micellar solutions containing 0.25 mM the micelle, 10 μM pyrene, 10 mM DMA, and 0.2 mM MV^{2+} gives rise to the distinctive absorption due to $\mathrm{MV}^{+\bullet}$. The yield of $\mathrm{MV}^{+\bullet}$ for micelles of r = 25 Å is 9 times higher than that for r = 12.2 Å.

ET from pyrene anions to MV^{2+} occurs for both surfactants either cationic or anionic. Triplet pyrene is quenched by MV^{2+} associated with the water pools constructed with anionic surfactants, but with less efficiency by water pools constructed with cationic surfactants. These results indicate that ET from pyrene anion to MV^{2+} occurs inside the water pool, when the water pool is large enough to hold the solvated radical ion pairs. When the water pool is smaller, the exciplex cannot penetrate into the water pool and is quenched only by enhanced intersystem crossing at the interface region, probably as the result of distortion of the steric arrangement of the exciplex.

Acknowledgment. We are greatly indebted to Professor J. K. Thomas for his helpful discussion and for reviewing the paper. We are also grateful to Professor H. Kokubun for his interest in this work and for generous support.

Registry No. MV^{2+}, 4685-14-7; $\mathrm{MV}^{+\bullet}$, 25239-55-8; pyrene, 129-00-0; *N*,*N*-dimethylaniline, 121-69-7; 2-ethylhexylsulfosuccinate sodium salt, 577-11-7; benzyldimethylhexadecylammonium chloride, 122-18-9; heptane, 142-82-5; water, 7732-18-5; benzene, 71-43-2.

References and Notes

(1) Kikuchi, K.; Thomas, J. K. *Chem. Phys. Lett.* **1988**, *94*, 2476.

(2) (a) Kikuchi, K.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1545. (b) Kikuchi, K. *Chem. Phys. Lett.* **1991**, *183*, 103.

(3) Tokumura, K.; Kikuchi, K.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1309.

(4) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

(5) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.

(6) Leonhardt, H.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 791.

(7) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 257.

(8) Grellmann, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 469.

(9) Weller, A. *Z. Phys. Chem.* (*Munich*) **1982**, *130*, 129.

(10) Schulten, K.; Staerk, H.; Weller, A.; Werner, H.-J.; Nickel, B. *Z. Phys. Chem.* (*Munich*) **1976**, *101*, 371.

(11) Werner, H.-J.; Schulten, Z.; Schulten, K. *J. Chem. Phys.* **1977**, *67*, 646.

(12) Werner, H.-J.; Staerk, H.; Weller, A. *J. Chem. Phys.* **1978**, *68*, 2419.

(13) Baumann, D.; Ulrich, T.; Steiner, U. E. *Chem. Phys. Lett.* **1987**, *137*, 113.

(14) Adrian, F. J. In *Chemically Induced Magnetic Polarization*; Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pedersen, J. B. D., Eds.; Reidel: Dordrecht, 1977; p 77.

(15) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

Polypyrrole-Based Anion-Exchange Polymers

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(Received: January 3, 1992)

The preparation and electrochemistry of two polypyrroles with cationic substituents in the 3-position, and a precursor alkyl bromide substituted polymer, are reported. The electrochemical and ion-exchange properties of the new cationic polymers are similar to those of a previously reported N-substituted analogue. However, their lower redox potentials (ca. −0.1 V vs SSCE) mean that they become conductive at less oxidizing potentials. This is shown to be advantageous in the catalysis of ascorbate oxidation. The enhanced conductivity at low potentials also greatly accelerates the electrochemistry of electrostatically bound ferrocyanide. Surprisingly, the maximum conductivity of the new 3-substituted cationic polymers is lower than that of the N-substituted analogue. Poly[3-(3-bromopropyl)pyrrole] and cationic copolymers formed by its partial reaction with trimethylamine were used to probe the origin of this difference. Swelling of the polymers with electrolyte solution and associated morphological changes appear to be important factors.

Introduction

During the past decade a great diversity of conducting polymers have been generated by the introduction of functional groups into a few basic parent polymers.[1] Many of these new polymers are derived from pyrroles, thiophenes, and benzenes, a wide variety of which have been found to polymerize when oxidized either chemically or electrochemically. These molecules have a long established and rich synthetic chemistry and methods have been developed for the introduction of most types of functional group. Consequently, an almost unlimited variety of chemically tailored conducting polymers can be envisaged.

There have been a number of reports of the incorporation of ionic functional groups into polypyrroles and polythiophenes. Such groups can modify ion transport in the polymer, leading to faster anion transport[2] or to cation rather than anion transport.[3,4] Ionic functional groups also endow the conducting polymers with a permanent ion-exchange capacity. This has been exploited to bind transition-metal complexes within the polymer[5-11] and to preconcentrate ions in electroanalysis.[7]

To date, most reported polypyrroles with cationic functional groups are substituted at the pyrrole nitrogen.[7,8,11,12] Although this is synthetically the most expedient position for substitution of pyrrole, it is generally not the position of choice because it substantially decreases the conductivity of the resulting polypyrrole.[13] A second effect of N-substitution is a shift of the redox potential, and onset of conductivity, to higher potential. This would be an advantage in a battery,[14] for example, but may be a disadvantage in electroanalysis or electrocatalysis.[7]

We now elaborate upon our previous report[15] of the synthesis and properties of two polypyrroles with cationic substituents at the 3-position of the pyrrole ring (structures **1** and **2**). The pentyl analogue of **2** (poly[1-(5-pyrrol-3-ylpentyl)pyridinium bromide]) has also recently been reported.[11] As expected,[13] these materials exhibit significantly lower redox potentials than the N-substituted analogues. However, surprisingly they are less conductive. Other surprising features of our results include the failure of (pyrrol-3-ylmethyl)dimethylamine (**3**) to polymerize and the lack of electroactivity of a precursor polymer, poly[3-(3-bromopropyl)pyrrole] (**4**), in aqueous media.

