Pergamon

0014-3057(95)00011-9

Eur. Polym. J. Vol. 31, No. 7, pp. 635–641, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0014-3057/95 \$9.50 + 0.00

SYNTHESIS OF CONDUCTING POLYPYRROLE AND POLYCARBAZOLE CONTAINING HYDROXAMIC ACID GROUPS

S. H. HOSSEINI and A. ENTEZAMI*

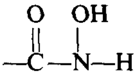
Laboratory of Polymer Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

(Received 1 February 1994; accepted in final form 11 July 1994)

Abstract—Although conducting polyheteroaromatics have been widely investigated, those containing hydroxamic acid groups have not been studied. In this work we have synthesized various N-(carbohydroxamic acid)pyrrole and N-(carbohydroxamic acid)carbazole derivatives from a series of N-substituted ester groups. The compounds obtained were then chemically polymerized in the presence of oxidants such as ammonium persulphate, and Iron (III) perchlorate. The conductivity of these polymers was measured by four probe methods. The compounds N-(2-ethane-carbohydroxamic acid)pyrrole (VI), 9-(carbohydroxamic acid)carbazole (VII), and 9-(2-ethanecarbohydroxamic acid)carbazole (XII) were successfully electropolymerized by a cyclic voltametry method under 6×10^{-3} M of monomer, 0.1 M tetrabutylammonium perchlorate, 20 ml acetonitrile, Pt disk working electrode, and SCE as a reference electrode condition. These compounds gave coloured complexes with certain metals.

INTRODUCTION

Research in new electronic conductive polymeric materials has grown intensively during the last decade as a consequence of their important technological application, such as rechargeable all-plastic batteries, electro-optical displays, and conductive coatings [1]. Ease of preparation at the laboratory scale has also contributed to the promotion of interest in these conductive materials. Typical examples of this new class of conductors are heterocyclic polymers, such as polypyrrole. In recent years N-functionalized polypyrroles have attracted more and more attention [2–5]. However, N-substituted polypyrrole containing hydroxamic acid groups has not been studied. On the other hand, groups containing hydroxamic acid

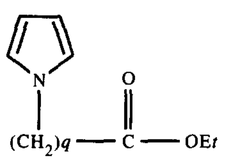


$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{N}-H$$

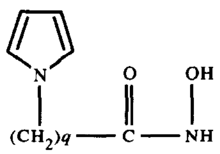
are an important class of organic compound that have been widely studied and show many reaction characteristics of functional groups in the molecule [6]. Hydroxamic acids have long been known for their special ability to form complexes with heavy metals [7–10].

EXPERIMENTAL

Part A: preparation of monomers

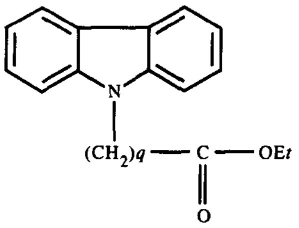


I–III

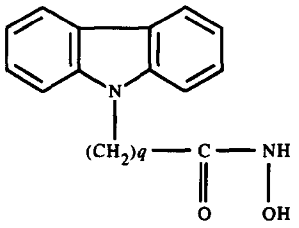


IV–VI

q = 0,1,2



VII–XI



X–XII

---

*To whom all correspondence should be addressed.

N-ethylpyrrole-1-carboxylate (I, q = 0). N-pyrrole potassium salt (0.05 M) treated with ethylchloroformate (0.05 M) in 10 ml anhydrous ether at 5°C, was dropped into a suspension. After a few hours filtration of the mixture, water (20 ml) was added to the filtrate, and the organic layer was separated and evaporated to give the crude C— and O— acylation derivatives. The compound (I) was purified by Alumina column chromatography with appropriate solvents (petroleum ether/ethylacetate/methanol: 1/5/15), or by distillation under reduced pressure, b.p. 70°C/20 mm Hg. IR: 3100, 2980, 1755 cm^{-1}; u.v.: λ_{max} = 227.6 nm in CH_3CN, mass spectrum, chemical ionization (200 eV); *m/e*: 139 as calculated for Z(M), ^{1}H-NMR in CC14, 7 (*q*, 2H), 5.95 (*q*, 2H), 4.2 (*q*, 2H), 1.3 (*t*, 3H).

