Polyheterocyclic Conductors from *N*-(*ortho*-Substituted Phenyl)pyrroles

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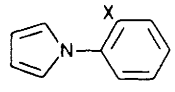
Voltammetric studies are reported which show that both electronic and steric effects are important in the electrosynthesis of organic metal films from *N*-(*ortho*-substituted phenyl)pyrroles in agreement with n.m.r. studies reported by other workers; the resulting films employed as electrodes yield well defined cyclic voltammograms similar to those obtained with other solid electrodes.

Electrochemistry offers a novel and potentially useful method for the preparation of various types of polyheterocyclic conductors, especially by anodic oxidation.[1] Here we describe the effect of the *ortho* substituent on the electropolymerization of some *N*-(*ortho*-substituted phenyl)pyrrole monomers which produce films with high quality performance as electrodes.

Cyclic voltammograms of the *N*-(*ortho*-substituted phenyl)pyrrole monomers (1)—(7) resemble those of other pyrrole monomers with characteristic shapes for an irreversible process[2] plus a small peak at *ca.* 1.2 V which was not assigned. Plots of the i_{pa} values of (1)—(7) are linear with $v^{1/2}$ in the potential sweep range of 20 to 100 mV s^{-1} and exhibit slope values close to that of the parent *N*-phenylpyrrole. These correlations agree with a reaction of dissolved species which do not adhere to the electrode.

The E_{pa} values of (1)—(7) shown in Table 1 increase progressively in the order OMe $<$ H $<$ Cl $<$ F $<$ NO_2 $<$ Br $<$ CF_3 with variations in electronic and steric effects of X. In these measurements, the electrode surface was cleaned after each scan because the voltammograms were modified by film deposit. In addition, the substituents induce diamagnetic shifts of the pyrrole α-protons in the ^1H n.m.r. spectra which decrease gradually in the order NO_2 $>$ CF_3 $>$ Cl $>$ Br $>$ OMe $>$ F $>$ H. Analysis of the shifts in the α-proton resonances confirms electronic and steric interactions of the *ortho*-substituents with the pyrrole ring and also suggests a tendency towards free rotation of the two rings with minimal interaction.[3]

The electrochemical measurements and film growth were performed in a single compartment cell using Pt as the working electrode, Pt wire as the counter electrode, and a calomel electrode in an aqueous saturated potassium chloride solution as the reference electrode. Each electrolytic solution contained 10^{-3} M of the substrate [N-(*ortho*-substituted phenyl)pyrrole monomer or ferrocene] plus 0.1 M tetraethylammonium tetrafluoroborate in distilled acetonitrile. The films were grown on the 0.5 cm² Pt electrode by electro-



(1) X = OMe

(2) X = H

(3) X = Cl

(4) X = F

(5) X = NO_2

(6) X = Br

(7) X = CF_3

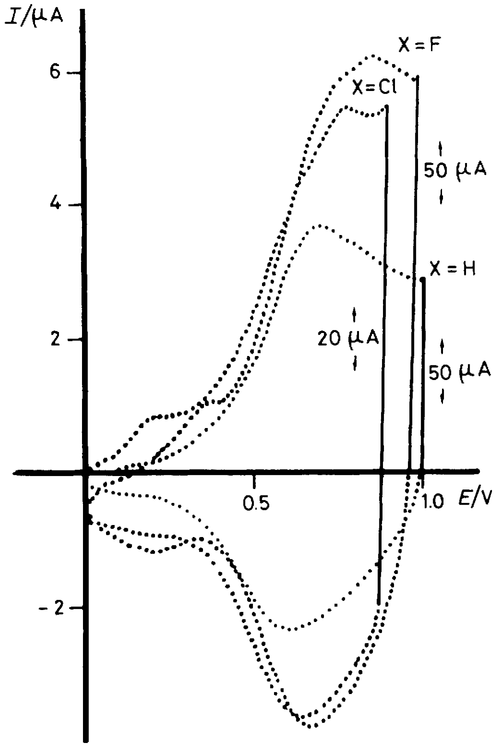


Figure 1

oxidation of a 0.03 M solution of each substituted phenylpyrrole monomer containing the electrolytic salt and by applying 20 mC cm^{-2} of charge to control the film thickness.

Electropolymerization of (**1**)—(**7**) performed at a constant potential of 1.233 V yielded very high quality films for X = Cl, F, Br, H, and OMe. Polymerization was inhibited for X = NO_2 and CF_3. Therefore, as in the *N*-alkyl series, a steric effect is manifested in the monomers with large *o*-groups.[2]

Table 1

Compound	Monomer E_{pa}/V	Polymer film E_{pa}/V	Polymer film E_{pc}/V	Polymer film E_0/V
(**1**)	1.410	0.623	0.400	0.511
(**2**)	1.470	0.690	0.595	0.652
(**3**)	1.505	0.770	0.630	0.700
(**4**)	1.527	0.850	0.660	0.752
(**5**)	1.530	—	—	—
(**6**)	1.540	0.845	0.260	0.552
(**7**)	1.560	—	—	—

Figure 1 shows the cyclic voltammograms of thin films of (**2**)—(**4**) at a 100 mV s^{-1} scan rate. The oxidation and reduction current (i_{pa} and i_{pc}) values are almost equal in each voltammogram showing a reversible redox process. The films are stable and can be cycled repeatedly between conducting and insulating state. The *ortho*-substituent effect was clearly manifested in the E_{pa}, E_{pc}, and E_0 values of the films of (**1**)—(**7**) (Table 1). Furthermore when the films were used as electrodes in the ferrocene–ferrocinium$^{\cdot +}$ redox reaction, the E_{pa}–E_{pc} separations increased in the order H < Cl < F < Br < OMe showing a *quasi*-reversible reaction with defined E_{pa} and E_{pc} peaks. From our results it can be concluded that *N*-phenyl-, (*o*-Cl-phenyl)-, and (*o*-F-phenyl)-pyrrole polymers are the most stable and give the best performance as electrodes. The detailed electrochemistry and use of these polymers as electrodes will be published elsewhere.

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