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Preliminary note

Redox behaviour of a poly(pyrrole) modified electrode where the pyrrole has *N*-substituted 9-cyanoanthracene groups

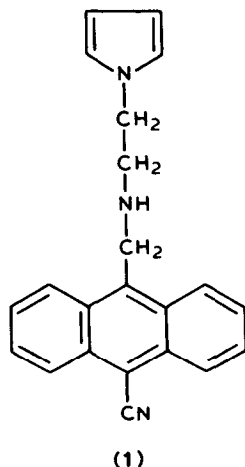
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INTRODUCTION

Poly(pyrrole) has the useful property of forming a tough matrix which moulds to the electrode support. In view of the growing interest in redox materials held on an electrode surface by covalent attachment to poly(pyrrole) [1–6], we were led to examine the redox behaviour of some materials in this class. We report here the behaviour of the 9-cyanoanthracene group in an electrode coating formed by oxidative polymerization of 1-[2-(9-cyanoanthracene-10-ylmethylamino)ethyl]pyrrole (**1**). The behaviour of this polymer [poly(**1**)] on cyclic voltammetry (CV) and chronoamperometry (CA) in the cathodic region, where the 9-cyanoanthracene group is electroactive, is strikingly different from the behaviour of most other electroactive polymers.



EXPERIMENTAL

Reaction between 9-bromomethyl-10-cyanoanthracene and 1-(2-aminoethyl)pyrrole gave (1), m.p. 107–108°C (Found: C, 81.2; H, 5.7; N, 13.2%; $C_{22}H_{19}N_3$ requires C, 81.2; H, 5.9; N, 12.9%; $M^+ m/z$ 325).

A coherent, thin, polymeric coating formed on a spherical Pt anode (diameter 1–2 mm) after oxidation of (1) at 1.2 V vs. SSCE (saturated sodium chloride calomel electrode) from 20 mM solution in acetonitrile containing 0.1 M Pr_4NClO_4 and a slight excess of perchloric acid. Acid is necessary to give a coherent coating and probably prevents attack by the amine-nitrogen lone pair on pyrrole radical-cation intermediates. The coated Pt sphere was transferred to a fresh solution of electrolyte in acetonitrile for the experiments described below.

RESULTS AND DISCUSSION

A typical CV of a thin film of poly(1) is shown in Fig. 1. The current flow is associated with the redox behaviour of the 9-cyanoanthracene group. For comparison, E° for (1) in acetonitrile is -1.47 V vs. SSCE. Peak current is proportional to scan rate as expected for a thin film. The shape of the cathodic peak is quite different from that expected for thin films [7,8]. The cathodic current decreases sharply to almost zero at negative potentials while the anodic peak has more nearly the expected bell shape with a 75 mV width at half-height.

A typical CA–Cottrell plot for poly(1) is shown in Fig. 2. Clearly there is no linear relationship between current and $1/t^{1/2}$. What is observed is very rapid charging of the film and then a sudden cessation of current flow. The type of behaviour we describe during CA and CV can be repeated many times with the same sample of polymer.

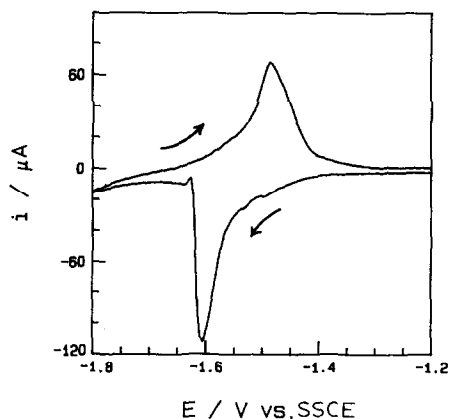


Fig. 1. Cyclic voltammetry of poly(1) on Pt (area 0.131 cm²) in acetonitrile, 0.1 M Pr_4NClO_4 ; $v = 0.070$ V s⁻¹; $\Gamma = 8.7$ nmol cm⁻² (by CA); charge passed for polymerization = 7.30 mC cm⁻².

