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Electrochemically Induced Substitution of Polythiophenes and Polypyrrole

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The electrochemically induced substitution of thin films of polypyrrole, polythiophene, poly(3-methylthiophene), and poly(2,2′-bithiophene) with the nucleophiles Cl$^-$, Br$^-$, methanol, and 3-bromopropanol has been investigated by cyclic voltammetry, electron microprobe analysis, IR spectroscopy, and NMR spectroscopy. The degree of substitution obtained is potential dependent and varies between nucleophile/polymer combinations. Thus, reaction of polythiophene, poly(3-methylthiophene), or polypyrrole with Cl$^-$ at 1.4 V vs SSCE results in chlorination of approximately 80% of the rings, while for poly(2,2′-bithiophene) only 20% substitution is obtained. Reaction with 3-bromopropanol, results in 25−35% substitution for both poly(3-methylthiophene) and polypyrrole. The substituted polymers are electroactive and conductive. However, for substitution of the polythiophenes by Cl$^-$, electrochemically deactivated intermediates with low conductivity can be isolated. Reaction of poly(3-methylthiophene) with methanol results in solubilization of the polymer in acetonitrile.

A major factor responsible for the widespread interest in electronically conducting polymers such as polythiophenes and polypyrroles is the diversity of different properties that can be obtained by using substituted monomers. The "tailoring" of the properties of conductive materials provides fascinating opportunities to produce novel types of materials with novel application.[1,2]

Much progress has been made in the synthesis of tailored conducting polymers from substituted monomers. Much of the early work employed electrochemical polymerization,[3−5] which was found to be an easy route to many substituted polythiophenes,[6] polypyrroles,[7,8] and polyanilines (e.g., refs 9−12). However, as the field has developed in sophistication, chemical methods[2] which produce more well defined and processible materials have generally superseded the electrochemical method.

Despite the massive amount of work that has already been done on the synthesis of substituted polypyrroles and polythiophenes, there is still a need for routes to new materials. One approach that is receiving increasing attention is functionalization after polymerization.[13−18] The precursor polymer, which can be prepared either chemically or electrochemically, can then be selected based on factors such as morphology, stability, solubility, and melting point, and processed into the desired form before functionalization. A somewhat similar strategy is used in the preparation of poly(phenylenevinylenes) from processible nonconjugated precursor polymers.[19]

We have recently shown[20,21] that overoxidation of poly(3-methylthiophene) in the presence of chloride or bromide and subsequent reactivation results in substitution of the hydrogen at the 4-position by the halide. This type of electrochemically induced substitution, which is well established for heteroaromatic monomers,[22] could provide a valuable route to novel polythiophenes and polypyrroles. We have therefore begun to investigate its generality. In this paper, we demonstrate the electrochemically induced substitution of polypyrrole and several polythiophenes with chloride and two alcohols. In addition to its synthetic utility,

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electrochemically induced substitution with an alcohol provides a method for solubilizing electrochemically formed polymers so that they can be better characterized.

The reactions of overoxidized polypyrroles and polythiophenes with nucleophiles have been the subject of a considerable research effort.[23] Additions of water, hydroxide, methanol, bromide, and chloride[24] to polypyrrole[25] and methanol, bromide, and chloride to polythiophene[26] have been reported. However, in all of these cases an electrochemically deactivated and nonconducting polymer was formed. The importance of our work is that we report electrochemically induced substitution methods that yield substituted polymers that are electroactive and conductive.

Experimental Section

All electrochemical experiments were carried out in conventional glass cells under argon at ambient temperature (21 ± 2 °C). The working electrode was a platinum disk (0.0052 cm^2) sealed in glass for cyclic voltammetry, a glassy carbon (Tokai, 0.071 cm^2) disk sealed in epoxy for X-ray emission analysis, a Pt flag ($\sim$2 cm^2) for IR spectroscopy, and a large-area Pt gauze for the preparation of soluble methoxylated poly(3-methylthiophene). A SSCE reference electrode was used.

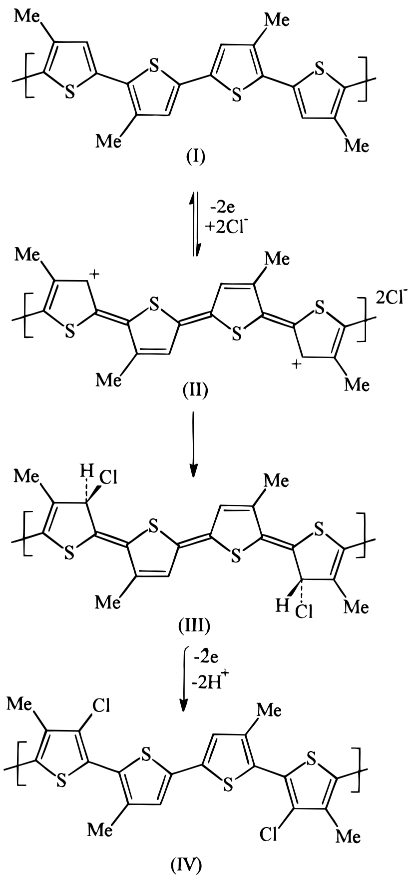
Thiophene (Aldrich), 2,2′-bithiophene (Aldrich), 3-methylthiophene (Aldrich), pyrrole (Aldrich), 3-bromopropanol (Aldrich), tetraethylammonium perchlorate (Fluka, $>$99%), acetonitrile (Fisher HPLC grade), methanol (ASC grade), and other chemicals were used as received.