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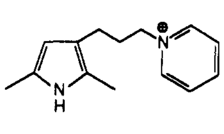
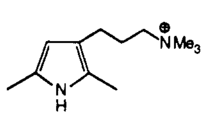
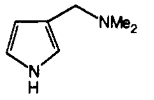


1, poly-PPP$^{\oplus}$



2, poly-PPTA$^{\oplus}$



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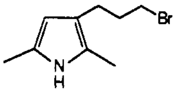
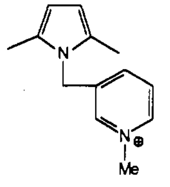


4, poly-BPP



5, poly-MPMP$^{\oplus}$

Experimental Section

Electrochemistry. Electrochemical experiments were carried out in conventional three-compartment glass cells under an argon atmosphere at 23 ± 2 °C. All potentials were measured and are quoted with respect to the sodium chloride calomel electrode (SSCE). The counter electrode was a Pt wire. Pt disk working electrodes sealed in glass (1.3×10^{-4} or 0.0052 cm^2) or PTFE (Pine Instruments rotating disk electrode; 0.458 cm^2) were polished with 0.3-μm alumina before use. Dual electrode conductivity measurements[16,17] utilized two adjacent Pt disks (1.3×10^{-4} cm^2) sealed in glass. The polymer film was coated onto one electrode and an evaporated gold layer provided electrical contact between the outer surface of the polymer film and the second electrode. In this way the potentials at each interface of the film could be controlled with a four-electrode potentiostat. Electrochemical instrumentation consisted of a Pine Instruments RDE4 potentiostat/galvanostat, a BBC MDL780 X-Y recorder, and a Pine Instruments ASR electrode rotator.

Monomer Synthesis. *(Pyrrol-3-ylmethyl)dimethylamine.* *N,N*-Dimethylpyrrole-3-formiminium chloride was prepared from 1-(triisopropylsilyl)pyrrole[18] using the Vilsmeier-Haack reagent.[19] Reduction to (pyrrol-3-ylmethyl)dimethylamine was accomplished in 60% yield with NaBH$_3$CN in methanol at ambient temperature. ^{1}H NMR (CDCl$_3$) δ (ppm): 2.26 (s, 6 H); 3.40 (s, 2 H); 6.18 (m, 1 H); 6.65 (m, 1 H); 8.68 (m, 1 H); 9.02 (s, 1 H). MS: m/z 124.00.

3-(3-Bromopropyl)pyrrole. The synthesis of 3-(3-bromopropyl)pyrrole followed the literature method[20] with the following modification. In the bromination of 1-(triisopropylsilyl)pyrrole[18] (in THF), *N*-bromosuccinimide was added as the solid rather than in solution to minimize its decomposition. Yields for this bromination as high as 92% (after chromatographic purification) were obtained in this way. 3-(3-Bromopropyl)pyrrole was purified on a silica gel column with 10% acetone in hexane.

1-(3-Pyrrol-3-ylpropyl)pyridinium Tetrafluoroborate (PPPBF$_4$) and (3-{Pyrrol-3-yl}propyl)trimethylammonium Tetrafluoroborate (PPTABF$_4$). A solution of 3-(3-bromopropyl)pyrrole (1 mmol) and pyridine (10 mmol; or 5 mmol trimethylamine) in methanol was stirred overnight in the dark. After removal of methanol under reduced pressure and washing of the residue with hexane to remove excess pyridine, the salt was dissolved in methanol and 1 equiv of silver tetrafluoroborate (Fluka) in methanol was added to precipitate AgBr. The product obtained after removal of the solvent was recrystallized from methanol (75–80% yield). PPPBF$_4$: ^{1}H NMR (CD$_3$OD) δ (ppm): 2.15 (p, 2 H); 2.61 (t, 2 H); 4.66 (t, 2 H); 5.92 (s, 1 H); 6.55 (s, 1 H); 6.62 (s, 1 H); 8.10 (t, 2 H); 8.58 (t, 1 H); 8.98 (d, 2 H). MS: m/z = 186.99. PPTABF$_4$: ^{1}H NMR (CD$_3$OD) δ (ppm): 2.04 (p, 2 H); 2.58 (t, 2 H); 3.30 (t, 2 H); 6.01 (m, 1 H); 6.60 (s, 1 H); 6.67 (m, 1 H). MS: m/z = 167.07.

TABLE I: Optimum Polymerization Conditions at Constant Current in Acetonitrile Containing 0.1 M Et$_4$NBF$_4$

polymer	concn of monomer, mM	oxidation potential,[a] V	optimum current density, mA/cm^2	potential during polymerizn, V vs SSCE
poly-PPP$^+$	24	0.70	0.58	0.7–0.8
poly-PPTA$^+$	40	0.80	0.40	0.7–0.8
poly-BPP	20	0.75	0.21	0.7–0.8

[a] Approximate potential at which polymerization begins under potential cycling conditions.

Chemicals. Ascorbic acid (Aldrich, Gold Label), tetraethylammonium perchlorate (Fluka), tetraethylammonium tetrafluoroborate (Fluka), lithium perchlorate (Fluka), acetonitrile (Fisher, HPLC grade), and all other chemicals were used as received.

Results and Discussion

Electrochemical Polymerization. All polymers described in this work were prepared as thin films on electrodes by anodic polymerization of the appropriately substituted pyrrole in acetonitrile containing 0.1 M Et$_4$NBF$_4$, without forced convection. In order to control thickness, polymers were prepared galvanostatically, although they could also be prepared at constant potential or under potential cycling conditions. The optimum current density for preparation of each polymer (Table I) was determined by growing a series of films using an identical charge but differing current densities. The resulting films were assessed by cyclic voltammetry, the film exhibiting the highest peak currents and the smallest peak separation being judged as optimal. The polymerization potential increases with current density and so deactivation of the polymer by overoxidation limits the rate at which it can be prepared. However, if the current density is too low, coverage of the electrode is uneven, with polymer only being deposited at the center of the Pt disk. Uneven coverage may be the result of insufficient nucleation or the diffusion of oligomers away from the electrode before they precipitate.[21] The latter explanation is supported by the observation that polymer deposition is inhibited if the polymerization solution is stirred. Furthermore, this would explain the failure of polymer deposition at the edges of the electrode where the diffusion rate is highest.

Electrochemical oxidation of (pyrrol-3-ylmethyl)dimethylamine does not form a conductive film, even in the presence of acid. The failure of pyrroles with a nucleophilic nitrogen to form conductive polymers is well documented[12] and appears to arise from nucleophilic attack on the radical cation intermediate.[22] Consequently, the presence of excess acid normally allows conductive polypyrroles to be prepared.[12] The numerous reports of the polymerization of 3-substituted pyrroles (e.g., 3,4-diethylpyrrole[23]) make it unlikely that steric factors prevent the polymerization of protonated (pyrrol-3-ylmethyl)dimethylamine. We are left to speculate that electrostatic repulsion prevents coupling of the expected radical-dication intermediates. The proximity of the positive charge to the ring appears to be an important factor since the (3-{pyrrol-3-yl}propyl)trimethylammonium ion, for example, does polymerize.