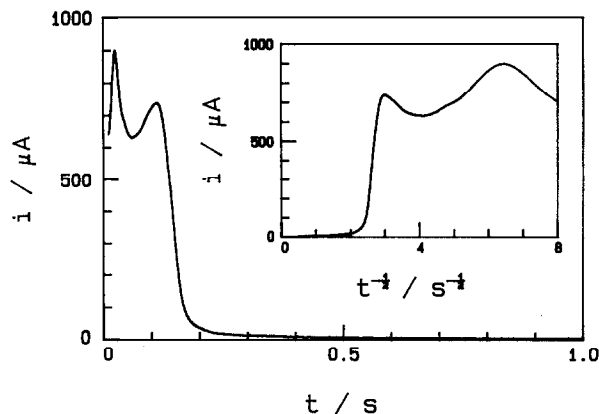


Fig. 2. Chronoamperometry of poly(1) on Pt (area 0.112 cm^2) in acetonitrile, $0.1 \text{ M Pr}_4\text{NClO}_4$; potential step $0 \rightarrow -1.8 \text{ V vs. SSCE}$; $\Gamma = 10 \text{ nmol cm}^{-2}$; charge passed for polymerization = 7.83 mC cm^{-2} .

Similar behaviour on CV and anomalous CA curves has been observed for films composed from the thiofulvalenium cation in a Nafion matrix [9,10]. The rapid electron transport into these films which occurs at negative potentials has been taken to indicate that the acceptor units are confined or stacked within zones. We can rationalise the behaviour of poly(1) in a related manner.

There cannot be the usual random distribution of electroactive groups in the polymer; this would lead to normal behaviour on CV and CA. Rather, groups of cyanoanthracene units must be organised close to each other in the matrix to form zones with a high density of electroactive groups which are surrounded by regions with a much lower density of these groups. With this arrangement, rapid transport of electrons can be expected through the high density zones together with counter-

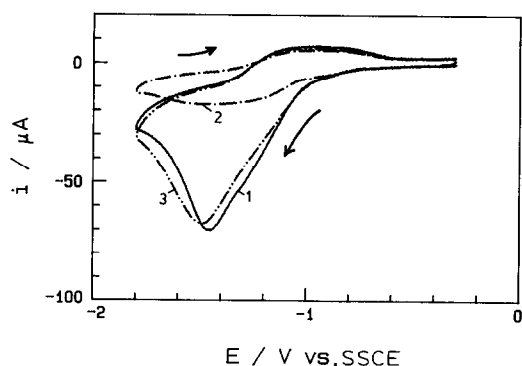
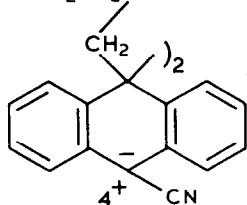


Fig. 3. Cyclic voltammetry of poly(1) on Pt (area 0.182 cm^2) in acetonitrile, 0.1 M LiClO_4 ; $\nu = 0.070 \text{ V s}^{-1}$; $\Gamma = 25 \text{ nmol cm}^{-2}$ (by CA); charge passed for polymerization = 4.0 mC cm^{-2} . (1) First CV; (2) third CV; (3) subsequent CV after 10 min rest at 0 V vs. SSCE .

Poly(pyrrole)CH₂CH₂NH

(2)

ions and solvent molecules. On this model, the cathodic branch of the CV curve is expected to commence with a normal shape. However there is also a limit to which the polymer lattice can expand to accept the counter-ions. When this limit is reached, electron transport into the film will suddenly cease as observed during CV and CA, even though unreduced cyanoanthracene units are available.

This type of behaviour is not observed with electroactive polymers based on the lattices of poly(styrene) [11,12] and poly(amino acids) [13-15].

In the presence of lithium ions in acetonitrile, the electrochemical behaviour of thin films of poly(1) is entirely changed. The apparent surface coverage from CV and CA is considerably increased and the CA now shows normal Cottrell behaviour. On the CV, a broad cathodic peak is observed for the first cycle with no corresponding anodic peak (Fig. 3). After passage of this first cathodic current, the film behaves as an insulator. When this insulating film is allowed to rest for a few minutes at 0 V vs. SSCE, the original CV behaviour is restored.

We believe this behaviour in the presence of lithium ions to be due to dimerization of the 9-cyanoanthracene radical-anion to form (2). The rate of the corresponding anodic process is then dependent on a slow carbon-carbon bond cleavage in the dimer. An alternative explanation is the formation of a tight ion-pair that is not easily oxidised.

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