Immobilization of Redox Anions in Poly(Amphiphilic Pyrrolylalkylammonium) using a simple and Monomer-saving One-step Procedure in Pure Water Electrolyte

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The pyrrolylalkylammonium tetrafluoroborate monomer **1** can be electropolymerised in aqueous electrolytes when adsorbed on an electrode surface and electroactive bulky anions can be incorporated either in polymer films of **1**, or by electropolymerisation of a coating containing the anion along with **1**; cyclic voltammetry peak splittings suggest a regular surface arrangement.

Recently there has been considerable interest in new methods for processing modified electrodes by anchoring electroactive polymer films with a well-defined molecular structure. Thus, it has been demonstrated that electrically conducting polypyrroles prepared by chemical polymerisation[1] or electropolymerisation[2] in Langmuir–Blodgett films are effective for stabilising organised assemblies.

In this paper, we present our preliminary results about the electropolymerisation of the amphiphilic substituted pyrrole **1**.†

Films of poly(**1**) could be electrodeposited onto an electrode surface by using a novel procedure requiring only small amounts of monomer and carried out in aqueous electrolyte. The electropolymerisation of pyrrole in water is usually carried out using a high concentration of monomer (0.1–1 mol dm^{-3}). Furthermore, homopolymers from substituted pyrroles obtained in aqueous electrolytes are uncommon.

Monomer **1** has a low solubility in water at ambient temperature. From turbidity measurements, the solubility of this monomer is estimated to be less than 8×10^{-5} and 2×10^{-5} mol dm^{-3} in pure water and in $LiClO_4$ (0.1 mol dm^{-3}) aqueous electrolyte respectively. In a similar way that surfactant vesicles are prepared,[3] sonication in pure water initially disperses **1** into a turbid solution, which then becomes optically transparent and is stable for days. Preliminary experiments demonstrate that organised aggregates of **1** are formed. Work is in progress to characterise this stable dispersion.

On a platinum or glassy carbon electrode the cyclic voltammogram of **1** (4×10^{-3} mol dm^{-3}) in Et_4NClO_4–MeCN (0.1 mol dm^{-3}) exhibited only the irreversible oxidation peak of the pyrrole moiety at 1.05 V *vs.* Ag/10^{-2} mol dm^{-3} Ag^+. Films of poly(**1**) could be grown on the electrode surface by controlled potential oxidation at 0.85 V. The resulting modified electrode exhibited the quasi-reversible redox peak system at 0.4 V, typical of a *N*-substituted polypyrrole.[4]

From dispersions of **1** in $LiClO_4$–H_2O (0.1 mol dm^{-3}) it is also possible to electrodeposit thin polymer films of **1** on carbon surfaces by controlled-potential oxidation at 0.76 V *vs.* standard calomel electrode (SCE). This polymerisation seems to be due to an adsorbed layer of the insoluble monomer on the electrode surface.

Thicker polymer films of **1** could be easily obtained by using the uncommon and monomer-saving electropolymerisation process described hereafter. A drop of monomer **1** stock

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† Compound **1** was obtained by refluxing for 16 h in ethanol 12-(pyrrol-1-yl)dodecyl-*p*-toluenesulphonate with an excess of triethylamine. Anion-exchange on an Amberlite IRA-93 resin in BF_4^- form afforded **1** as a red-brown oil. Its structure was established by fast atom bombardment mass spectrometry (*m*/*z* positive mode C^+ 335) and ^1H NMR ($CDCl_3$) δ *vs.* Me_4Si: 1.29 (t, 9 H, *J* 7.5 Hz), 1.41 (m, 20 H), 3.08 (m, 2 H), 3.24 (q, 6 H, *J* 7.5 Hz), 3.79 (t, 2 H, *J* 7 Hz), 6.06 (t, 2 H, *J* 2 Hz), 6.58 (t, 2 H, *J* 2 Hz).