Polymer films were prepared at a constant current density of 1.0 mA cm^{-2} from 0.1 M solutions of the monomer (except 20 mM for bithiophene and 0.5 M pyrrole for the IR experiment) in acetonitrile containing 0.1 M Et_4NClO_4 (0.2 M Et_4NBF_4 for the IR experiment). In the case of polythiophene, ca. 2 mM bithiophene was added to the deposition solution as a catalyst.[27] Film thicknesses were estimated from the polymerization charge using relationships of 0.4 C cm^{-2}/μm for polythiophene and poly(3-methylthiophene),[28] 0.2 C cm^{-2}/μm for polybithiophene, and 0.24 C cm^{-2}/μm for polypyrrole.[29]

Electrochemically induced substitutions were generally carried out at constant potential. In a typical procedure, an approximately 0.2 μm thick film on a glassy carbon or Pt electrode was held at the stated potential (e.g., +1.4 V) for the stated time (e.g., 3 min) in a 0.1 M solution of the nucleophile in CH_3CN. The potential was then returned to 0 V. Details are provided in the text and in figure captions.

Most X-ray emission (electron microprobe) analyses were obtained using a Hitachi S-570 scanning electron microscope with a Tracor Northern 5500 energy-dispersive analyzer and Microtrace 70152 silicon detector. However, since this instrument cannot detect elements lighter than Na, a Cameca SX50 electron microprobe with a Link energy-dispersive X-ray detector was used for the determination of Cl:N, Br:N, and O:N ratios in polypyrroles. All films were on glassy carbon electrodes and were rinsed well with acetone and dried in air before analysis. Procedures and calibration of the Hitachi S-570 for S:Cl ratios have been previously described.[21] Calibration for S:Br ratios using 4-bromobenzene sulfonyl chloride (Aldrich, 98%)/poly(4-vinylpyridine) films followed a similar procedure. Cl:N and O:N ratios from the Cameca SX50 were corrected using the results for two electrodes coated with poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium perchlorate],[30] which has a Cl/N ratio of 1/2 and a O/N ratio of 2 in its unoxidized form. Br:N ratios were not corrected.

Scheme 1



FTIR reflectance spectra were recorded using a Mattson Polaris spectrometer with a Specac P/N 19900 Series diffuse reflectance accessory. A clean Pt foil was used for the background spectrum.

Results and Discussion

Halogenation. *Poly(3-methylthiophene).* The electrochemical halogenation of poly(3-methylthiophene) has been demonstrated and discussed elsewhere.[20,21] In a typical procedure, an approximately 0.2 μm thick film on a glassy carbon or Pt electrode was held at +1.40 V for 3 min in a 0.1 M Et_4NCl/CH_3CN solution. This causes addition of Cl^- to the polymer (Scheme 1, structure III), and results in a loss of conductivity and electrochemical activity. Reactivation of the film at +1.40 V in 0.1 M Et_4NClO_4/CH_3CN yields Cl-substituted poly(3-methylthiophene) (Scheme 1, structure IV). Electron microprobe (X-ray emission) analysis indicated that this procedure results in substitution of ca. 85% of the thiophene rings. Repeating the procedure increases the level of substitution to ca. 100%. The same procedure with Bu_4NBr in place of Et_4NCl results in ca. 50% bromination of the polymer, while no halogenation is observed with Bu_4NI.[21] These results are summarized in Figure 1. The reactivity of the halides follows their nucleophilicity in aprotic solvents, $Cl^- > Br^- > I^-$ (opposite to the order in water), and is consistent with the proposed mechanism.

