Electrochemical Synthesis of Ferrocene-functionalized Polypyrrole Films

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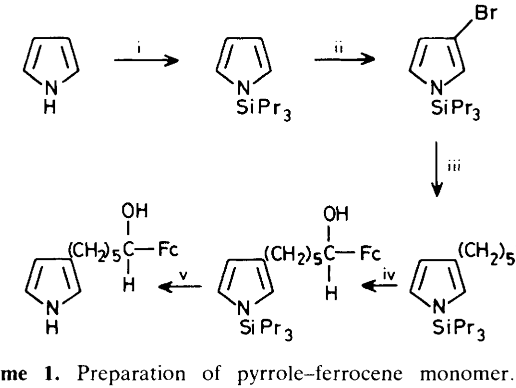
Electrochemical copolymerization of pyrrole and 3-(6-ferrocenyl-6-hydroxyhexyl)pyrrole yields a ferrocene functionalized polypyrrole with a controllable amount of ferrocene functionalization.

Conducting polypyrrole can be chemically modified to produce films with a wide variety of highly specific electroactive properties by attaching substituents to the pyrrole monomer prior to polymerization[1—5] or to polypyrrole films,[6] or by incorporating electroactive and electro-optic molecules as counterions.[7—10] Herein we report the synthesis and electrochemical behaviour of thin films of poly[3-(6-ferrocenyl-6-hydroxyhexyl)pyrrole] (PP–Fc) and copolymers with pyrrole. These materials are of interest as modified electrodes for organic and bio-electrochemistry.



Scheme 1. Preparation of pyrrole–ferrocene monomer. (Fc = ferrocenyl). *Reagents*: i, NaH, Pr_3SiCl; ii, *N*-bromosuccinimide; ii, Bu^nLi, $Br(CH_2)_5Br$; iv, Mg, ferrocenecarbaldehyde; v, Bu_4NF, H_2O.

The pyrrole–ferrocene (P–Fc) monomer was synthesized as shown in Scheme 1. Thin polymer films (500—5000 Å) were grown by electrochemical oxidation of monomers from acetonitrile (MeCN) solution, on sputtered Pt-on-glass electrodes with a Pt counter electrode and a saturated calomel reference electrode (s.c.e.).†

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† The films were grown at a constant potential of 1.00 V *vs.* s.c.e. and the charge passed was 100 mC cm^{-2}. The films incorporating the P–Fc moieties were copolymers of P–Fc and unsubstituted pyrrole. Homopolymers of P–Fc were difficult to produce in thin film form and attempts resulted only in uneven film deposits on the electrode. The copolymers were made from electrolyte–monomer solutions of P–Fc (0.02 M), tetraethylammonium tetrafluoroborate ($TEABF_4$) (0.1 M, recrystallized twice from MeOH), and freshly distilled pyrrole (0.1, 0.5, or 1.0 M) in MeCN (distilled twice over CaH_2). The solutions were thoroughly deoxygenated prior to polymerization. The films were rinsed thoroughly with MeCN and EtOH and placed in fresh $TEABF_4$–MeCN solutions for cyclic voltammetry studies.

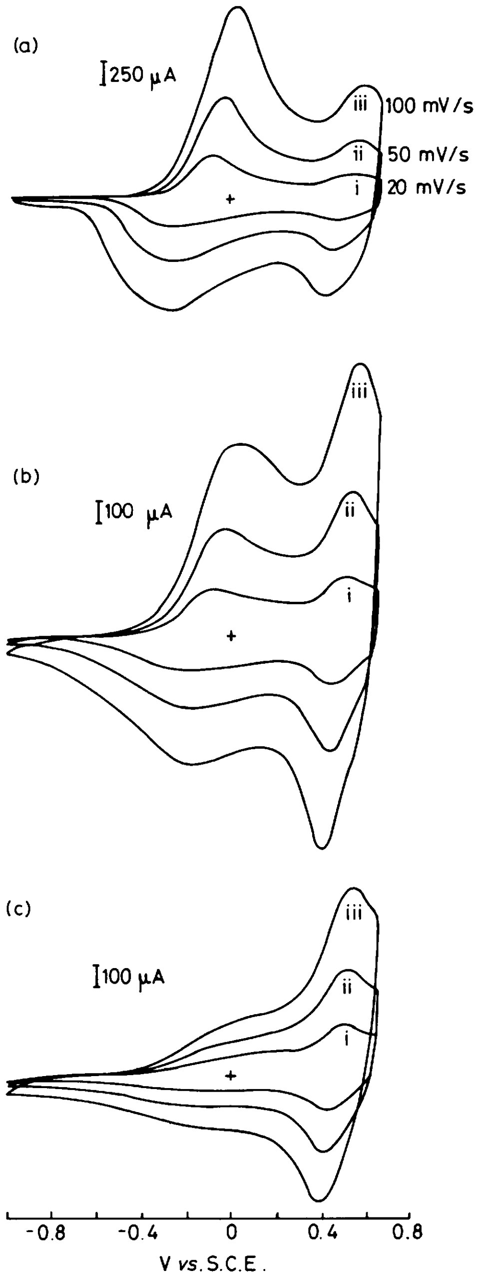

Figure 1. Cyclic voltammograms for copolymers of pyrrole and P–Fc from polymerizing solutions of three different relative concentrations of pyrrole and P–Fc: (a) 1.0 M pyrrole, 0.02 M P–Fc; (b) 0.5 M, pyrrole, 0.02 M P–Fc; (c) 0.1 M pyrrole, 0.02 M P–Fc. The scan rates were (i) 20, (ii) 50, and (iii) 100 mV sec^{-1} in $TEABF_4$–MeCN (0.1 M) electrolyte.

Cyclic voltammetry of the PP–Fc films in deoxygenated $TEABF_4$–MeCN electrolyte revealed two different redox processes corresponding to the reduction/oxidation of the polypyrrole backbone and the ferrocene moiety, respectively (Figure 1). The $E_{\frac{1}{2}}$ value of the ferrocene moiety in the copolymer film is not appreciably different from that in the P–Fc monomer or in unsubstituted ferrocene in MeCN solution. The films could be cycled repeatedly, thereby confirming the persistence of the covalent link to the Fc moiety.

The ΔE value for the incorporated ferrocene was dependent on scan rate, but was apppreciable even at low scan rates (60 mV *vs.* s.c.e. at 20 mV s^{-1}). Since no peak separation is expected for a Nernstian process for a surface adsorbed species, this may indicate a structural hysteresis associated with ion movement in and out of the polymer in addition to an *iR* drop.

Evidence for the existence of the ferrocene moiety in the films is also seen in the u.v.–visible spectra of thin films deposited on indium–tin oxide electrodes. The characteristic ferrocene absorption band had a peak at 435 nm, both for the copolymer film and the monomer in MeCN solution.

As can be seen from Figure 1, the amount of ferrocene incorporated in the film can be controlled by varying the composition of the electropolymerizing solution. The exact composition is difficult to determine from electrochemical data alone since the electroactivity, as measured by peak heights for polypyrrole, is sensitive to solvents and composition. Additional experiments to characterise the films fully are in progress.

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