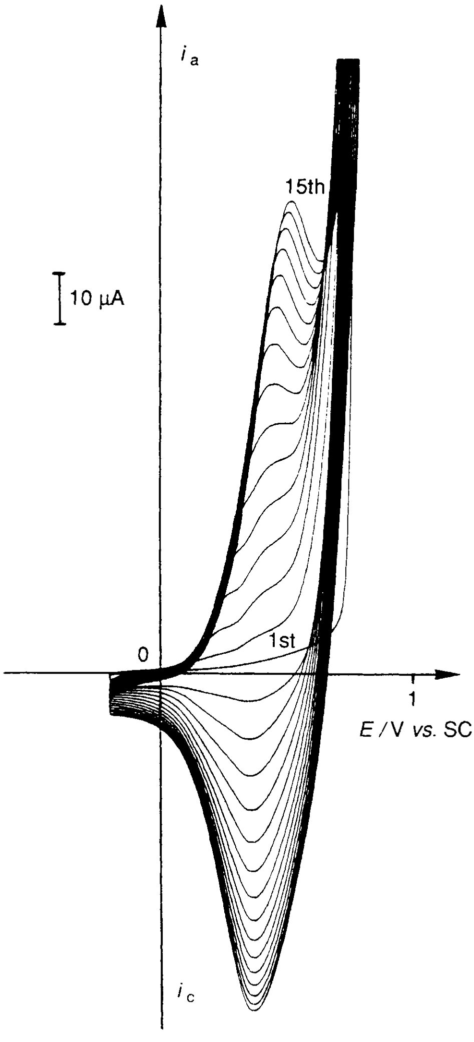

Fig. 1 Electropolymerisation of **1** (5.1×10^{-8} mol deposited on a 5 mm diameter Pt electrode) by repeated potential scanning in $LiClO_4$–H_2O (0.1 mol dm^{-3}), 1st to 15th scan; sweep rate v = 50 mV s^{-1}

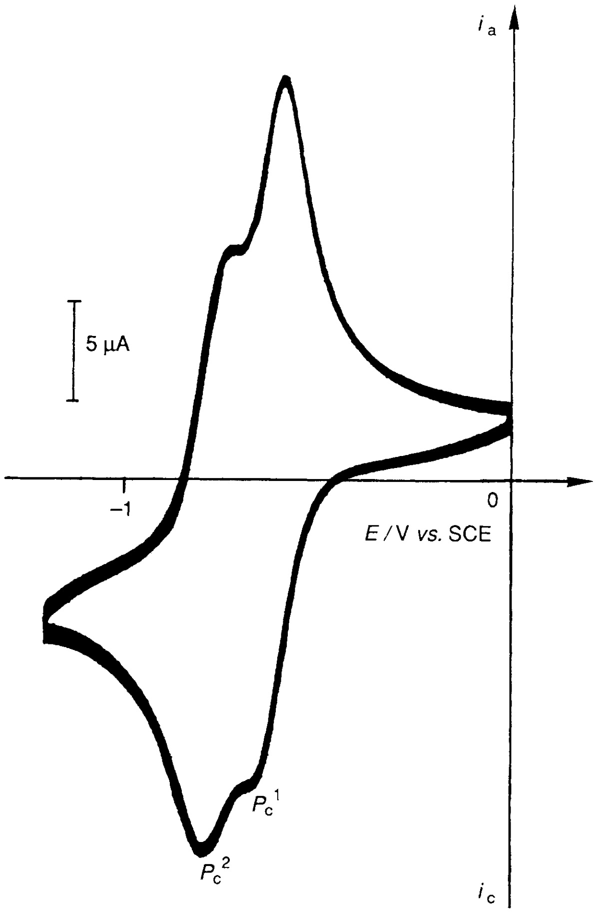

Fig. 2 Cyclic voltammetry curve for a C/poly (**1**-AS) modified electrode prepared, as described in the text, and cycled in $LiClO_4$–H_2O (20 mmol dm^{-3}; $\Gamma_{AS} = 10^{-8}$ mol cm^{-2}), the first 6 scans are represented; v = 50 mV s^{-1}