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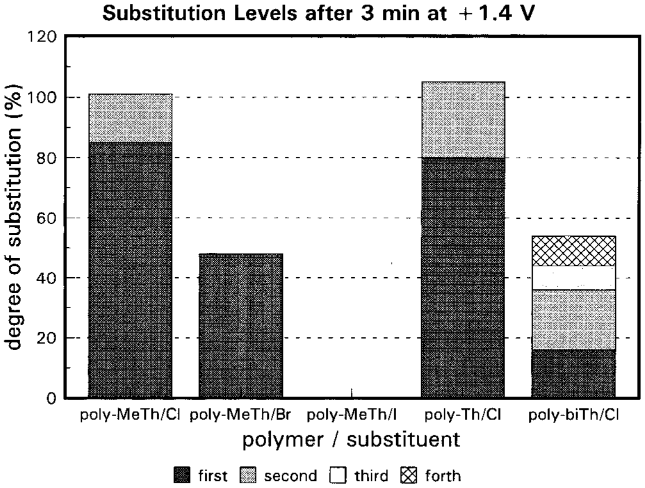

Figure 1. Substitution levels determined by electron microprobe analysis of 0.2 μm poly(3-methylthiophene), polythiophene, and poly(2,2′-bithiophene) films following 3 min at +1.4 V in acetonitrile containing 0.1 M Et_4NCl (or Bu_4NBr or Bu_4NI), reactivation at 1.4 V in 0.1 M Et_4NClO_4/CH_3CN, and reduction at −0.2 V (2 min) to expel counterions.

It should be noted that the structures given in Scheme 1 are simplified examples of the types of structures that would be expected. Obviously, a large number of alternate substitutions patterns can occur, and the actual structure will be a mixture of these.

For chlorination, the various steps in the overall substitution process described above can be observed by cyclic voltammetry.[20] Typical results for the chlorination of poly(3-methylthiophene) are shown in Figure 2A for comparison with results for polythiophene and poly(2,2′-bithiophene). Oxidation of the polymer film in the Cl^--containing solution (curve b) results in a large (note that the current scale is 4 times larger) irreversible wave centered at ca. 0.9 V. The absence of redox waves for the polymer on the reverse scan and subsequent scans (not shown) shows that the film has become electrochemically inactive (deactivated) in the Et_4NCl solution. On transfer to a Et_4NClO_4 solution (curve c), the deactivated film is not oxidized at the normal peak potential of ca. 0.6 V (as in curve a) but does begin to be oxidized at potentials above ca. 0.7 V. A large and sharp oxidation wave at ca. 1.2 V results in reactivation of the film's reversible electrochemistry (curve d), which now appears at a slightly higher potential than that of the virgin polymer (compare curve d with curve a) because of the electron-withdrawing effect of the chloro substituent.[31]

Conductivity changes accompanying the various steps in the electrochemical chlorination of a poly(3-methylthiophene) film were followed by observing the film's ability to mediate the electrochemistry of ferrocene in acetonitrile (Figure 3). Cyclic voltammograms of ferrocene at a pristine poly(3-methylthiophene)-coated electrode (solid line) were not significantly different from those at bare Pt (not shown), indicating that the polymer is conductive in this potential range and can mediate the electrochemistry of ferrocene. The polymer film was then deactivated in a chloride-containing solution in the normal way and transferred back to the solution containing ferrocene. It can be seen from the resulting voltammograms (dashed lines) that ferrocene oxidation is blocked by the deactivated film (i.e., on the first forward scan, a), indicating that the deactivated polymer is nonconductive and therefore presumably poorly conjugated. Once the film becomes reactivated at potentials above 1.2 V, it mediates ferrocene oxidation at potentials as low as +0.4 V (parts b and c of the dashed line), indicating that conduction (conjugation) has been restored.