Film Thickness and Morphology. Figure 1A shows a scanning electron micrograph of a poly-PPP$^+$ film on an indium/tin oxide electrode. The electrode was broken to reveal a cross section of the polymer. Although this method provides only a crude estimate of film thickness because of the uneveness of the dried polymer, estimated thicknesses did increase approximately linearly with the polymerization charge density. A charge density of ca. 95 mC cm^{-2} is required to produce a 1-μm poly-PPP$^+$ film. This relationship was used to estimate the thickness of films used in electrochemical experiments from their polymerization charge. The thicknesses of poly-PPTA$^+$ films could not be satisfactorily estimated in this way because they form as very rough deposits or buckle during drying (Figure 1B). The charge to thickness

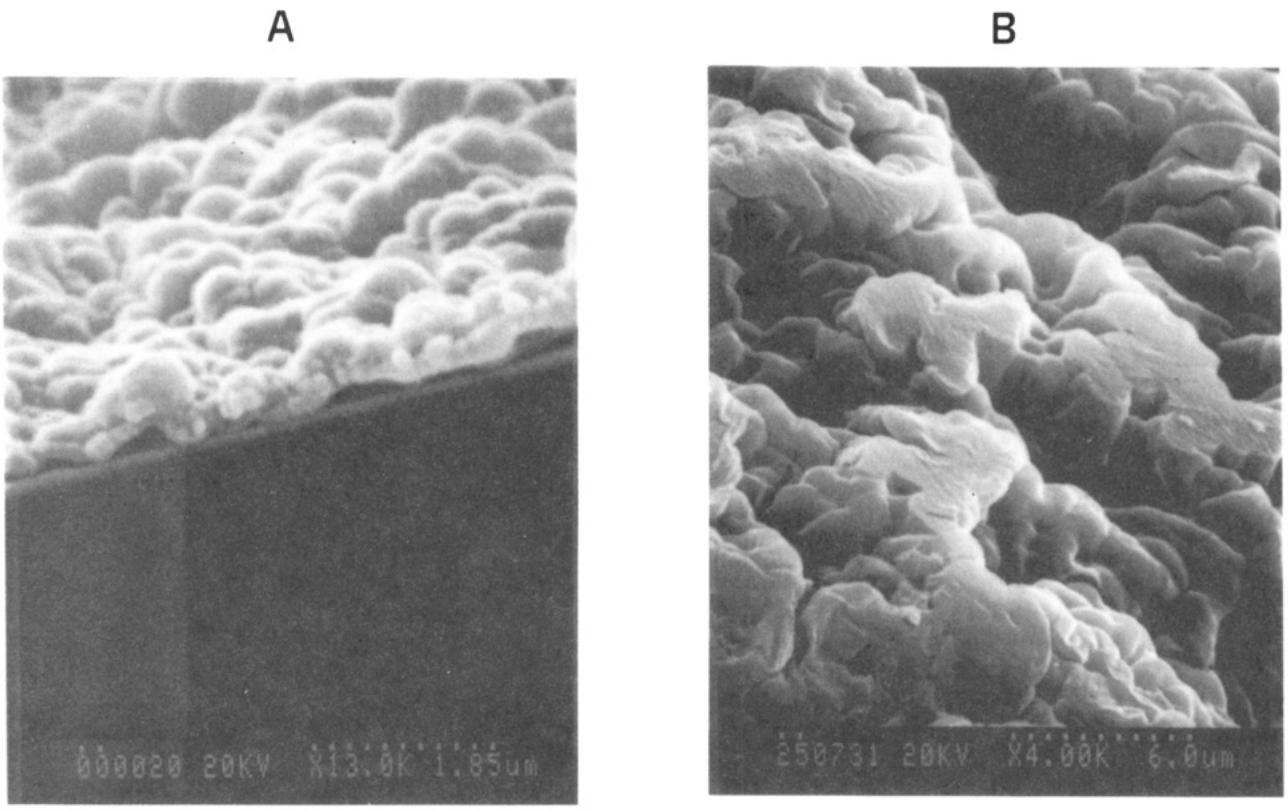


Figure 1. (A) Scanning electron micrograph of a poly-PPP$^+$ film on indium/tin oxide coated glass. The coated electrode has been broken to reveal a cross section of the polymer film. (B) Scanning electron micrograph of a poly-PPTA$^+$ film. The film has been removed from the indium/tin oxide electrode to reveal the side contacting the electrode.

conversion factor determined for poly-PPP$^+$ was therefore also used for poly-PPTA$^+$.

The morphologies of poly-PPP$^+$ and poly-PPTA$^+$ are significantly different from that of the similar N-substituted polymer, poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium]$^+$ (poly-MPMP$^+$, **5**). MPMP$^+$ produces unusually smooth films which adhere to the electrode well and exhibit no resolvable internal structure.[7] The rougher morphology of the new polymers described here may result from a difference in the solubility of the oligomers. This could lead to a lower density of nucleation and the formation of larger clumps of polymers. Alternatively, the rougher morphology of the new polymers may be a result of increased swelling in the acetonitrile electrolyte solution from which they are prepared.

Cyclic Voltammetry of Polymers. Figure 2 shows examples of cyclic voltammograms for poly-PPP$^+$ and poly-PPTA$^+$. Apparent formal potentials (measured as the average of the cathodic and anodic peak potentials) from these voltammograms range from −0.04 to −0.125 V depending on the scan rate and are close to values reported for polypyrrole (ca. −0.2 V vs SSCE)[24] and other 3-substituted polypyrroles.[13] From the voltammograms shown in Figure 2, the formal potential of poly-PPTA$^+$ appears to be slightly higher than that of poly-PPP$^+$, but this is probably not significant given the variability between different batches of monomer and polymer. For both polymers, peak currents increased linearly with scan speed, indicating that there are no kinetic limitations at scan rates up to 200 mV s^{-1} for these 0.5-μm films. This conclusion is supported by the near zero peak separations.

Figure 3 shows a cyclic voltammogram of poly[3-(3-bromopropyl)pyrrole] (poly-BPP) in acetonitrile. Two oxidation and reduction peaks appear at apparent formal potentials of −0.35 and +0.08 V. The reasons for the appearance of two distinct processes in this case are under further investigation.

