Electroactive Copolymers of Pyrrole Containing Covalently Bound Dopant Ions: Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulphonate]}

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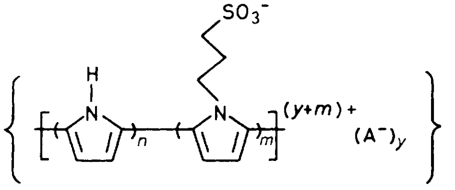
A self-doped electroactive copolymer, poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulphonate]}, in which the charge balancing counterion is covalently attached to the polymer chain, has been synthesized and cation controlled charge transport parameters have been evaluated.

The redox conductivity of polyheterocycles, such as polypyrrole, is strongly dependent on the degree of oxidation of the polymer and the rate of electrochemical charge transport through the film.[1] During oxidative doping in a supporting electrolyte, ion mobility can occur *via* either incorporation of a dopant anion into the polymer film or expulsion of a resident cation out of the film leaving an anion for charge compensation. This phenomenon is dependent on the nature of the electrolyte and is controlled by the polymer ion interactions.[2]

We report here the synthesis and evaluation of charge transport properties of a pyrrole copolymer, poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulphonate]} (**1**) having a covalently bound dopant ion attached to the polymer chain. This bound ion serves as an internal dopant ion, thus causing the polymer to be 'self-doped.' The sulphonate species was chosen in view of its well known low reactivity in electrochemical redox processes. In this manner, the ionic transport in the conductive polymer can be modulated by a high density of anionic sites, thus requiring the cation to be the mobile species. Chronocoulometric experiments at these copolymer electrodes can then yield information on the diffusion of cationic species without the complication of having to determine the identity of the diffusing species. The situation is comparable, to a certain extent, to that of the ionomeric Nafion–redox polymer composites[3,4] and the poly(vinyl sulphate)–polypyrrole composites[5] reported previously.

Potassium 3-(pyrrol-1-yl)propanesulphonate (**2**) was synthesized by the reaction of pyrrole with potassium and then with 1,3-propanesultone. The product was washed repeatedly with hot tetrahydrofuran to remove any unreacted sultone and dried at 60 °C *in vacuo* for 24 h. The product was characterized by diffuse reflectance Fourier transform (F.t.)-i.r. (KBr): $\tilde{\nu}$ 3097, 2935, 2878, 1501, 1447, 1201, 1192, 798, 729, 609, and 532 cm^{-1}; ^{1}H n.m.r. (D$_2$O): δ 6.89 (br. t, 2H), 6.18 (t, 2H), 4.13 (t, 2H), 2.99—2.77 (m, 2H), 2.20—2.13 (m, 2H); and elemental analysis.

Cyclic voltammetric (c.v.) oxidation of monomer (**2**) in acetonitrile containing $Bu^n_4NBF_4$ as supporting electrolyte at a platinum electrode resulted in a broad peak around 1.1 V [*vs.* Ag/Ag$^+$ (0.1 M)] as shown in Figure 1(a). The oxidation rendered the electrode surface non-conducting as shown by the absence of any significant anodic current in succeeding scans. C.v. examination of an equimolar mixture of monomer (**2**) and pyrrole in the same medium showed an anodic peak around the same potential, but the magnitude of the peak current increased [Figure 1(b)], demonstrating the co-oxidation of both monomers at this potential. During the c.v. scan a conducting copolymer film was deposited on the electrode. The film was blue in the oxidized state and switched to brown upon reduction. Similar results were obtained in other supporting electrolytes, such as LiClO$_4$–MeCN. The cyclic voltammogram of the film-covered electrode in a solution of LiClO$_4$ in MeCN without monomer exhibited an anodic peak around 0.2 V and a broad reduction peak in the cathodic region [Figure 1(c)].



(**1**)

Elemental analysis of the copolymer prepared in the oxidized form indicated a pyrrole : pyrrolesulphonate ratio of 3 : 1 and a BF$_4^-$: pyrrole ring ratio of 1 : 16. This is due to the random incorporation of the bound sulphonate ions along the polypyrrole chain that participate in the charge-transfer complex and thus reduce the BF$_4^-$ content in the polymer as compared to the typical poly(pyrrole tetrafluoroborate) structure where the BF$_4^-$: pyrrole ring ratio is about 1 : 3. Thus it is clear that the polymer is 'self-doped.'

