Electropolymerization of 4-(3-pyrrolyl)-4-oxobutyric acid by *in situ* potentiodynamic pre-reduction/oxidation

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Electrochemical polymerization of 4-(3-pyrrolyl)-4-oxobutyric acid and its copolymerization with pyrrole produces electroactive polymers and copolymers, respectively. This study highlights the advantages to be gained by using transient potential waveforms for production of polymer materials.

(Keywords: 4-(3-pyrrolyl)-4-oxobutyric acid; electropolymerization; conducting polymer)

INTRODUCTION

Previous investigations into 3-substituted pyrroles have shown that: the alkyl substituents[1-3] determine the lipophilicity of the resultant polymers; the alkylsulfonate substituents[4] enable water-soluble self-doped polymers to be produced; polymers are obtained from ketopyrrole derivatives[5]; a pyrrole-ferrocene monomer can be copolymerized with pyrrole to produce ferrocene-functionalized polypyrrole films[6]; a 3-alkyl substituted chiral pyrrole can be copolymerized with pyrrole[7]. Our interest in 3-substituted pyrroles, however, stems from the need to produce more hydrophilic polymers or copolymers which would be stable in water, methanol or acetonitrile as a minimum requirement. The intention is to apply these new polymers or copolymers in the fields of transport across membranes[8-18], and new chromatographic stationary phases[19-22]. Towards these ends, we now report the organic synthesis of 4-(3-pyrrolyl)-4-oxobutyric acid (POBA), **I**, its electropolymerization, and its electrocopolymerization with pyrrole.

EXPERIMENTAL

The organic synthesis was carried out so that 1-(phenylsulfonyl)pyrrole[23] gave the 4-[(1-phenylsulfonyl)-3-pyrrolyl]-4-oxobutyric acid by the $AlCl_3$ catalysed Friedel Crafts acylation reaction[24]. Subsequent alkaline hydrolysis gave POBA. All the synthesized compounds were characterized according to literature methods[23,24], and are in agreement with published results.

Electrochemical experiments were performed in a three-electrode cell where the working electrode was a glassy carbon (GC) disc (BAS), the auxiliary electrode was a Pt mesh and the reference electrode was Ag/AgCl (3 M NaCl) (BAS).

Typical solution conditions for the electropolymerizations were as follows:

1. POBA (**I**): POBA (0.1–0.2 M) in H_2SO_4 (2 M)/CH_3OH or HCl (2 M)/CH_3OH or $HClO_4$(2 M)/CH_3OH;
2. 4-(3-pyrrolyl)-4-butyric acid (PBA, **II**): PBA (0.1 M)/ H_2SO_4 (2 M)/CH_3OH;
3. POBA with pyrrole: POBA (0.1 M)/pyrrole (0.1 M)/ $HClO_4$ (2 M)/CH_3OH. The potentiodynamic scan rate used was $1.0 V s^{-1}$.

Cyclic voltammetric characterization of the polymers was performed at a scan rate of $100 mV s^{-1}$ in 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB)/ CH_3OH. The potential limits were -2.0 V and $+1.2$ V.

RESULTS AND DISCUSSION

The resultant cyclic voltammograms over the potential range from -2.0 V to $+1.2$ V show that POBA can be electropolymerized only by pre-reducing the keto group of the molecule prior to oxidation. This irreversible reduction process only occurred in the presence of acid. The above behaviour is illustrated by the cyclic voltammogram (*Figure 1*) where the initial scan (0.0 to $+1.2$ V, scan 1) did not result in monomer oxidation. However, after the monomer was reduced ($Ep_{(c)} = -1.48$ V, scan 2) an oxidation response was evident ($Ep_{(a)} = 1.00$ V, scan 2). The dark brown polymers obtained were electroactive and this is best depicted by the cyclic voltammogram of the polymer (*Figure 2*). In fact, the degree of electroactivity (peak currents) increased with an increased number of scans.

Further evidence showing that electropolymerization of this monomer can only be achieved by the pre-reduction/oxidation technique, is given by the absence of any polymer formed when potential cycling was confined between the potential limits of (a) 0.0 and $+1.2$ V, and (b) -2.0 and 0.0 V.