solution in MeCN or suspension in water (typically 20 and 40 μl respectively) is laid on the electrode surface (Pt or C disk, diameter 5 mm) and the solvent evaporated to dryness under a sunlight lamp. Then the electrode is placed in pure $LiClO_4$–H_2O (0.1 mol dm^{-3}) electrolyte. The oxidative electropolymerisation of **1** can be accomplished either by repetitive scanning over the −0.2 to 0.8 V range (Fig. 1), or by controlled-potential oxidation at 0.76 V.

The modified electrodes exhibited a stable electrochemical response in aqueous and MeCN electrolytes of *N*-substituted polypyrroles, with quasi-reversible redox peak systems around 0.5 V and 0.4 V respectively. Apparent surface concentrations Γ_{N^+}‡ of pyrrole, and thus the alkylammonium unit, from 2.5×10^{-8} to 1.5×10^{-7} mol cm^{-2} could be easily obtained from the concentration of **1** in the stock MeCN solution or suspension in H_2O. Thicker films, with Γ_{N^+} up to 4.6×10^{-7} mol cm^{-2} have been made from diluted (2–5 mmol dm^{-3}) solutions or suspensions by repeating the deposition procedure.

The alkylammonium groups confer on the polymer films of **1** anion-exchange properties similar to those demonstrated for related poly(pyrrolylalkylammonium or pyridinium);[4] multicharged organic and inorganic anions have been incorporated in these preformed polymer films.

More attractive is the fact that the incorporation of an electroactive anion in a polymer film could also be accomplished in one step, by the electropolymerisation of a monomer-anion mixture in water spread and dried on the electrode surface. As an example, Fig. 2 depicts the cyclic voltammetry for a C/poly(**1**)-AS§ modified electrode obtained upon controlled-potential polymerisation in aqueous electrolyte of a coating containing 0.19 μmol of **1** and 0.22 μmol of an AS sodium salt. The electropolymerisation appeared less efficient than with **1** alone. This could be due to the quenching effect of sulphonate groups on the pyrrole polymerisation.

It is noteworthy that the AS reversible reduction system gives two distinct redox couples at −0.63 and −0.76 V. No peak splitting was observed for AS incorporated in a non-amphiphilic poly(pyrrolylalkylammonium) film.[4] Cycling over the +0.72 to −1.2 V range, or potentiostating the electrode at −1 V resulted in an increase of the $i_{pc}{}^1/i_{pc}{}^2$ ratio.

This behaviour is identical to that already reported for $[Ru^{II}(2,2'\text{-bipyridine})_3]^{2+}$ incorporated in a poly(styrenesulphonate) matrix[5] and these observations suggest that AS anions trapped in the polymer film are in at least two distinct environments with different redox potentials. Furthermore, similar doubled-peak voltammograms have also been reported for electroactive amphiphilic molecules in a Lang-

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‡ Calculated from the integrated charge under the polypyrrole oxidation wave, assuming that one in three pyrrole units is oxidised.

§ AS is anthroquinone 2-sulphonate.

muir–Blodgett monolayer form[6] and amphiphiles from a liposome solution adsorbed on an electrode surface,[7] or with a polyvinylferrocene film containing liquid crystalline dopants.[8] Specific interactions were postulated to be responsible for the formation of discrete species having different redox potentials. Finally, a theoretical model[9] based on a statistical mechanical description of surface-bound monomolecular films containing redox species, suggests that one-electron transfer splitting occurs when surface arrangement is regular.

The amphiphilic pyrrole **1** appeared to have unusual features which allow its electropolymerisation in aqueous electrolytes when it is adsorbed on an electrode surface. Electroactive anion-containing polymer modified electrodes could be synthesised by the electropolymerisation of a **1**-electroactive anion coating. This novel monomer and anion-saving procedure will be applied to the preparation of enzyme and cofactor-containing films as biosensors.

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