Diffuse reflectance F.t.-i.r. spectra of the copolymer showed features common to the homopolymers of both pyrrole and pyrrolesulphonate ($\tilde{\nu}$ 1215, 1184, 1054, 1041 cm^{-1}). The S–O stretching bands in the 1200 cm^{-1} region are characteristic of the sulphonate group[6] and indicate that the groups did not undergo any undesirable electrochemical degradation.

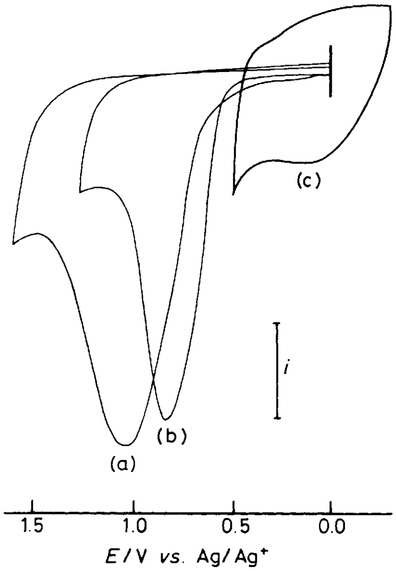


Figure 1. Cyclic voltammograms for the redox processes, (a) oxidation of 3-(pyrrol-1-yl)propanesulphonate (*ca.* 7 mM) in MeCN–$Bu^n_4NBF_4$ electrolyte at a Pt electrode (A = 1.8 mm^2), scan rate 100 mV/s, i = 10 μA ; (b) oxidation of a 1 : 1 mixture of pyrrole and 3-(pyrrol-1-yl) propanesulphonate under the same conditions, i = 20 μA; (c) redox reaction of poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulphonate]} in MeCN–0.1 M LiClO$_4$ electrolyte, i = 5 μA.

The conducting and electroactive properties of the copolymer films were examined using an electrochemical probe. The facile oxidation of ferrocene at a copolymer-modified electrode in $Bu^n_4NBF_4$–MeCN demonstrated the conductive nature of the surface. However, the cathodic peak for the reduction of the ferricenium ion was considerably broadened, suggesting kinetic limitations relative to polypyrrole. It was expected that the copolymer, containing nitrogen-bound substituents, would have lower conductivity as is the case with *N*-alkyl substituted pyrrole homopolymers and their copolymers.[7] This was expected to lead to slower electrochemical response characteristics.

Chronocoulometry was used to estimate charge transport in the films during oxidative doping in supporting electrolyte solutions of $LiClO_4 \cdot 3H_2O$, $LiBF_4$, and $Bu^n_4NBF_4$ in MeCN. A potential step, from an initial potential of -0.2 V to $+0.5$ V, was applied to the working electrode covered with copolymer film and the resulting charge-time curves were monitored. From the slopes of the charge Q *vs.* $t^{1/2}$ plots, the transport rate was obtained as D/L^2, where D is the apparent diffusion coefficient and L represents the thickness of the solvent swollen film.[4] The values of D/L^2 for $LiClO_4 \cdot 3H_2O$, $LiBF_4$, and $Bu^n_4NBF_4$ are 0.05 (±0.01), 0.28 (±0.07), and 0.08 (±0.02) s^{-1}, respectively.

Since the ClO_4^- and BF_4^- anions are similar in size and charge density, the variation in D/L^2 must be due to the mobile cation; the bulkier tetrabutylammonium ion moves slower, as would be expected, than the smaller non-hydrated Li^+ ion. However, since the hydrated Li^+ ion in $LiClO_4$ is bulkier than the non-hydrated Li^+ in $LiBF_4$ the value of D/L^2 is much smaller. A complete study of the interaction of the mobile cationic species with the bound-ion polymer is in progress. A dry film thickness for the copolymer films can be estimated from a charge–thickness relationship[8] as 0.5 μm, and if a solvent swelling factor of 2 is assumed[9] it can be seen that the diffusion coefficients are of the order of 10^{-10} $cm^2 s^{-1}$, in good agreement with values obtained by other workers[10] for polypyrrole films.

Financial support through grants from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research, the Texas Advanced Technology Research Program, the Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Received, 21st November 1986; Com. 1656

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