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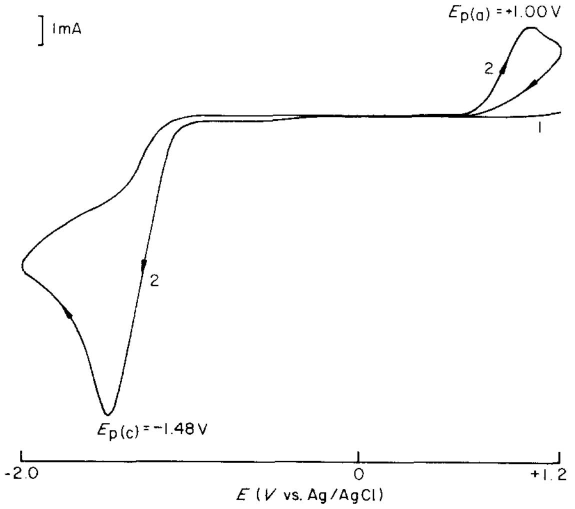


Figure 1 Potentiodynamic electropolymerization of POBA. Monomer solution: POBA (0.2 M) in H_2SO_4 (2 M)/CH_3OH. Scan rate 1.0 V s^{-1}

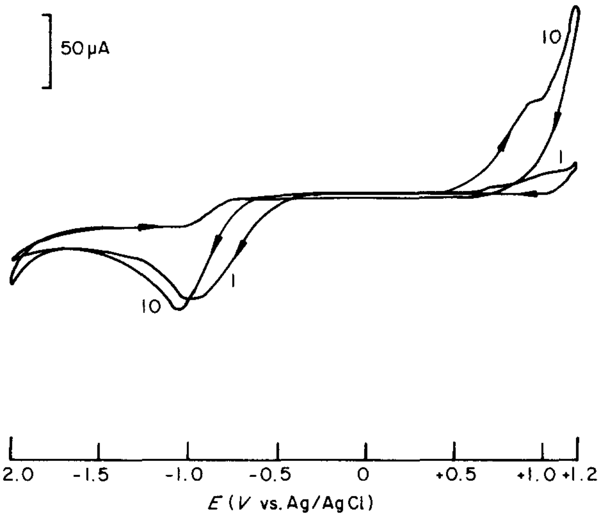


Figure 2 Cyclic voltammogram of the polymer (poly-PBA-perchlorate) modified GC electrode in TBATFB (0.1 M)/CH_3OH. Scan rate 100 mV s^{-1}

In a separate experiment, 4-(3-pyrrolyl)-4-butyric acid (PBA, **II**) in H_2SO_4 (2 M)/CH_3OH was electropolymerized by potentiodynamic cycling between the potential limits of 0.0 and + 1.2 V. The oxidation peak potential obtained for PBA was + 1.00 V (*Figure 3*) which corresponds exactly with the oxidation potential of POBA after pre-reduction (*Figure 1*).

All this electrochemical evidence suggests that the electropolymerization of POBA to produce poly(4-(3-pyrrolyl)-4-butyric acid) (**III**) proceeds as shown in *Scheme 1*.

Polymerization from a mixture of POBA and pyrrole in $HClO_4$ (2 M)/CH_3OH, using the same potentiodynamic conditions as above, was investigated (*Figure 4*). The earlier onset of oxidation in the presence of pyrrole and the nucleation crossover observed in the voltammogram are indicative of increased polymer growth in the presence of pyrrole[25]. The black copolymers formed were electroactive and display cyclic voltammograms (*Figure 5a*) that are different from the cyclic voltammogram of polypyrrole (*Figure 5b*). This difference is apparent even though the cyclic voltammograms of the individual comonomers show that pyrrole is more rapidly oxidized than POBA.

In conclusion, these preliminary studies show that the technique of potentiodynamic pre-reduction/oxidation

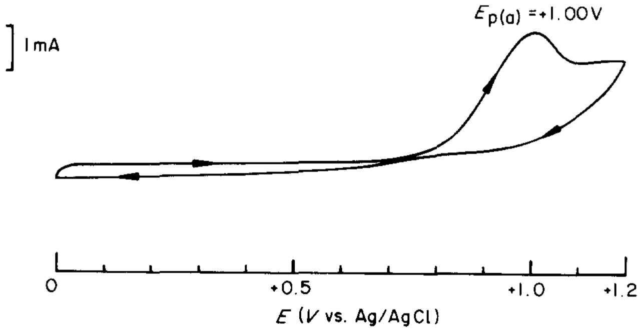
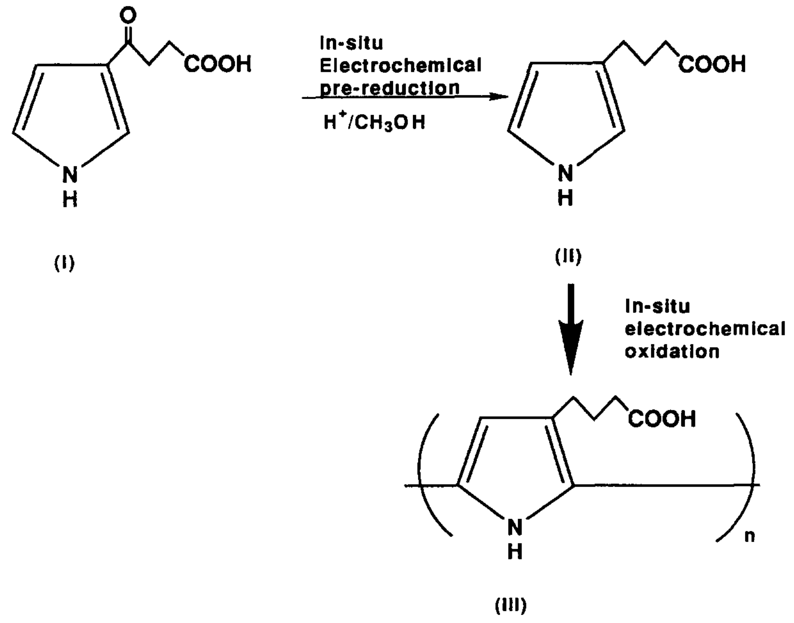