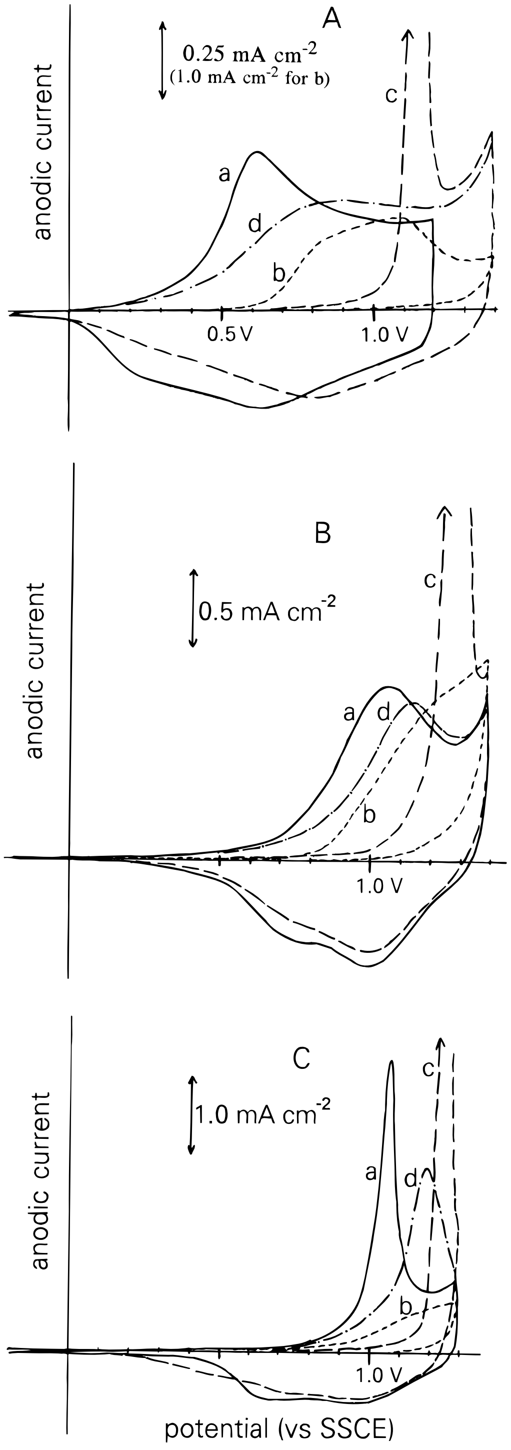

Figure 2. Cyclic voltammograms of Pt/poly(3-methylthiophene) (A), Pt/polythiophene (B), and Pt/poly(2,2′-bithiophene) (C) electrodes in 0.1 M Et_4NClO_4/CH_3CN before (a) and after (c and d) potential cycling in 0.1 M Et_4NCl/CH_3CN (b). Scan rate = 100 mV/s. The polymer films were all nominally 0.1 μm thick.

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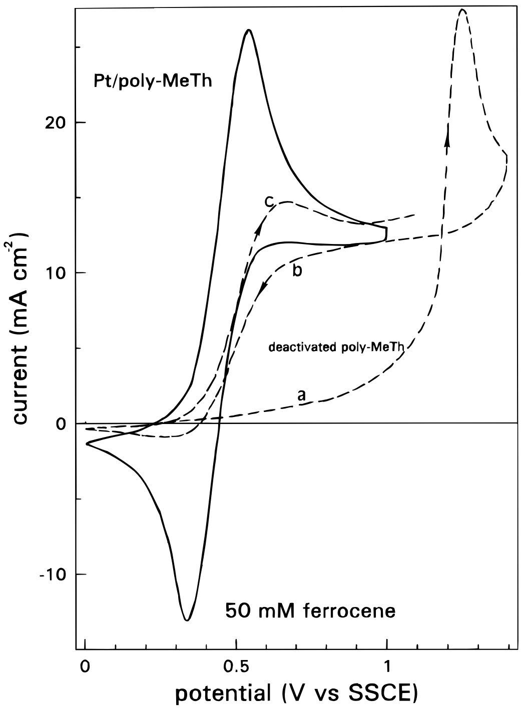


Figure 3. Cyclic voltammograms of 50 mM ferrocene in 0.1 M Et_4NClO_4/CH_3CN at a Pt electrode coated with ca. 0.1 μm of pristine (solid line) or deactivated (dashed line) poly(3-methylthiophene). The polymer was deactivated for 3 min at 1.4 V in 0.1 M Et_4NCl/CH_3CN.

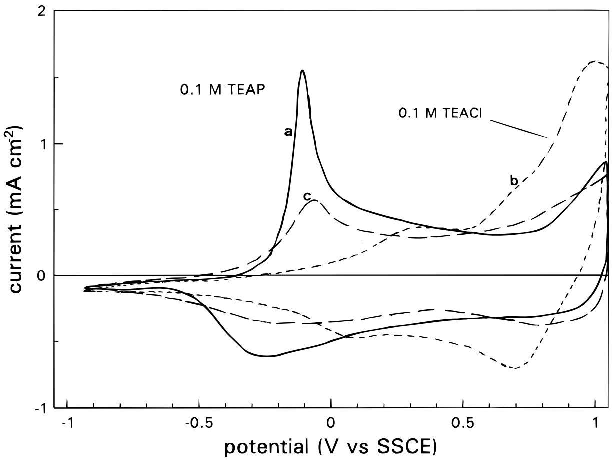


Figure 4. Cyclic voltammograms of a Pt/polypyrrole (ca. 0.1 μm) electrode in 0.1 M Et_4NClO_4/CH_3CN, before (a, second cycle) and after (c, first cycle) potential cycling in 0.1 M Et_4NCl/CH_3CN (b, eighth cycle). Scan rate = 100 mV/s.