N-(ethylacetate)pyrrole (II, q = 1), N-(β-ethylpropionate)pyrrole (III, q = 1). These compounds were prepared with the N-pyrrole potassium salt and corresponding chloroesters under the same conditions. Compounds (II); b.p. = 85°C/20 mm Hg. Compound (III): b.p. = 85°C/5 mm Hg. IR: 3150, 2990, 1750, 1485, 1405, 1375, 1190 and 740 cm^{-1}. u.v.: λ_{max} = 209 nm in acetonitrile.

N-(carbohydroxamic acid)pyrrole (IV). Compound (IV) was prepared by addition of hydroxylamine hydrochloride (5.56 g, 0.08 M) to a solution of compounds (I) (2.78 g, 0.02 M) in 40 ml methanol. Then a solution of potassium hydroxide (5 g, 0.02 M) in 20 ml methanol was dropped. The mixture was stirred for 36 hr at room temperature and filtered, and evaporated on a rotatory evaporator. The resulting material was acidified by 20 ml (50/50) acetic acid and water, then extracted by 50 ml ethylacetate. Compound (IV) was obtained by distillation (b.p. = 57°C/5 mm Hg) or by column chromatography with appropriate solvents (petroleum ether/chloroform/ethylacetate 1/2/10), evaporation of the solvent afforded pure compound (IV). IR: 3000–3400, 1720, 1420, 1380, 1320, 1260 and 1050 cm^{-1}. u.v.: λ_{max} = 205.6, 256.8 in acetonitrile.

N-(methanecarbohydroxamic acid)pyrrole (V). Compound (V) was prepared with compounds (II) as starting material and the same conditions as compound (IV). b.p. = 65°C/5 mm Hg, yield 72%. IR: 3350–3000, 2990, 1695, 1420, 1260 and 1025 cm^{-1}. u.v.: λ_{max} = 217 nm in acetonitrile. ^{1}H-NMR in CDC13; 7–9 (noresol., 1H), 6.58 (*q*, 2H), 6.05 (*q*, 2H), 3.97 (*s*, 2H), 2.5 (*s*, 1H).

N-(2-ethanecarbohydroxamic acid)pyrrole (VI). Compound (VI) was prepared with compound III as starting material and the same conditions as compounds IV. b.p. = 72°C/5 mm Hg, yield 87%. IR: 3480, 3520, 3090, 2990, 1680, 1400, 1260 and 1090 cm^{-1}. u.v.: λ_{max} = 220 and 270 nm in acetonitrile. ^{1}H-NMR in CC14; 7–9 (noresol., 1H), 6.75 (*q*, 2H), 6.3 (*q*, 2H), 3.9 (*t*, 2H), 3 (*t*, 2H), 2.4 (noresol., 1H).

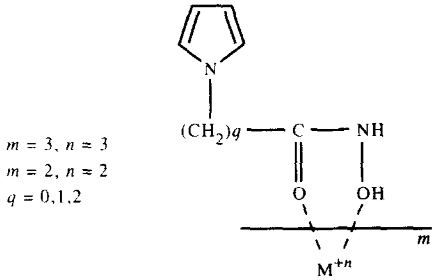
Ethylcarbazole-9-carboxylate (VII). N-carbazole potassium salt (0.05 M) was suspended in 100 ml water, and a solution of ethylchloroformate (5.42 g, 0.05 M) in 50 ml ether at 0°C was dropped into the above suspension during half an hour. This was then stirred for 1 hr at room temperature. 200 ml water was added to the mixture, stirred for 1 hr, and then extracted by 50 ml ether. The evaporation of solvent gave crude material which was purified by column chromatography with appropriate solvents (petroleum ether/ethylacetate, 2/10). IR: 3119, 2990, 1760, 1480, 1410, 1340, 1040 and 740 cm^{-1}. u.v.: λ_{max} = 205 and 227 nm in acetonitrile.

9-(ethylacetate)carbazole (VIII) and 9-(3-ethylpropionate)carbazole (IX). Compounds VIII and IX were prepared with starting materials such as ethylchloroacetate and ethylchloropropionate respectively, and the same conditions as compound VII. Compound VIII. IR: 3080, 2990, 1720, 1450, 1390, 1240, 1075 and 750 cm^{-1}. u.v.: λ_{max} = 208.4 nm in acetonitrile. Compound IX. IR: 3100, 2990, 1750, 1490, 1460, 1380, 1240 and 1050 cm^{-1}. u.v.: λ_{max} = 210.6 in acetonitrile.