Interestingly, poly-BPP was not electrochemically active in an aqueous 0.1 M H_3PO_4/KH_2PO_4 buffer (pH 2.5). Presumably, this polymer is so hydrophobic that it does not absorb enough water to facilitate ion ejection or insertion. Poly-BPP films did become electroactive in water after conversion of some of the bromo-groups to more hydrophilic alkylammonium groups by treatment with trimethylamine. Evidence for the occurrence of this reaction was obtained by measuring the polymer's ability to bind ferrocyanide. For example, after reaction with 0.1 M NMe_3 in methanol at ambient temperature for 12 h, the ferrocyanide saturation concentration (see below) of a 0.5-μm poly-BPP film had increased from zero to 35% of the value for a poly-PPP$^+$ film of similar thickness. This indicates approximately 35% conversion of bromo- groups to alkyl ammonium groups.

Electronic Conductivity. Small-amplitude dual electrode voltammetry[17] on polymer films sandwiched between a Pt disk electrode and a porous gold film[16] was used to obtain in situ conductivities as a function of potential. A dual electrode voltammogram for poly-BPP is shown in Figure 3 with the cyclic voltammogram of the same film before it was coated with gold. Surprisingly, no significant conductivity seems to be associated with the first oxidation process of poly-BPP at −0.35 V. As is normally observed for conducting polymers,[17] the conductivity of poly-BPP at any particular potential depends on whether it is being oxidized or reduced; the forward and reverse scans do not overlap.

Figure 4 shows plots of log (conductivity) vs potential for two poly-BPP films. For simplicity, conductivities from the anodic and cathodic scans have been averaged. A linear region at low potential (slope ~ 70 mV per decade) indicates that this polymer behaves like a redox conductor in this potential region.[25,26] At potentials above the second formal potential (0.08 V), conductivity becomes independent of potential, exhibiting a maximum value of ca. 10^{-2} S cm^{-1}.

Poly-PPP$^+$ and Poly-PPTA$^+$ sandwich electrodes did not give acceptable dual electrode voltammograms. Conductivities measured in situ were either negligible or unreasonably high and did not change with potential in the expected way. Presumably, the excessively rough surfaces of these polymers (Figure 1) lead to fracture of the gold film when the film swells in the electrolyte. In some cases shorts occur where the polymer has peeled from the Pt electrode. The conductivities of poly-PPP$^+$ and poly-PPTA$^+$ could be estimated, however, from resistance measurements on dry sandwich electrodes. Some results are listed in Table II. The polymer films were in the oxidized form prior to gold coating so

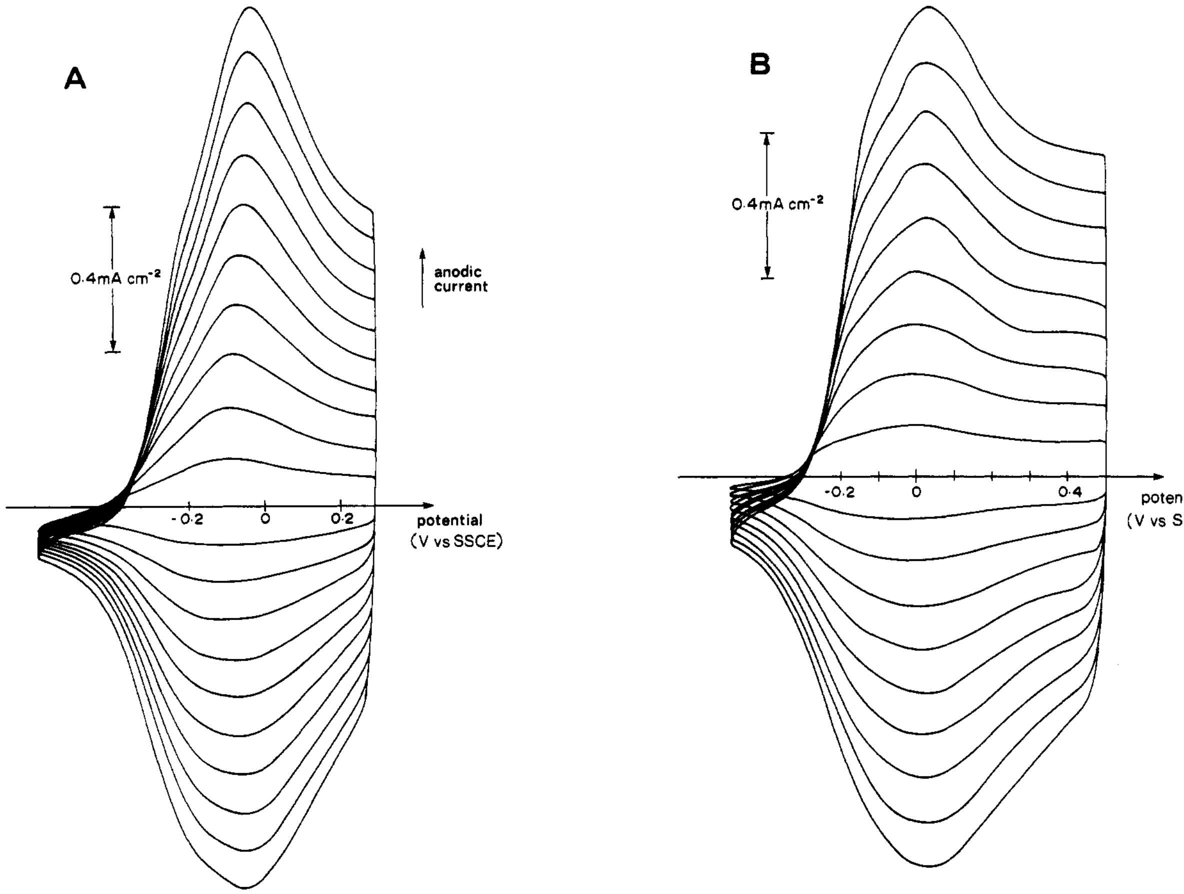


Figure 2. Cyclic voltammograms of poly-PPP$^+$ (A) and poly-PPTA$^+$ (B) coated Pt electrodes in acetonitrile containing 0.1 M Et_4NBF_4. Both films were approximately 0.5 μm thick. Scan rates were from 20 to 200 (A) or 180 (B) mV s^{-1} in 20 mV s^{-1} increments.

