	4.3×10^{-5}	9.2×10^{-5}
Poly (VI)	—	7.8×10^{-5}	3.2×10^{-4}
Poly (VIII)	—	6.4×10^{-5}	2.9×10^{-4}
Poly (X)	—	9.4×10^{-4}	2.4×10^{-4}

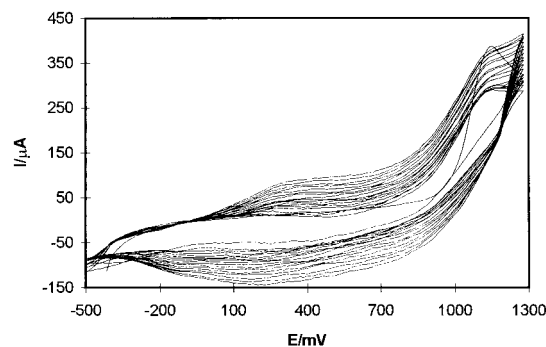


Figure 1 Cyclic voltammograms of 1,1-di-(*N*-pyrrolyl) methane hydroxamic acid (II; 6×10^{-3}) in acetonitrile and LiClO₄ (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s (16 cycles).

tion were freshly prepared using acetonitrile distilled from calcium hydride and stored over 3 Å molecular sieves. Lithium perchlorate (Merck) was treated with bubbling dry oxygen free nitrogen for at least 20 min before each polymerization. Polymers were grown on GC disk electrode under scan potential in the range of -500-2000 mV. Cyclic voltammetry and electrochemical polymerizations were carried out using an E.G. & G PARC Model 273 potentiostat/galvanostat and digital potentiostat DP8 (home made).

RESULTS AND DISCUSSION

Synthesis of the precursors

The principle of the syntheses of these polymers is different from the traditional method used by others since 1984 to make polypyrrole films that are covalently anchored to a transition metal complex.²⁸ Classically, an electroactive group that is chemically linked as a pendant moiety to a pyrrole ring was used as a polymer precursor. However, *N*-substituted polyheteroaromatics, such as polypyrrole, polycarbazole, and polyindole, are less electrically conducting than

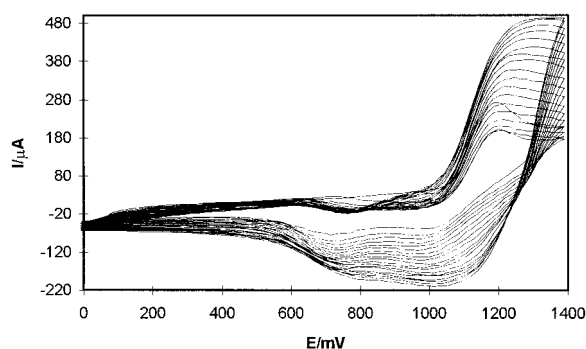


Figure 2 Cyclic voltammograms of 1,1-di-(*N*-carbazoyl) ethyl acetate (V; 6×10^{-3}) in acetonitrile and LiClO₄ (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s (20 cycles).

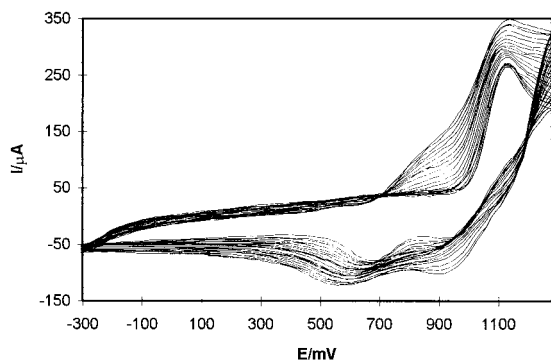


Figure 3 Cyclic voltammograms of 1,1-di-(*N*-carbazoyl) methane hydroxamic acid (**VI**; 6×10^{-3}) in acetonitrile and LiClO_4 (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s (20 cycles).

their parent homopolymers because of the steric constraints imparted by their bulky substituents.