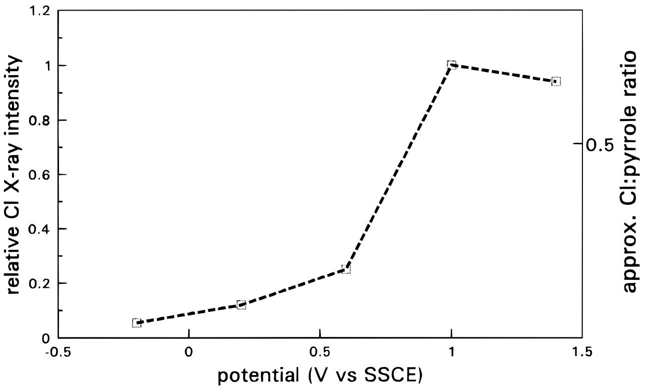


Figure 5. Relative Cl X-ray intensity from electron microprobe analysis (Hitachi S-570) vs potential for polypyrrole films (0.2 μm) that had been oxidized at constant potential for 2 min in 0.1 M Et_4NCl/CH_3CN. Films were immersed in stirred 0.1 M Bu_4NBr/CH_3CN for 6 min before analysis to replace Cl^- counterions with Br^-. Results have been normalized with respect to the 1.0 V result, which corresponds to a Cl:N ratio of 0.70 (Cameca SX50).

Polythiophene. The electrochemically induced chlorination of polythiophene occurs in essentially the same way as for poly(3-methylthiophene) (Figure 2B). The procedure described above for poly(3-methylthiophene) results in deactivation (loss of electroactivity, curve b of Figure 2B), reactivation (curve c), and ca. 80% chlorination (i.e., an average of 0.8 Cl/thiophene ring, which may include some disubstitution, Figure 1). Repeating the procedure once leads to essentially 100% substitution (one Cl/ring). The voltammetric response of the polymer during the various stages is qualitatively similar to that observed for poly(3-methylthiophene) (compare parts A and B in Figure 2). The key differences being that poly(3-methylthiophene) is more easily oxidized than polythiophene (curves a) and hence begins to deactivate at a lower potential (curve b). This indicates that the rate of addition of Cl^- to the oxidized polymer backbone depends on the oxidation level of the polymer rather than directly on the potential. This supports our postulated[21] mechanism (Scheme 1) involving addition of Cl^- to cationic (oxidized) sites on the polymer (see below) but is incompatible with mechanisms involving electrochemically generated Cl_2.

Polybithiophene. Although somewhat surprising, it is well-known that electrochemically produced poly(2,2′-bithiophene) is a material distinctly different from polythiophene.[6] This difference is clearly reflected in their electrochemical chlorination (compare parts B and C in Figure 2). Poly(2,2′-bithiophene) is slightly more difficult to oxidize than polythiophene (curves a), because of its shorter mean conjugation length,[6] and its oxidation wave is much sharper, perhaps reflecting a narrower molar mass distribution. Deactivation in the presence of Cl^-, requires a slightly higher potential than for polythiophene (curves b), which is consistent with the lower mean conjugation length and hence lower concentration of cationic sites at any particular potential.

Chlorination of poly(2,2′-bithiophene) at 1.4 V for 3 min results in only about 20% substitution, much less than the ca. 80% substitution observed for poly(3-methylthiophene) and polythiophene under the same conditions (Figure 1). Although the degree of chlorination of poly(2,2′-bithiophene) can be increased by repeating the procedure, only 50% substitution was observed after four treatments (Figure 1). These low substitution levels may reflect the failure of short chains in the polymer to form dications, which may be required for substitution to proceed (Scheme 1).

Polypyrrole. In contrast to the polythiophenes, cyclic voltammetry of polypyrrole in Et_4NCl/CH_3CN did not give a clear indication that Cl^- reacts with the polymer (Figure 4). Peaks for Cl^- oxidation (0.95 V) and Cl_2 reduction (0.65 V) appeared superimposed on the electrochemistry of the polymer (curve b), and there was a ca. 0.4 V anodic shift of the polymer's redox waves (compare curves a and b), but no indication of deactivation of the polymer. On transfer to a Cl^--free electrolyte solution (curve c), the polymer's electrochemistry was similar to that before cycling in the Cl^- solution, with

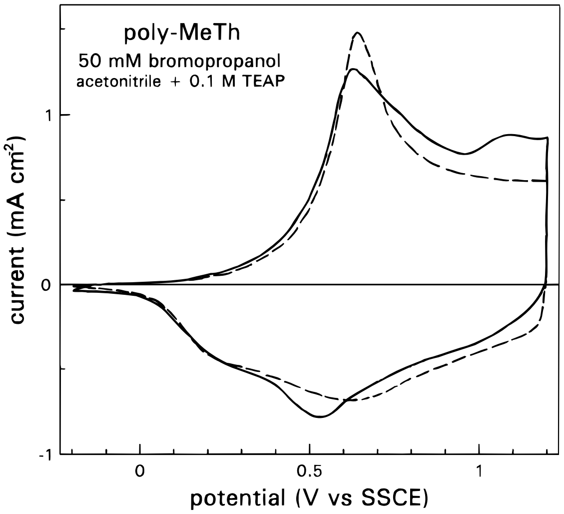


Figure 6. Cyclic voltammograms (first scans) of a Pt/poly(3-methylthiophene) (0.1 μm) electrode in 0.1 M Et_4NClO_4/CH_3CN in the absence (dashed line) and presence (solid line) of 50 mM 3-bromopropanol. Scan rate = 100 mV/s.