9-(carbohydroxamic acid)carbazole (X). Compound VII (4.78 g, 0.02 M) was dissolved in 70 ml methanol and hydroxylamine hydrochloride (5.56 g, 0.08 M) was added. The mixture was stirred and 4.2 g (5 M) KOH was added and stirred for 36 hr at room temperature. The mixture was filtered and evaporated on a rotary evaporator, acidified by 20 ml (50/50) acetic acid–water, and extracted twice with 50 ml ether. The evaporated solvent gave a crude material which was purified by column chromatography with appropriate solvents (petroleum ether/ethylacetate, 2/10). The pure compound was adsorbed by silica gel and dissolved by the addition of methanol. Evaporated methanol gave pure compound with a yield of 43%. IR: 3340–3000, 1690, 1440, 1290 and 1020 cm^{-1}. u.v.: 210, 217 and 254 nm, in acetonitrile.

9-(methanecarbohydroxamic acid)carbazole (XI), 9-(2-ethanecarbohydroxamic acid)carbazole (XII). Compounds XI, XII were prepared under the same conditions as compound X. The yield for XI was 77% and for XII was 82%. Compound XI, IR: 3400–2990, 1705, 1450, 1260 and 1020 cm^{-1}. u.v.: λ_{max} = 208.2, 230 and 254.3 nm in acetonitrile. Compound XII, IR: 3400–2990, 1720, 1410, 1270, 1020 cm^{-1}. u.v.: λ_{max} = 215, 235 and 259.8 nm in acetonitrile.

Part B: preparation of metals complexes



M = Fe, m = 3, n = 3, q = 0. The compound IV (0.518 g, 4.11 mM) was added under a N_2 atmosphere to a solution of anhydrous $FeCl_3$ (0.191 g, 1.17 mM) in 50 ml THF containing a few ml of pyridine. The mixture stirred for 5 hr at room temperature, and evaporated under reduced pressure gave a solid residue, which was washed several times with ether, then dissolved in 100 ml dichloromethane, washed with water. The organic layer was separated, and evaporation of the solvent gave the red colour complex. FTIR: 3425, 3000, 1579, 1412 and 1043 cm^{-1}. u.v.: λ_{max} = 254 and 327 nm.

M = Rh, m = 3, n = 3, q = 0. The compound IV (4.41 g, 0.035 M) was dissolved in 10 ml ethanol. This solution was added to a solution of 45 ml water containing dissolved $RhCl_3$ (2.094 g, 0.01 M) and sodium acetate (2 g). The mixture was heated for 10 min until boiling, then cooled. The precipitate was separated, as an orange colour complex, recrystallized with ethanol. FTIR: 3452, 3076, 1593, 1531, 1445, 1068 and 885 cm^{-1}.

M = Ir, m = 3, n = 3, q = 0. $(NH_4)_3IrCl_6$ (4.591 g, 0.01 M) and sodium acetate (0.9 g) were dissolved in 10 ml water, and ethanol was added until a gel precipitate was obtained. Then a solution of compound IV (3.78 g, 0.03 M) in 10 ml ethanol was added. The mixture was heated to 50°C for 2 hr, cooled, then 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). The red colour complex was recrystallized in dichloromethane/ethanol. FTIR: 3420, 3050, 1601, 1420 and 1050 cm^{-1}.

Table 1. The conductivity δ of poly(N-substituted)pyrrole and carbazole containing esters groups measured by the four-probe method

Polymer	Oxidant	δ (S × cm^{-1})
Polypyrrole	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	10^{-2}
Polycarbazole	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	5×10^{-4}
Poly(I)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	2.3×10^{-5}
Poly(II)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	8.9×10^{-5}
Poly(III)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	2.2×10^{-5}
Poly(VII)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	7.5×10^{-5}
Poly(VIII)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	5.3×10^{-5}
Poly(IX)	$Fe(ClO_4)_3$, $9H_2O$ in $HClO_4$, 9.1 M	8.4×10^{-5}

$M = Cr$, $m = 3$, $n = 3$, $q = 0$. $Cr(NO_3)_3$. $9H_2O$ (3.2 g, 8 mM) was dissolved in 30 ml water, stirred magnetically, and compound IV (3.93 g, 32 mM) dissolved in 150 ml of water was added. Then, 0.1 of NaoAc–HoAc at fixed pH = 4.7 was added. The mixture was stirred for 12 hr at room temperature. After filtration, the solid precipitate obtained was purified with THF. FTIR: 3440, 3010, 1588, 1435 and 1018 cm^{-1}.