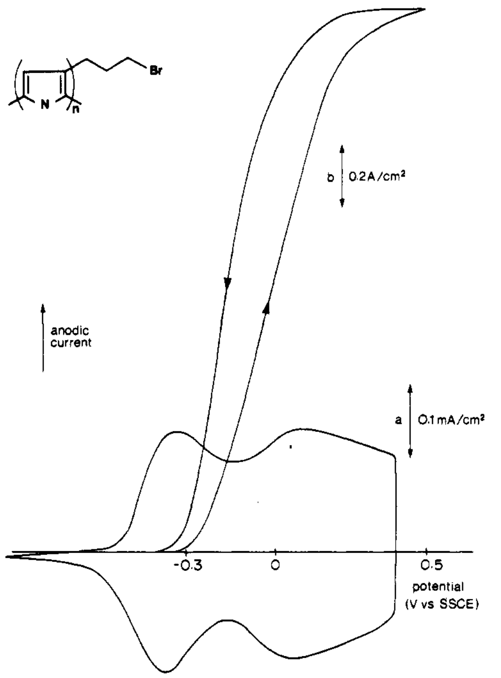


Figure 3. Cyclic voltammogram (a, 50 mV s^{-1}) and small-amplitude (ΔE = 20 mV) dual electrode voltammogram (b, 3 mV s^{-1}) for a 0.4-μm poly-BPP film in acetonitrile containing 0.1 M Et_4NBF_4.

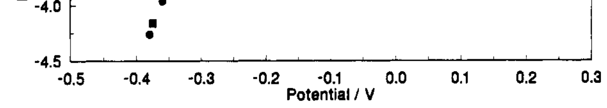


Figure 4. log (conductivity) vs potential for poly-BPP from dual electrode voltammetry (e.g., Figure 3b; averages for anodic and cathodic scans). Film thicknesses were 0.4 μm (●) and 0.6 μm (■).

TABLE II: Conductivities of Oxidized Poly-PPP$^+$ and Poly-PPTA$^+$ Films, from Resistance Measurements on Dry Sandwich Electrodes

polymer	film thickness, μm	conductivity, $\sigma \times 10^5$, S cm^{-1}	av $\sigma \times 10^5$, S cm^{-1}
poly-PPP$^+$	0.46	6.1	
	0.90	5.7	
	1.0	6.0	
	2.8	6.7	6.1 ± 0.4
poly-PPTA$^+$	0.5	1.6	
	1.8	3.2	
	2.7	5.9	
	3.6	2.8	3.4 ± 1.8

we assume that these are the conductivities of the oxidized polymer (corresponding to the potential independent region in Figure 4).

Surprisingly, poly-PPP$^+$ and poly-PPTA$^+$ appear to be less conductive than the similar N-substituted polymer, poly-MPMP$^+$ (maximum conductivity ~ 10^{-4} S cm^{-1}).[26] To ensure that the results presented in Table II are good estimates of maximum conductivities, and to investigate the reasons for the low conductivity of poly-PPP$^+$, the following experiment was conducted.

After in situ conductivity measurements by dual electrode voltammetry, a poly-BPP sandwich electrode was immersed in a methanol solution of trimethylamine to convert some of the

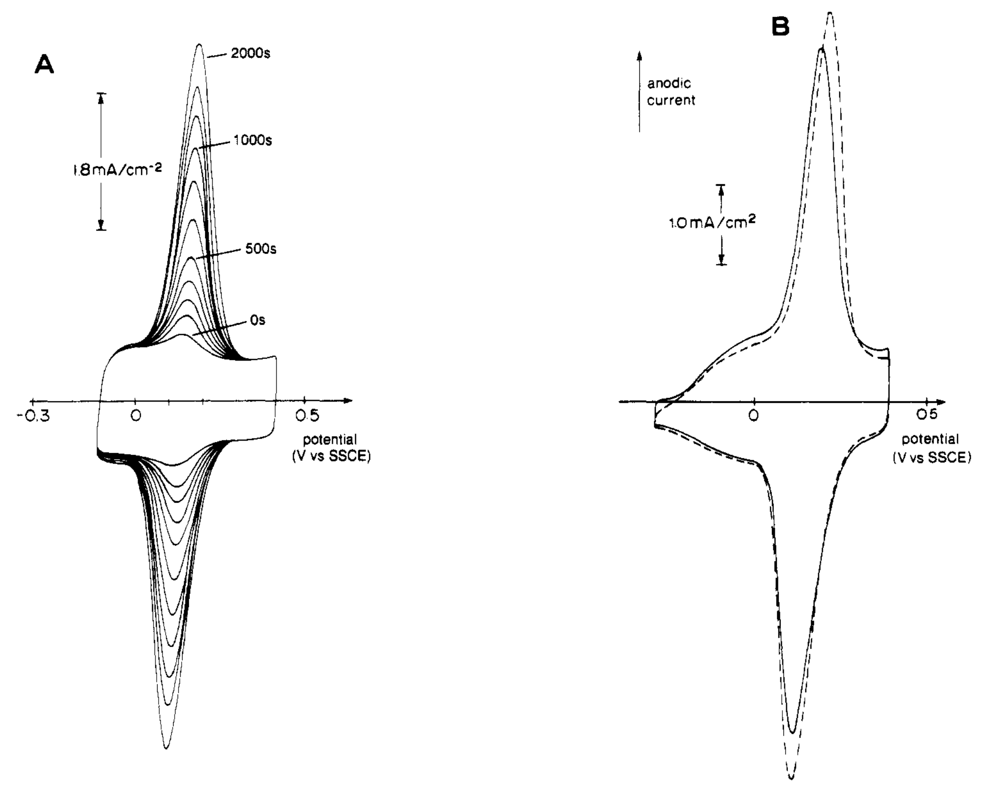


Figure 5. (A) Cyclic voltammograms at 100 mV s^{-1} of a poly-PPTA$^+$ (0.5 μm) coated Pt electrode after various times of continuous potential cycling in a 0.1 M H_3PO_4/KH_2PO_4 buffer (pH 2.5) containing 0.1 mM $K_4Fe(CN)_6$. (B) Cyclic voltammograms at 100 mV s^{-1} of a $Fe(CN)_6^{4-}$-saturated poly-PPP$^+$ film (0.4 μm) in 0.1 M phosphate buffer (pH 2.5), in the presence (---) and absence (—) of 0.1 mM $K_4Fe(CN)_6$.