only a small loss of electroactivity, and a slight positive shift of the redox peaks. There is little indication that any substitution had occurred. However, electron microprobe analysis clearly showed that the polypyrrole had been electrochemically chlorinated, even at potentials as low as 0.2 V. Figure 5 shows relative Cl X-ray emission intensities for films subjected to various constant potentials for 2 min in a Et_4NCl/CH_3CN solution. The Cl content of the polymer clearly increases with increasing potential. In a separate experiment, the Cl:N ratio for a film chlorinated at 1.0 V for 2 min was determined to be 0.70, indicating that a maximum of ca. 70% chlorination can be achieved in one treatment.

The small loss of electroactivity in CH_3CN/Et_4NClO_4 following chlorination in CH_3CN/Et_4NCl (compare curves a and b in Figure 4) suggests that the polymer's conjugated structure had been partially disrupted. This kind of damage is understandable given the high potentials used and probably results mainly from attack of water on the highly oxidized polymer.[23] The shift of the polymer's main redox waves in the Cl^- solution (curve c in Figure 4) occurred over a number of cycles and may be due to a decrease in the average conjugation length caused by partial deactivation. Upon transfer to the Cl^--free solution (curve c), the peaks immediately moved back to almost their original positions, indicating a restoration of conjugation. The slight residual shift is presumably due to the electron-withdrawing effect of the Cl substituent.

Alkoxylation. 3-Bromopropanol was used in some of these experiments so that the presence of the alcohol in polymer films could be detected and quantified more easily by microprobe analysis of Br. The bromo substituent is also of potential value for further functionalization of the polymer.

Poly(3-methylthiophene). Cyclic voltammograms of poly(3-methylthiophene) films in acetonitrile/0.1 M Et_4NClO_4 containing 50 mM bromopropanol differ only slightly from those recorded in the absence of the alcohol (Figure 6). They show no apparent evidence of reaction of the polymer with the alcohol (the small additional peaks at ca. 1.05 V (anodic) and ca. 0.65 V (cathodic) are presumably due to the redox chemistry of the alcohol (see also Figure 8)). However, electron microprobe analysis of films held at +1.40 V in the bromopropanol solution clearly demonstrated incorporation of bromine, presumably as covalently bound ω-bromopropoxy groups (reaction 1). Three min at 1.40 V results in ap-