$M = Cu$, $m = 2$, $n = 2$, $q = 0$. $CuCl_2$, $2H_2O$ (0.042 g, 0.25 mM) was dissolved in 20 ml water. Then, compound IV (0.063 g, 0.25 mM) was added at, pH = 4–5 regulated with dilute H_2SO_4. A green colour complex was obtained by washing with water and ether and then dried. FTIR: 3390, 3005, 1608, 1414 and 1018 cm^{-1}.

$M = Ni$, $m = 2$, $n = 2$, $q = 0$. $NiCl_2$, $2H_2O$ (0.095 g, 0.25 mM) was dissolved in 10 ml water. Then, a solution of (IV) (0.063 g, 0.5 mM) was dissolved in 20 ml water. Dilute wash was added to fix the pH at 8.3. After washing with water and ether, a pure complex with a blue colour was obtained. FTIR: 3642, 3579, 3010, 1617, 1375 and 1017 cm^{-1}.

Table 2. The conductivity of δ of poly(N-substituted)pyrrole and carbazole containing hydroxamic acid groups measured by four-probe method

Polymer	Oxidant	Before doping δ (S × cm^{-1})	After doping δ (S × cm^{-1})
Poly(IV)	$(NH_4)_2S_2O_8$, HCl 1 N	5.4×10^{-5}	3.2×10^{-4}
Poly(V)	$(NH_4)_2S_2O_8$, HCl 1 N	4.7×10^{-5}	7.1×10^{-4}
Poly(VI)	$(NH_4)_2S_2O_8$, HCl 1 N	9.3×10^{-4}	3.3×10^{-3}
Poly(X)	$(NH_4)_2S_2O_8$, HCl 1 N	7.3×10^{-6}	3.5×10^{-5}
Poly(XI)	$(NH_4)_2S_2O_8$, HCl 1 N	9.3×10^{-6}	6.5×10^{-5}
Poly(XII)	$(NH_4)_2S_2O_8$, HCl 1 N	2.2×10^{-5}	1.2×10^{-4}

Part C: polymers; general procedure

Chemical and electrochemical polymerization of pyrrole and carbazole containing ester groups. The synthesis of the conducting polymer films was carried out in a conventional reaction vessel. The bottom of the reaction vessel was covered with 25 ml $HClO_4$ 9.1 M containing an oxidant, such as $Fe(ClO_4)_3$, $9H_2O$. 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 short time the polymeric film formed at the interface of the aqueous/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 hr.

All electrochemical polymerizations were performed using a conventional three electrode system with a saturated calomel reference electrode (SCE), platinum wire counter

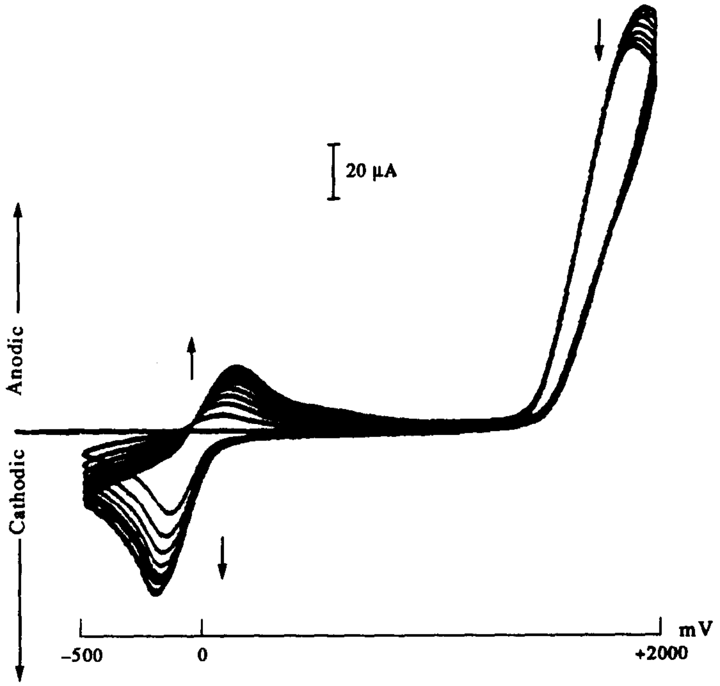


Fig. 1. Cyclic voltametry of ethylpyrrole-1-carboxylate (I) (6×10^{-3} M) in acetonitrile tetrabutylammoniumperchlorate 0.1 M Pt disk electrode SW = 100 mV/sec, potential range 500–2000 mV vs SCE (9 cycles).

