Electrochemical Synthesis and Preliminary Characterization of Poly(thieno[3,2-*b*]pyrrole)

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Electrochemical polymerization of thieno[3,2-*b*]pyrrole leads to thin conducting films, which have been studied by *X*-ray photoelectron spectroscopy, both in the oxidized and reduced states.

There has been much recent interest in heteroaromatic-based conducting polymers such as polypyrrole[1] and polythiophene,[2] in view of their greater chemical stability than polyacetylene, and their simple one-step electrochemical synthesis. More recently, new compounds such as polyselenophene[3] and polypyridazine[4] have been obtained using the same polymerization process. We now describe the electrochemical preparation, preliminary characterization, and some properties of a new conducting polymer based on the sulphur–nitrogen bicyclic monomer, thieno[3,2-*b*]pyrrole (**1**).

The polymerization was carried out in argon atmosphere under potentiostatic conditions, using a three-electrode single-compartment cell, with solutions containing electrolyte salt (0.1 M; Et_4NBF_4 or $LiClO_4$) and monomer (1 mM) in acetonitrile. Film formation occurs on the anode at +0.6 V *vs.* Ag–$AgNO_3$ (0.1 M) reference electrode. Application of the potential for 10—20 min leads to thick, but rather brittle, black deposits (up to 10 μm). Preliminary conductivity measurements on these samples give values around 5×10^{-3} Ω^{-1} cm^{-1}.

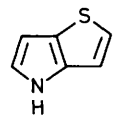
Table 1. X.p.s. binding energies (eV) of BF_4^--doped and undoped polythieno[3,2-*b*]pyrrole.

	C 1s	N 1s	S $2p_{3/2}$	F 1s	O 1s
Doped	285.2	400.5	164.3	686.4	—
Undoped	284.4	399.4	163.6	—	531.4

Thin films (1—5 min polymerization) can be driven cathodically to a reduced state. At −0.3 V they turn from a black to a red-brown colour; more cathodic potentials induce no additional change. The polymer in its reduced form becomes dark-green when exposed to air for several days.

X-Ray photoelectron spectroscopy (x.p.s.) measurements carried out on the as-grown films reveal the incorporation of the electrolyte anion (BF_4^- or ClO_4^-) into the polymer. Furthermore, C 1s, N 1s, and S 2p binding energies (Table 1) are typical of positively charged atoms, indicating that the polymer is doped in the oxidized state. The doping level, determined from the intensity of N 1s, F 1s, and Cl 2p core lines, is ~35%.

In contrast, the spectrum of the reduced form does not show any significant dopant signal and the binding energies of the polymer levels (Table 1) are considerably lowered, suggesting that the chains are in the neutral state. However, features corresponding to oxidized nitrogen and sulphur species



(1)

appear in the spectrum, which could be correlated with the sensitivity to the atmosphere of the neutral polymer. In fact, the oxygen content increases from 3—4% (atomic ratio) immediately after reduction to 10% one week later.

The polymer structure is expected to consist of a repetition of thienopyrrole units, consistent with the elemental composition derived from x.p.s. core line intensities. Since we observed that the polymerization is prevented by substitution α to the nitrogen atom, α–α' couplings must account for the majority of the linkages between the monomer units. A more complete characterization of the polymer, including in particular i.r. and u.v.–visible studies, which we intend to carry out, should give further information on this point. We have thus shown that electropolymerization of thieno[3,2-*b*]pyrrole leads to doped conducting films, which can be changed to a reduced undoped state along with a concomitant colour change.

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