TABLE III: Maximum in Situ (Acetonitrile + 0.1 M Et_4NBF_4) Conductivity of a Poly-BPP Film after Various Reaction Times in 0.1 M NMe_3 in Methanol

reaction time, h	max. conductivity, S cm^{-1}	reaction time, h	max. conductivity, S cm^{-1}
0.0	1.0×10^{-2}	12	4.7×10^{-5}
1.0	1.0×10^{-3}	24	3.8×10^{-6}

bromo- groups to alkylammonium groups (see above). Dual electrode voltammograms of the sandwich electrode were obtained in 0.1 M Et_4NBF_4/CH_3CN after various reaction times. Maximum conductivities, measured from the plateau region of the cathodic scan, are given in Table III. The conductivity drops by 4 orders of magnitude as the neutral bromo- group is replaced by the cationic alkylammonium group. Although this may be simply due to the increased bulkiness of the substituent,[27] increased swelling of the polymer is likely a contributing factor. The cationic substituent and its associated anion will cause the polymer to absorb extra solvent which will decrease the electron hopping rate between the polypyrrole chains. Electron microscopy suggests that poly-PPP$^+$ swells more than poly-MPMP$^+$ in acetonitrile (see above) and this may therefore explain why poly-PPP$^+$ is less conductive than poly-MPMP$^+$. The micrographs in Figure 1 also suggest that increased swelling influences the morphology of the polymers when they are dried and this might explain why the two 3-substituted polymers are also poorly conductive when dry.

Electrostatic Binding of Ferrocyanide. The ability of a conducting polymer to bind metal complexes is an important property and can lead to applications in electrocatalysis[28] and electroanalysis.[29] The electrostatic binding of anionic complexes was one of the motivations for the synthesis of conducting anion-exchange polymers.[6,7] Ferrocyanide has often been used to investigate anion binding by polymer films and is therefore used here.

Figure 5A shows a series of cyclic voltammograms of a poly-PPTA$^+$ coated electrode in a 0.1 mM aqueous solution of $Fe(CN)_6^{4-}$. The increasing peaks at a formal potential of +0.13 V, superimposed on the charging current due to the oxidized polymer, are due to $Fe(CN)_6^{3-/4-}$ which becomes concentrated in the polymer film. The peaks ceased to increase after about 2000 s of continuous cycling, indicating saturation of the film by the incorporated ion. The redox peaks for the saturated film were more than 2 orders of magnitude larger than those at a bare Pt electrode in the same solution.

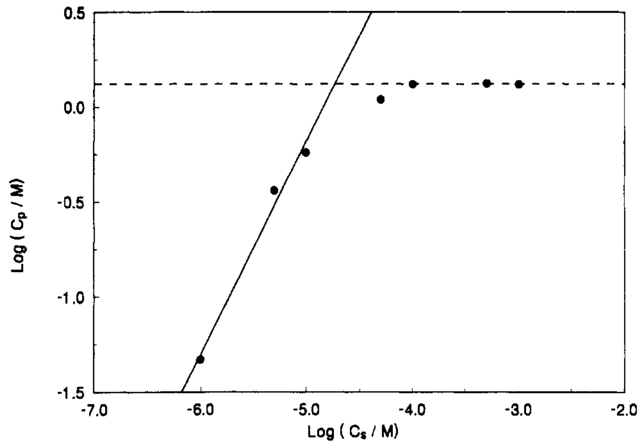


Figure 6. Equilibrium concentration of $Fe(CN)_6^{4-}$ in poly-PPP$^+$ (C_p) as a function of its solution concentration (C_s) in 0.1 M phosphate buffer (pH 2.5).

The binding of ferrocyanide by poly-PPP$^+$ is analogous. Figure 5B shows cyclic voltammograms for a ferrocyanide-saturated poly-PPP$^+$ film in the 10^{-4} M $Fe(CN)_6^{4-}$ loading solution (dashed line) and in a similar solution containing no ferrocyanide (solid line). Ferrocyanide is lost from poly-PPP$^+$ (or poly-PPTA$^+$) very slowly in ferrocyanide-free phosphate buffer; only about 5% was lost from a 0.2-μm film during continual potential cycling through the $Fe(CN)_6^{3-/4-}$ redox wave at 100 mV/s for $3^1/_3$ h, or during 15 h at open circuit.

The saturation concentration and the partition coefficient in 0.1 M phosphate buffer (pH = 2.3) were estimated for poly-PPP$^+$ as previously described.[7] A 0.2-μm film was allowed to equilibrate in stirred solutions containing different concentrations of ferrocyanide. The concentration of ferrocyanide accumulated in the

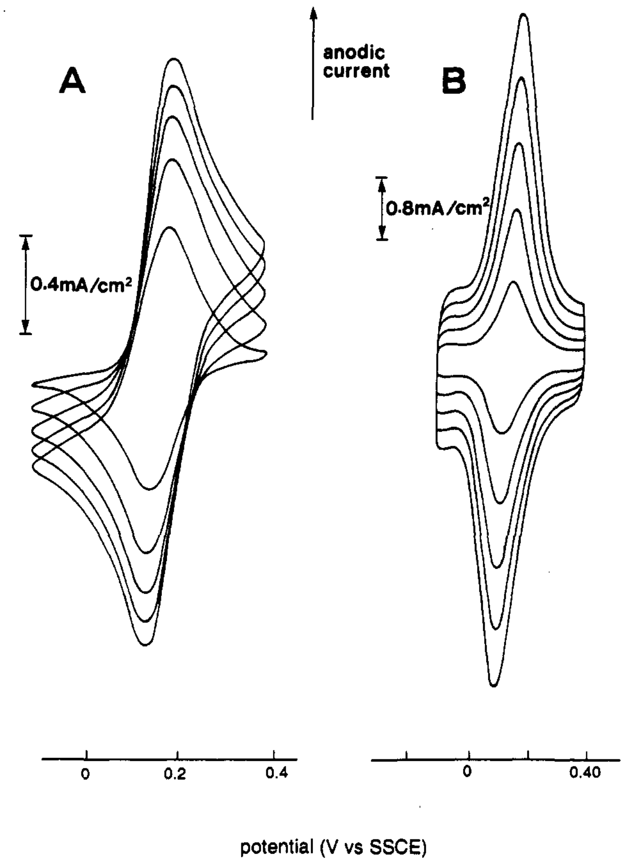


Figure 7. Cyclic voltammograms of ferrocyanide saturated poly-MPMP$^+$ (A, 0.2 μm) and poly-PPP$^+$ (B, 0.2 μm) films in 0.1 M phosphate buffer (pH 2.5). Scan rates from 20 to 100 mV s^{-1} in 20 mV s^{-1} intervals.