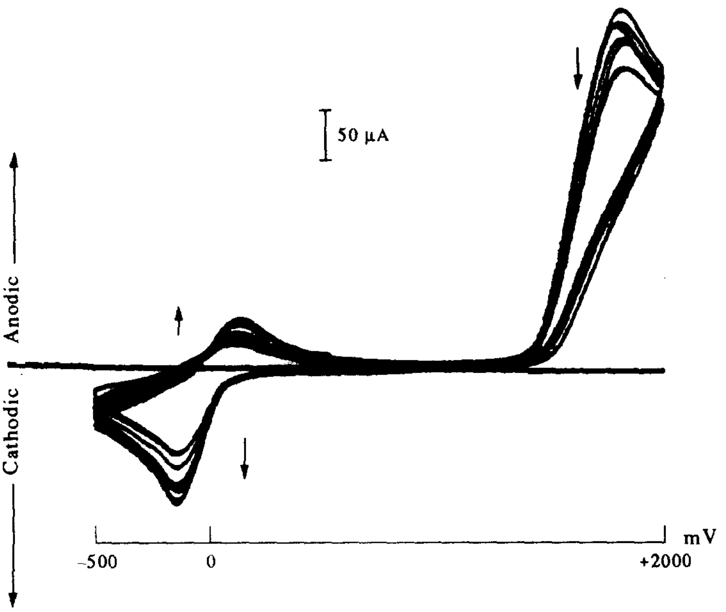


Fig. 2. Cyclic voltametry of N-(carbohydroxamic acid)pyrrole (IV) (6 × 10^{-3} M), in acetonitrile Bu4N ClO4 0.1 M pt disk electrode SW = 100 mV/sec potential range 500–2000 mV vs SCE (9 cycles).

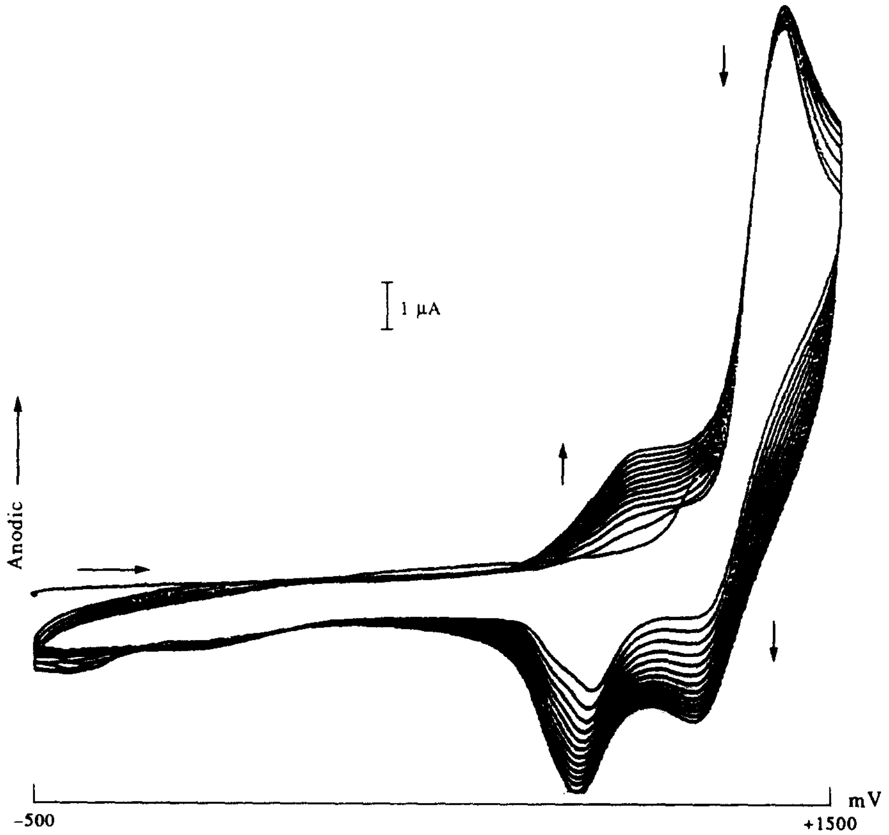


Fig. 3. Cyclic voltametry of N-(ethanecarbohydroxamic acid)pyrrole (VI) (3 × 10^{-3} M) in acetonitrile, Bu4N ClO4 0.1 M Pt disk electrode, SW = 100 mV/sec, potential range 500–2000 mV vs SCE (13 cycles).