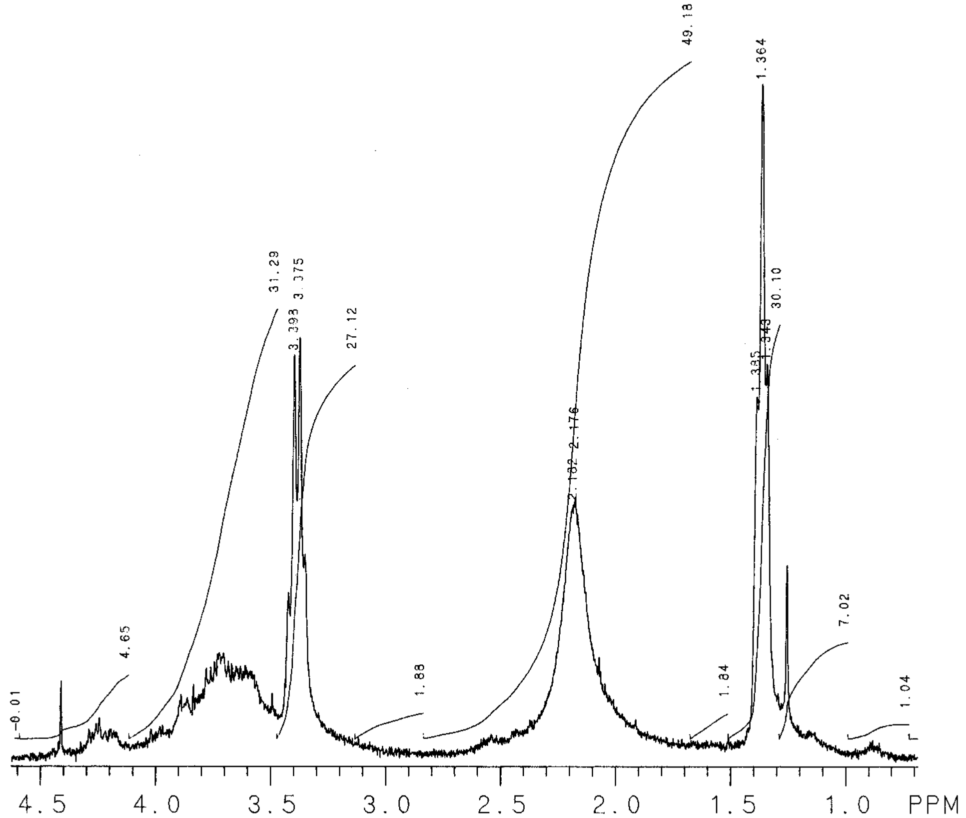


Figure 7. The 300 MHz H^1 NMR spectrum in $CDCl_3$ of the yellow material obtained by electrochemically dissolving poly(3-methylthiophene) at 1.4 V in 0.1 Et_4NClO_4/CH_3CN containing 10% methanol.

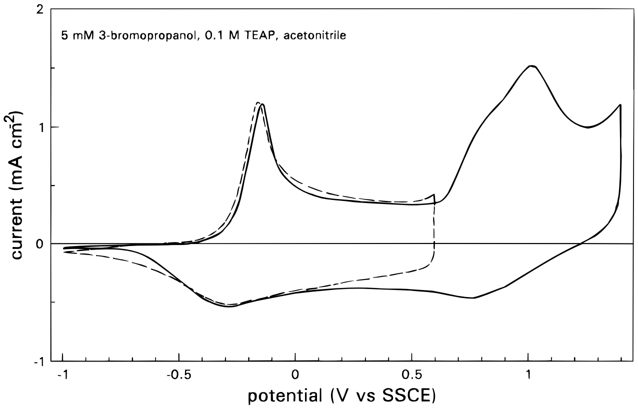
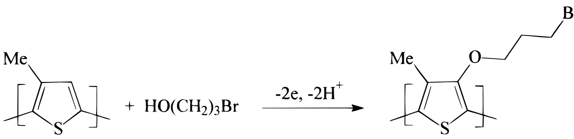


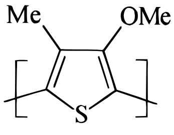
Figure 8. Cyclic voltammograms (second scans) of a Pt/polypyrrole (0.1 μm) electrode in 0.1 M Et_4NClO_4/CH_3CN in the absence (dashed line) and presence (solid line) of 50 mM 3-bromopropanol. Scan rate = 100 mV/s.

proximately 25% substitution (average for two films).



(1)

In CH_3CN/Et_4NClO_4 containing 10% methanol, poly(3-methylthiophene) films slowly dissolved when held at +1.40 V. Solutions were initially dark blue but became yellow on standing. To isolate a sample of this yellow material the solvents were removed under reduced pressure, and the Et_4NClO_4 was redissolved in water. The insoluble yellow material was extracted into chloroform, concentrated, and purified on a Sephadex G-10/$CHCl_3$ column. A 300 MHz H^1 NMR spectrum of the single yellow band is shown in Figure 7. The triplet at 1.36 ppm and quartet at 3.39 ppm are due to tetraethylammonium from the supporting electrolyte. No peaks due to aromatic or olefinic protons are present, indicating that there had been complete substitution at, or addition to, all 4-positions of the polymer. The broad bands at 2.18 and 3.7 ppm can be assigned to aromatic methyl and methoxy groups, respectively. They are broad because of the variety of different chemical environments that result from head–head, tail–tail, and tail–head coupling in the original 3-methylthiophene polymer. The band at 3.7 ppm provides strong evidence that the polymer has been methoxylated. The substituted polymer presumably has the basic structure shown in structure V.



V

Polypyrrole. Again cyclic voltammetry (Figure 8) revealed no apparent evidence of electrochemically induced substitution of polypyrrole by bromopropanol, but electron microprobe analysis indicated that both bromine and oxygen had become incorporated into the film, even at potentials as low as +0.20 V. The intensity of the Br X-ray intensity increased as the potential used for electrochemical substitution was increased (Figure 9). At +1.2 V, approximately 30% substitution occurs in 3 min, based on the relative intensities of the N and Br peaks. The O:N ratio was 0.57, higher than expected for 30% substitution (the ClO_4^- counterions had been exchanged with Cl^- before analysis). However, this figure contains an unknown oxygen contribution from reaction of the polypyrrole with trace water.[32]