We were the first to report the synthesis of *N*-substituted pyrrole- and carbazole-containing hydroxamic acid groups.²⁵ These monomers were chemically and electrochemically polymerized, and all their polymers showed high conductivity and could be precipitated completely on an electrode surface. Therefore, we must implement a new strategy because complexation of the polymers cannot take place on an electrode surface during electropolymerization. In a subsequent paper we will report in full the complexing metal and process of demetalation during the electropolymerization, with synthesis of bifunctional groups derivatives. In the preceding work, we evaluated the structure and the type of hydroxamic acid coordination by FTIR and UV-vis spectra data.¹³

In this research, we synthesized di-heteroaromatics from pyrrole, indole, and carbazole and their mixtures containing hydroxamic acid groups prepared from their *N,N*-substituted ester groups derivatives. These

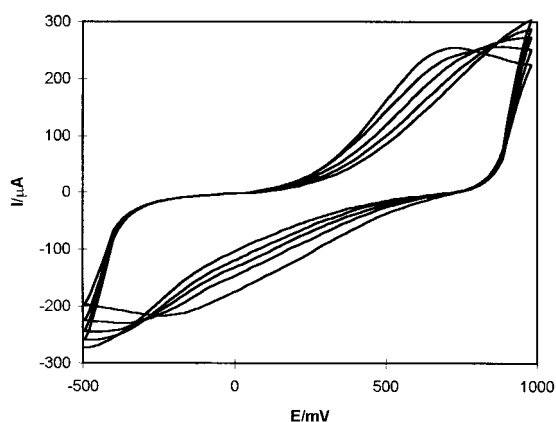


Figure 4 Cyclic voltammograms of poly[1,1-di-(*N*-pyrrolyl) ethyl acetate] (**I**) in acetonitrile and LiClO_4 (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s (5 cycles).

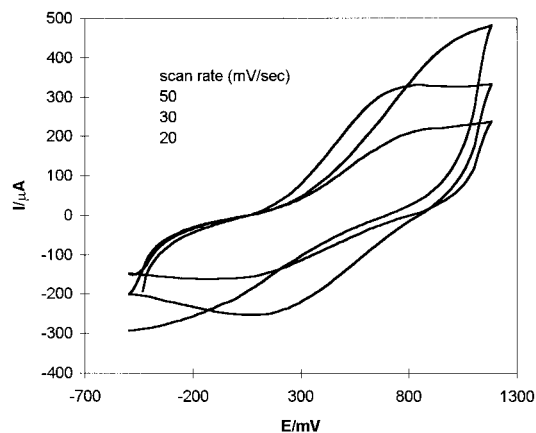


Figure 5 Cyclic voltammograms of poly[1,1-di-(*N*-pyrrolyl) methane hydroxamic acid] (**II**) in acetonitrile and LiClO_4 (0.1 M), using a GC disk electrode versus Ag/AgCl.

monomers were chemically and electrochemically polymerized, and the resultant polymers were shown to be conductive.

UV spectrophotometry

UV spectral results for **I**, **III**, **V**, **VII**, and **IX** (ester group compounds) and **II**, **IV**, **VI**, **VIII**, and **X** (hydroxamic acid group compounds) show a shift to higher wavelengths because of an increase in the density of electron intensity. On the other hand, comparison of UV spectra between **II** and the **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 a nonbonding interaction with the metal, which is another confirmation for coordination of metal with an oxygen atom.¹³

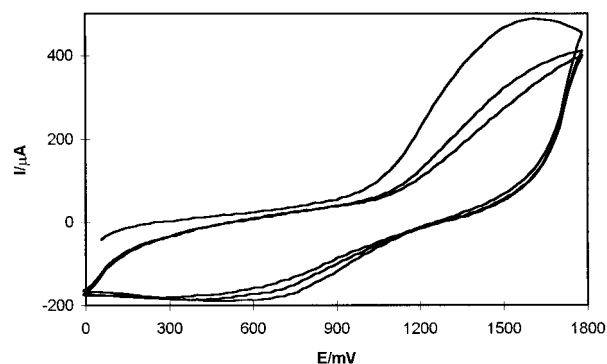
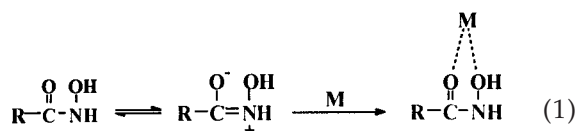


Figure 6 Cyclic voltammograms of poly[1,1-di-(*N*-carbazoyl)ethyl acetate] (**V**) in acetonitrile and LiClO_4 (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s (3 cycles).



Polymerization and conductivity

The mixtures of di-heteroaromatics from pyrrole-, indole-, and carbazole-containing ester groups were prepared at room temperature by interphase contacts between the aqueous solution of HClO_4 (9.1 M) containing $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ as oxidant and the monomer solution in benzene under N_2 atmosphere. Four-probe electrical conductivity data were measured on the compressed (6 ton/cm²) pellets of the polymers (Table I).