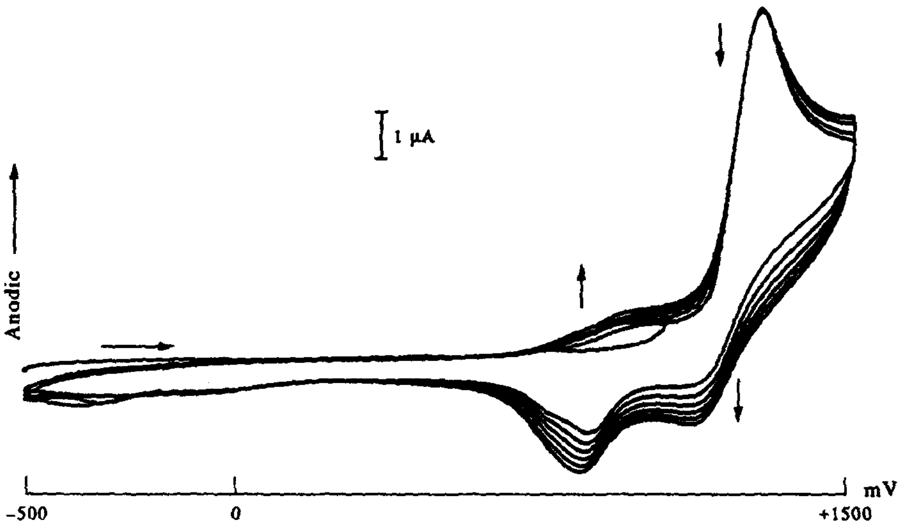


Fig. 4. Cyclic voltametry of 9-(3-ethylpropionate)carbazole (IX) (3×10^{-3} M) in acetonitrile, Bu4N ClO4 0.1 M, Pt disk electrode, SW = 300 mV/sec, potential range 500–2000 mV vs SCE (7 cycles).

electrode and platinum disk working electrode (Metrohm, 0.062 cm^2). All solutions for electrochemical polymerization were freshly prepared using acetonitrile distilled from calcium hydride and stored over 3 A molecular sieves. Tetrabutylammonium perchlorate (Merck) provided bubbling dry oxygen free nitrogen for at least 20 min before each polymerization. Polymers were grown on platinum disk electrodes at a scan potential in the range of 500–2000 mV.

Chemical and electrochemical polymerization of heteroaromatics containing hydroxamic acid groups. To a solution of heteroaromatics containing hydroxamic acid groups (0.057 M) in 75 ml HCl (1 M) was dropped a solution of ammonium persulphate (3 g) in 50 ml HCl (1 M). The mixture was cooled at 0–5°C. After a few minutes the colour of a solution changes and the powdered polymer was formed. The mixture was filtered and the powder washed with HCl (1 M) and acetone. The polymer was dried in vacuum.

Electrochemical polymerization. Electropolymerization of heteroaromatics containing hydroxamic acid groups was carried under the same condition as heteroaromatics containing ester groups.

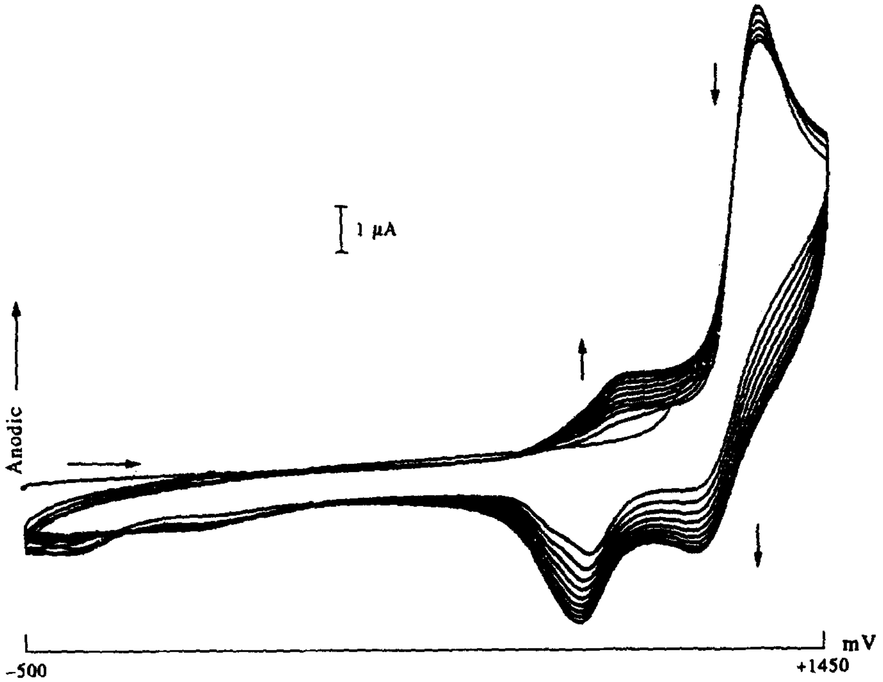


Fig. 5. Cyclic voltametry of 9-(2-ethanecarbohydroxamic acid)carbazole (XII) (3×10^{-3} M), in acetonitrile, Bu4N ClO4 0.1 M, Pt disk electrode SW = 200 mV/sec, potential range 500–2000 mV vs SCE (9 cycles).