Figure 3 Potentiodynamic electropolymerization of PBA. Monomer solution: PBA (0.1 M) in H_2SO_4 (2 M)/CH_3OH. Scan rate 1.0 V s^{-1}



Scheme 1

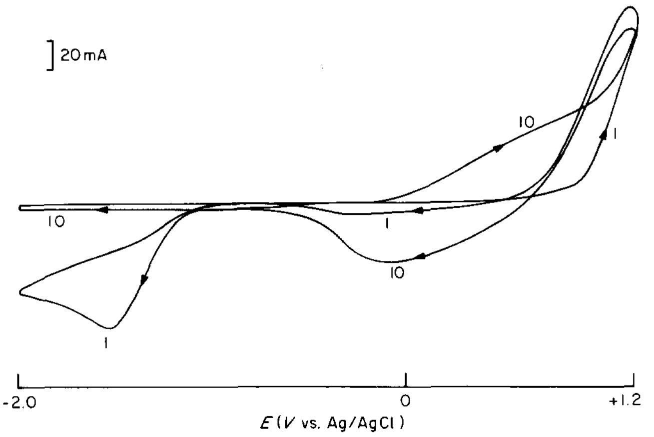


Figure 4 Potentiodynamic electrocopolymerization of POBA with pyrrole. Monomer solution: POBA (0.1 M)/pyrrole (0.1 M) in $HClO_4$ (2 M)/CH_3OH. Scan rate 1.0 V s^{-1}

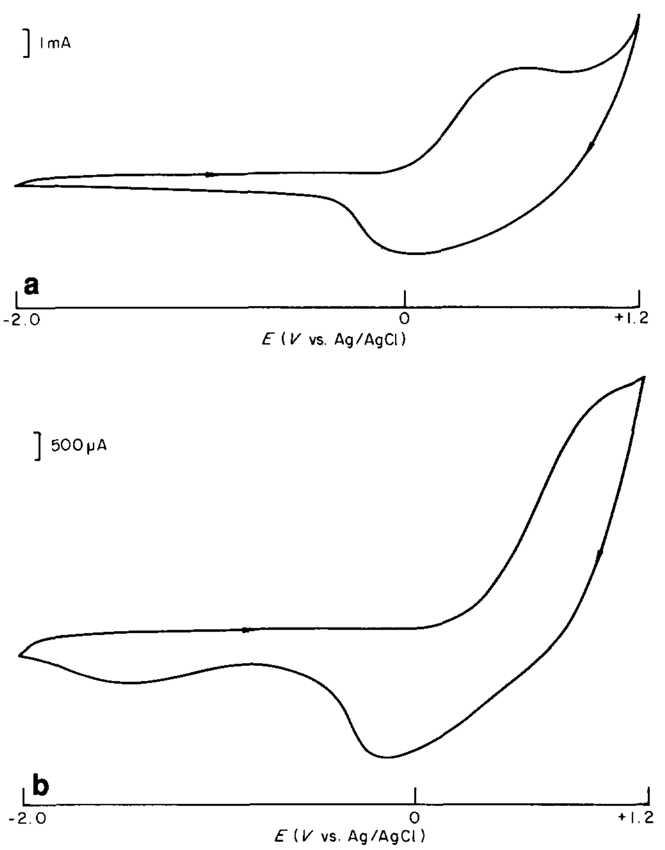


Figure 5 (a) Cyclic voltammogram of the copolymer (poly-[PBA/pyrrole]-perchlorate) modified GC electrode in TBATFB (0.1 M)/CH_3OH. Scan rate 100 mV s^{-1}. (b) Cyclic voltammogram of the polypyrrole-perchlorate modified GC electrode in TBATFB (0.1 M)/CH_3OH. Scan rate 100 mV s^{-1}

can achieve electropolymerization where other more conventional techniques fail. Furthermore, as reported, such polymeric products can be electroactive.

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