On the other hand, the di-heteroaromatics from pyrrole, indole, and carbazole and their mixtures containing hydroxamic acid groups were oxidatively polymerized in the presence of ammonium persulfate in an aqueous solution of HCl (1 M).²⁵ A powdered polymer was obtained after washing with HCl (1 M) and then with acetone, and then drying under vacuum. The conductivity of these polymers before and after doping with iodine vapor, measured by the four-probe method, is shown in Table II. It is evident that the values for conductance reported here are better than the values in our preceding work.²⁵

These monomers were electropolymerized in acetonitrile, with lithium perchlorate (0.1 M), by a cyclic voltammetry method, which used a GC disk working electrode and Ag/AgCl reference electrode. All the polymers obtained by electropolymerization were precipitated completely on an electrode surface. The cyclic voltammograms of some of these compounds in the absence of monomer are shown in Figures 1–3, and the cyclic voltammograms of their blank polymers are shown in Figures 4–7.

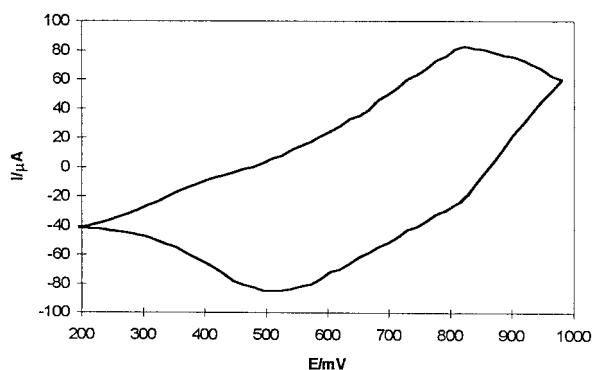


Figure 7 Cyclic voltammogram of poly[1,1-di-(*N*-carbazolyl)methane hydroxamic acid (VI)] in acetonitrile and LiClO_4 (0.1 M), using a GC disk electrode versus Ag/AgCl at a scan rate of 50 mV/s.

TABLE III
Oxidation Potential of Monomers and Oxidation and Reduction Potentials of Polymers

Sample	Oxid.(mV) monomer	Oxid.(mV) polymer	Red.(mV) polymer
Poly I	1200	675	-130
Poly II	1100	650	120
Poly V	1290	1400	700
Poly VI	1140	800	525

The oxidation potential of monomers and oxidation–reduction potential of polymers obtained on the electrode surface are shown in Table III. The minimum polymeric deposits produced from indole derivatives are brittle, like the parent polyindole, when obtained under these conditions. The electrical conductivities of pressed films of pyrrole, carbazole, and indole derivatives are considerably lower than those of the parent polymers. Furthermore, the electrical conductivities of polycarbazole and polyindole derivatives are also considerably lower than those of polypyrrole derivatives. As presented in Table III, the oxidation and reduction potentials of hydroxamic acid derivatives are lower than ester group derivatives because hydroxamic acids are better electron donors and the potential values obtained are not surprising.

CONCLUSION

In our preceding works,¹³ we presented a new method for synthesis of polyhydroxamic acid and studied its transition metal complexes in various pHs. In continuation of the latter work, we prepared polyheteroaromatics from pyrrole, indole, and carbazole containing one hydroxamic acid group.²⁵ This functional group was *N*-substituted with zero, one, and two methylene spacers, depending on the compound. Chemical and electrochemical polymerization samples without a spacer between the ring and hydroxamic acid are neither sufficient for growth nor high electrical conductivity. In contrast, samples with one and two methylene spacers show sufficient growth and high conductivity. These phenomena are due to the electron-withdrawing and deactivating effects of hydroxamic acid on aromatic rings. In the present research, we increased the reactivity, stability, and conductivity on the surface electrode with the synthesis of poly(di-heteroaromatics), such as pyrrole, indole, and carbazole and their mixtures containing a hydroxamic acid group. In addition, polymer growth on the surface electrode also occurred. But, complexation properties decreased because hydroxamic acid groups are unavailable on polymeric chains. On the other hand, the mixed compounds did not show sufficient growth on the surface electrode compared with similar di-heteroaromatics, but these polymers did have conductivity and mechanical properties.

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