polymer was estimated by cyclic voltammetry in a phosphate buffer containing no ferrocyanide. The results are shown in Figure 6. A partition coefficient of (5.5 ± 0.5) × 10^4 was obtained from the average C_P/C_S ratio for solution concentrations below 10^{-5} M. This is similar to the value (3.2 × 10^4) obtained for the analogous N-substituted poly-MPMP$^+$.[7] The saturation concentration is 1.3 M, the same as for poly-MPMP$^+$.[7] Surprisingly, the fact that poly-PPP$^+$ is oxidized at the formal potential of the $Fe(CN)_6^{3-/4-}$ couple (poly-MPMP$^+$ is reduced at this potential) does not appear to increase the saturation concentration. Excess ferrocyanide would be expected to be incorporated as dopant ions to counterbalance the positive charge on the polypyrrole backbone. We presumably have not detected this difference because of the uncertainties in film thicknesses (especially for poly-PPP$^+$) and absolute quantities of polymer.

Kinetics of Ferrocyanide Electrochemistry within the Polymers. A comparison of the cyclic voltammetry of a ferrocyanide saturated poly-PPP$^+$ (or poly-PPTA$^+$) film with a similar poly-MPMP$^+$ film[7] reveals a remarkable difference in kinetics. The voltammograms at scan rates over 40 mV/s for the N-substituted polymer (Figure 7A) exhibit a shape indicative of diffusion control.[30] The peaks are broad with significant diffusion tails (current decays with an approximately $t^{1/2}$ dependence). A plot of peak current vs scan rate was nonlinear while a (scan rate)$^{1/2}$ plot was approximately linear, again indicating diffusion control.

For poly-PPP$^+$, cyclic voltammograms exhibited sharp, symmetric peaks without diffusion tails for all scan rates studied (Figure 7B). A plot of peak current vs scan rate was linear. These characteristics indicate that charge transport within the polymer is fast compared with the time scale of the potential scan.[30] Clearly, the $Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_6^{3-}$ redox reaction can be accomplished much faster in poly-PPP$^+$ than in poly-MPMP$^+$.

This difference between the N- and 3-substituted polymers can easily be understood by considering the various ways in which charge can be transported to the $Fe(CN)_6^{3-/4-}$ sites in the polymer. This can occur by physical diffusion of the redox sites, by electron hopping between redox sites, or by electron transport through the polymer matrix. Electron hopping between $Fe(CN)_6^{3-/4-}$ sites appears to be slower than physical diffusion[31] and so will be neglected here. N-substituted polypyrroles are reduced at the formal potential of $Fe(CN)_6^{3-/4-}$ and so exhibit a very low electronic conductivity. The conductivity of poly-MPMP$^+$ is less than 10^{-11} S cm^{-1} at 0.14 V,[25] and charge transport to $Fe(CN)_6^{3-/4-}$ occurs solely by physical diffusion. In contrast, the 3-substituted poly-PPP$^+$ and poly-PPTA$^+$ are oxidized at 0.14 V and have electronic conductivities close to 10^{-5} S cm^{-1} (see above). Thus, charge transport to the $Fe(CN)_6^{3-/4-}$ occurs through the polypyrrole backbone and is very rapid.

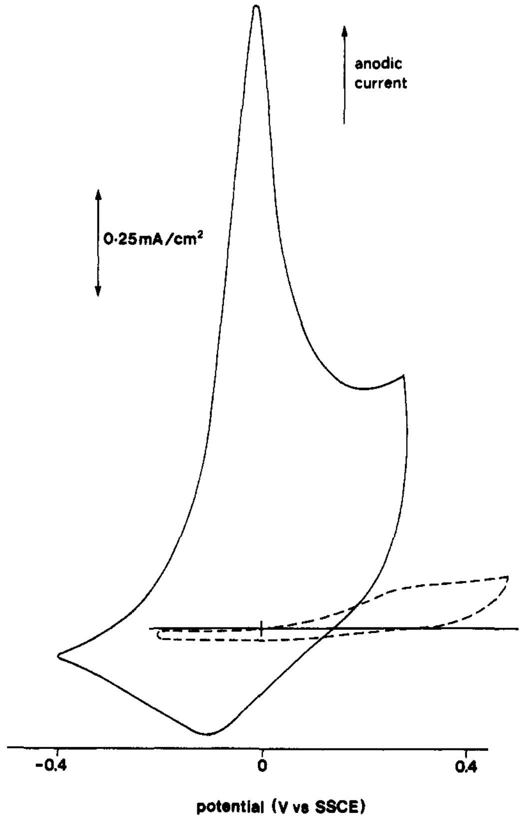


Figure 8. Cyclic voltammograms (50 mV s^{-1}) of ascorbate (0.5 mM) at naked (---) and poly-PPP$^+$ (1.4 μm) coated (—) Pt electrodes in 10 mM K_2HPO_4/KH_2PO_4 buffer (pH 7.4).

Ascorbic Acid Oxidation. Polypyrrole[32,33] and poly-MPMP$^+$[7] have been found to be promising electrode materials for ascorbic acid oxidation. Both polymers appear to catalyze the reaction via some type of electrostatic interaction. Poly-MPMP$^+$ therefore has a potential advantage over polypyrrole because of its higher concentration of cationic sites. The pyridinium sites also make poly-MPMP$^+$ more permeable than polypyrrole[2] and allow it to preconcentrate ascorbate,[7] which is useful in electroanalysis. However, the low electronic conductivity of poly-MPMP$^+$ at the ascorbate/ascorbic acid oxidation potential largely negates these advantages. Poly-PPP$^+$ and poly-PPTA$^+$ have the same advantages as poly-MPMP$^+$ but are conductive over the appropriate potential range.