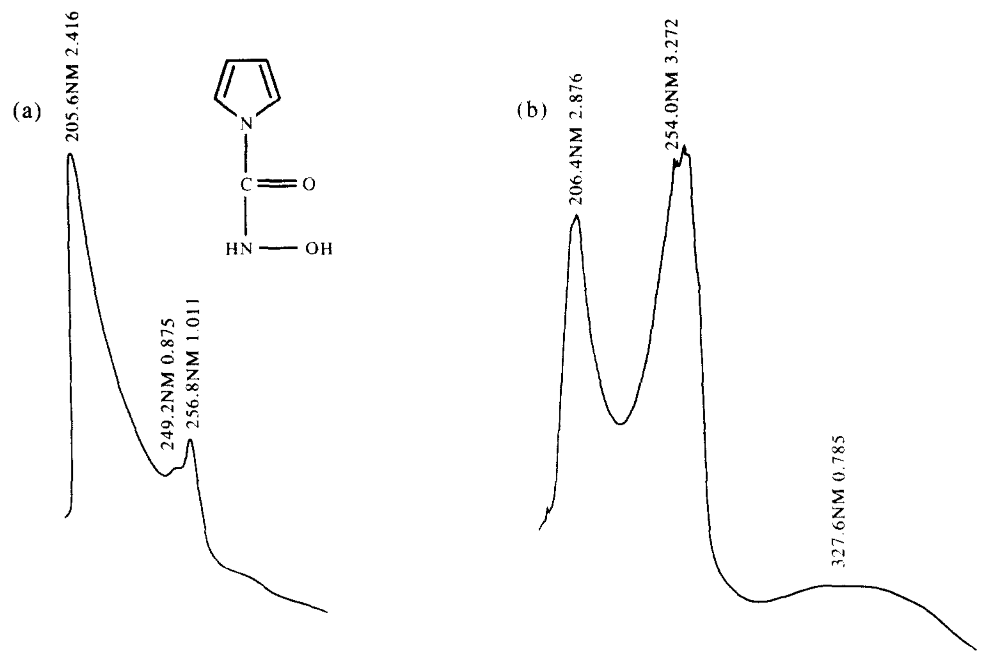


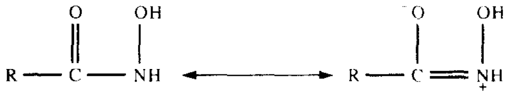
Fig. 6. u.v. spectra of compounds IV and IV-Fe.

RESULTS AND DISCUSSION

The special ability of hydroxamix acid groups to form complexes with heavy metals, e.g. Fe(III), Rh(III), Ir(III), Cr(III), Cu(II), Ni(II), . . . is of interest. From the FTIR spectrum of these complexes, we could evaluate the type of hydroxamic acid coordination.

The electronic structure of hydroxamic acids may be shown by hybrid resonance of (A) and (B).

(A) (B)



$$R-C(=O)-NH(OH) \longleftrightarrow R-C(O^-)=\overset{+}{N}H(OH)$$

If the coordination of hydroxamic acids occurs via a nitrogen atom, then the structural contribution of (B) will decrease. If this coordination occurs via an oxygen atom, then the structural contribution of (A) will decrease. The (C) and (D) forms are proposed for hydroxamic acid complexes, which show the coordination of oxygen and nitrogen atoms, respectively.