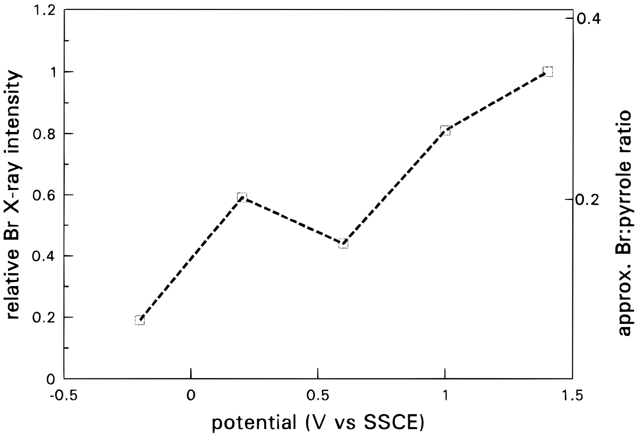


Figure 9. Relative Br X-ray intensity from electron microprobe analysis (Hitachi S-570) vs potential for polypyrrole films (0.2 μm) that had been oxidized for 2 min in 0.1 M Et_4NClO_4/CH_3CN containing 50 mM 3-bromopropanol. Results have been normalized with respect to the 1.4 V result, which corresponds to a Br:N ratio of 0.32 (Cameca SX50).

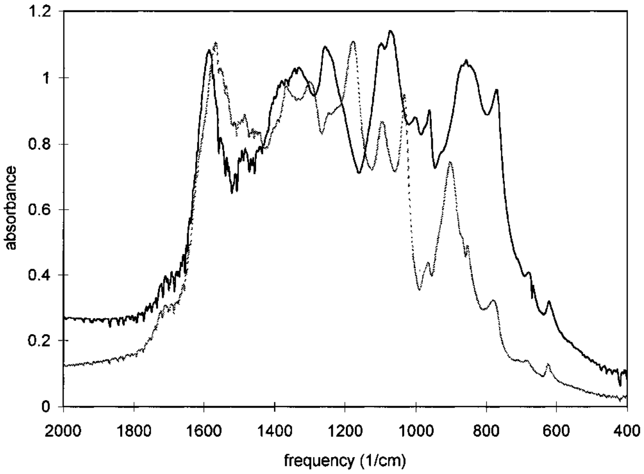


Figure 10. FTIR reflectance spectra of polypyrrole films (2 μm on Pt) that had been electrochemically cycled between −1.0 and +1.4 V (20 mV/s, 4 scans) in 0.1 M Et_4NClO_4/CH_3CN (solid line) and the same electrolyte containing 10% methanol (dotted line), and then held at 0 V for 5 min.

Further evidence for the reaction of oxidized polypyrrole with alcohols was obtained from infrared spectroscopy. Figure 10 shows FTIR reflectance spectra of polypyrrole films that had been electrochemically cycled (see caption) in 0.1 M Et_4NClO_4/CH_3CN (solid line) or the same electrolyte containing 10% methanol (dotted line), and then held at 0 V for 5 min. The cyclic voltammograms were similar, but there are substantial differences in the IR spectra. The new peaks at 1176 (a) and 1032 (b) cm^{-1} in the methanol treated film are characteristic of an aromatic (or vinylic) alkoxy group and therefore provide strong evidence that methoxylation had occurred. Loss of the peak at 1073 (c) cm^{-1}

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[32] Lei, J. T.; Liang, W. B.; Martin, C. R. *Synth. Met.* **1992**, *48*, 301–312.

due to the C−H deformation at the 4-position[33] indicates that substitution has occurred at the 4-position.

Conclusions

Substitution of electrochemically oxidized polythiophenes and polypyrroles by nucleophiles appears to be a quite general reaction. The reaction with water is well-known,[23] and we have now demonstrated reactions with Cl^-, Br^-, and some alcohols. However, there are exceptions such as the failure of I^- to substitute poly(3-methylthiophene).

The degree of substitution is potential dependent and under a certain set of conditions varies considerably between polymers and nucleophiles. The degree of oxidation of the polymer and the reactivity of the nucleophile appear to be the key factors that determine the substitution level. Enhanced substitution levels can be obtained by repeating the substitution procedure.

The new results reported here support our proposed mechanism[21] for the electrochemical chlorination of polythiophenes, which is outlined in Scheme 1. It is reasonable to suppose that a similar mechanism operates in the other substitution reactions reported here. The properties of the deactivated intermediate, which has been observed only for Cl substitution of polythiophenes, provide the main evidence for this mechanism. The postulated structure (III) is based on the observations that it contains covalently bound Cl,[21] is electrochemically inactive (Figure 2), and exhibits a low conductivity (Figure 3). The new results on the relative reactivities of polythiophene, polybithiophene, and poly(3-methylthiophene) are also consistent with this mechanism. An alternate mechanism, in which electrochemically produced Cl_2 reacts with the polymer, is ruled out by the fact that substitution can be observed at much lower potentials (e.g., Figure 5) than are required for Cl_2 formation (>+0.9 V).

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[33] Tian, B.; Zerbi, G. *J. Chem. Phys.* **1990**, *92*, 3886−3891.