Figure 8 shows cyclic voltammograms of ascorbate at bare and poly-PPP$^+$-coated Pt electrodes in a 0.01 M K_2HPO_4/KH_2PO_4 buffer (pH = 7.4). The ascorbate oxidation wave is greatly enhanced at the poly-PPP$^+$-coated electrode and appears superimposed on the polymer's voltammetric response. The peak potential is shifted by over 250 mV to a less oxidizing potential, indicating significant electrocatalysis. Peak currents, measured from a base line approximated by a cyclic voltammogram of the film in a solution containing no ascorbic acid, increased linearly with increasing film thickness. This can be attributed to preconcentration of ascorbate within the polymer before the voltammetric scan. Ascorbate oxidation at poly-PPTA$^+$-coated electrodes was similar, demonstrating that electrocatalysis and

TABLE IV: Cyclic Voltammetry Data for Ascorbate Oxidation at Polypyrrole-, Poly-MPMP$^+$-, Poly-PPP$^+$-, and Poly-PPTA$^+$-Coated Electrodes[a]

polymer	film thickness, μm	peak potential, mV	peak current, mA/cm^2
poly-MPMP$^+$ [b]	1.7	70	0.53
poly-PPP$^+$	1.4	−10	0.90
poly-PPTA$^+$	1.2	−40	0.46
polypyrrole[c]	0.08	0	0.18

[a] Experimental conditions: 0.5 mM ascorbic acid in 0.01 M phosphate buffer at pH = 7.4; scan rate 50 mV/s. [b] Data from ref 7. [c] Data from ref 32 (citrate and phosphate buffer containing 0.9% NaCl).

preconcentration are not strongly dependent on the nature of the positively charged group on the polymer.

Voltammetric data for ascorbate oxidation under similar conditions at the three polypyrrole-based anion exchange polymers (poly-MPMP$^+$, poly-PPP$^+$, and poly-PPTA$^+$) and polypyrrole are presented for comparison in Table IV. Ewing and co-workers[32] observed lower peak potentials and higher peak currents than Lyons et al.[33] for ascorbate oxidation at polypyrrole and so we have used data from their work.

All of the substituted polymers exhibit enhanced peak currents over polypyrrole, presumably due mainly to preconcentration of ascorbate by ion exchange. The low peak potentials at the 3-substituted polymers suggest that electrocatalysis is enhanced by the high concentration of cationic sites. This advantage over polypyrrole is lost with poly-MPMP$^+$ because of its low electronic conductivity at the ascorbate oxidation potential. The higher conductivity of poly-PPP$^+$ is also reflected in an enhanced peak current over poly-MPMP$^+$. It is not clear why the peak current at poly-PPTA$^+$ was lower.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Memorial University is gratefully acknowledged.

References and Notes

(1) Naarmann, H.; Theophilou, N. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1988; Vol. 1, pp 1–39.

(2) Mao, H.; Pickup, P. G. *J. Phys. Chem.* **1989**, *93*, 6480–6485.

(3) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151–159.

(4) Reynolds, J. R.; Sundaresan, N. S.; Pomerantz, M.; Basak, S.; Baker, C. K. *J. Electroanal. Chem.* **1988**, *250*, 355–371.

(5) Pickup, P. G. *J. Electroanal. Chem.* **1987**, *225*, 273–280.

(6) Pickett, C. J.; Moutet, J.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 188–189.

(7) Mao, H.; Pickup, P. G. *J. Electroanal. Chem.* **1989**, *265*, 127–142.

(8) Cosnier, S.; Deronzier, A.; Moutet, J.-C.; Roland, J. F. *J. Electroanal. Chem.* **1989**, *271*, 69–81.

(9) Keita, B.; Bousziz, D.; Nadjo, L.; Deronzier, A. *J. Electroanal. Chem.* **1990**, *279*, 187–203.

(10) Basak, S.; Rajeshwar, K.; Kaneko, M. *Anal. Chem.* **1990**, *62*, 1407–1413.

(11) Iyoda, T.; Alba, M.; Saika, T.; Honda, K.; Shimidzu, T. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1765–1769.

(12) Bartlett, P. N.; Chung, L.-Y.; Moore, P. *Electrochim. Acta* **1990**, *35*, 1273–1278.

(13) Delabouglise, D.; Roncali, J.; Lemaire, M.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1989**, 475–477.

(14) Novak, P.; Vielstich, W. *J. Electroanal. Chem.* **1991**, *300*, 99–110.

(15) Mao, H.; Pickup, P. G. *Electrochem. Soc.* **1990**. Abstract 815 of meeting in Montreal.

(16) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991–1998.

(17) Ochmanska, J.; Pickup, P. G. *J. Electroanal. Chem.* **1991**, *297*, 211–224.

(18) Muchowski, J. M.; Solas, D. R. *Tetrahedron Lett.* **1983**, *24*, 3455–3456.

(19) Bray, B. L.; Muchowski, J. M. *J. Org. Chem.* **1988**, *53*, 6115–6118.

(20) Stefan, K.-P.; Schuhmann, W.; Parlar, H.; Korte, F. *Chem. Ber.* **1989**, *122*, 169–174.

(21) John, R.; Wallace, G. G. *J. Electroanal. Chem.* **1991**, *306*, 157–167.

(22) Morse, N. J.; Rosseinsky, D. R.; Mortimer, R. J.; Walton, D. J. *J. Electroanal. Chem.* **1988**, *255*, 119–141.

(23) Casas, R.; Dicko, A.; Ribo, J. M.; Valles, M. A.; Ferrer-Anglada, N.; Bonnett, R.; Hanly, N.; Bloor, D. *Synth. Met.* **1990**, *39*, 275–280.

(24) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115–132.

(25) Mao, H.; Pickup, P. G. *J. Am. Chem. Soc.* **1990**, *112*, 1776–1782.

(26) Mao, H.; Pickup, P. G. *Chem. Mater.*, in press.

(27) Andrieux, C. P.; Audebert, P. *J. Electroanal. Chem.* **1989**, *261*, 443–448.

(28) Deronzier, A.; Moutet, J.-C. *Acc. Chem. Res.* **1989**, *22*, 249–255.

(29) Dong, S.; Wang, Y. *Electroanalysis* **1989**, *1*, 99–106.

(30) Murray, R. W. *Electroanal. Chem.* **1984**, *13*, 191.

(31) Qi, Z.; Pickup, P. G., manuscript in preparation.

(32) Saraceno, R. A.; Pack, J. G.; Ewing, A. G. *J. Electroanal. Chem.* **1986**, *197*, 265–278.

(33) Lyons, M. E. G.; Breen, W.; Cassidy, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 115–123.