(C) (D)

$$R-C(=O\cdots M)-NH(OH\cdots M) \qquad R-C(O\cdots M)-NHOH$$

Table 3. The oxidation potential of monomers and oxidation, reduction potential of polymers

Sample	Oxide (mV) monomer	Oxide (mV) polymer	Red (mV) polymer
I	+1860	+158	−160
IV	+1730	+114	−137
VI	+1750	+160	+27
IX	+1260	+1125	+1175, 950
XII	+1337	+976	+1186, 918

If in the IR spectra of complexes in comparison with free ligand (V), $\bar{\nu}$ (C=O) shifts to a higher frequency and $\bar{\nu}$ (C—N) shifts to a lower frequency, this will indicate ligand coordination via a nitrogen atom [(A) and (D)], and if $\bar{\nu}$ (C=O) shifts to a lower frequency and $\bar{\nu}$ (C—N) to a higher frequency, then it will indicate the ligand coordination via an oxygen atom [(B) and (C)], and so the $\bar{\nu}$ (O—H) should be eliminated. Considering the FTIR data in Table 4, the (B) and (C) forms are confirmed. On the other hand, comparison of u.v. spectra of compounds IV and IV-Fe (Fig. 6) shows that the decrease of bond intensity corresponding to a $n \rightarrow \pi^*$ transition of the oxygen atom of a carbonyl group, due to interaction with metal and increase of carbonyl group, due to interaction with metal and increase of bond intensity corresponding to a $n \rightarrow \pi^*$ transition of a nitrogen atom, due to non-bonded interaction with metal, is another confirmation for coordination of metal with an oxygen atom (B and C). Using Job's method, it is evident that the ratio of ligand to a two valence metal is 2:1 and to a three valence metal is 3:1.

The polymerization of N-substituted pyrrole and carbazole containing hydroxamic acid groups, due to their ability to complex formation and function in certain reactions, should be interesting.

For the first time, we report the synthesis of N-substituted pyrrole and carbazole containing hydroxamic acid groups. These monomers were chemically and electrochemically polymerized. The polymers obtained have conductivity. In the cases of N-substituted pyrrole and carbazole containing ester groups, polymeric films were prepared at room

Table 4. FTIR data (cm^{-1}) of free ligand and their complexes

IV-Cu	IV-Ni	IV	IV-Fe	IV-Ir	IV-Rh	IV-Cr	Vib. mode
1610	1617	1720	1578	1601	1593	1608	(C=O)
1382	1375	1370	1412	1420	1445	1414	(C—N)

temperature by contact between an aqueous solution of $HClO_4$ 9.1 M containing $Fe(ClO_4)_3$, $9H_2O$ as oxidant and monomer solution in benzene under N_2 atmosphere. Four-probe electrical conductivity data were measured on compressed (6 ton/cm^2) pellets of the polymers (Table 1).

On the other hand, the N-substituted pyrrole and carbazole containing hydroxamic acid groups were polymerized oxidatively in the presence of ammonium persulphate in an aqueous solution of HCl (1 M). A powdered polymer was obtained, after washing with HCl (1 M), then with acetone, and dried in vacuum. Table 2 shows the conductivity of these polymers, measured by the four-probe method. These monomers were electropolymerized by a cyclic voltametry method, in acetonitrile, with tetrabutylammonium perchlorate 0.1 M Pt disk working electrode, and SCE reference electrode. The polymers obtained by electropolymerization of compounds I, IV, VII, X cannot be precipitated completely on an electrode surface, but the polymers of compounds II, III, V, VI, VIII, IX, XI, XII were precipitated completely on an electrode surface. Figures 1–5 show the cyclic voltamograms of some of these compounds. Table 3 shows the oxidation potential of monomers and oxidation, reduction potential of polymers obtained on electrode surface.

REFERENCES

1. T. A. Skotheim. *Handbook of Conductive Polymers*, Vols 1 and 2 (1986).
2. M. Velasques and T. A. Skothime. *J. Electronal. Chem.* **185**, 297 (1985).
3. T. Inagaki and M. Hunter. *J. Chem. Soc. Chem. Commun.*, 126 (1988).
4. A. Haimerl and A. Merz. *Angew. chem. Int. Ed. Engl.* **25**, 180 (1986).
5. J. Grimshaw and S. D. Perera. *J. Electronal. Chem.* **266**, 336 (1989).
6. C. Bass and J. H. Yoe. *Talanta* **13**, 735 (1966).
7. H. L. Yale. *Chem. Rev.* **33**, 209 (1943).
8. J. B. Neilands. *Struct. Bond.* **7**, 59 (1966).
9. H. Maehr. *Pure appl. Chem.* **28**, 603 (1950).
10. R. E. Buckiles. *Analyt. Chem.* **22**, 676 (1950).
11. J. W. Munson. *Chem. Biol.* **1–3**, 94 (1982).
12. I. Ines and K. Horst. *IRc5 Med. Sci.* **13**, 579 (1985).
13. N. C. Billingham. *Elect. Cond. Poly. Appl. Sci.* In press.