Reactivation of Poly(3-methylthiophene) following Overoxidation in the Presence of Chloride

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Poly(3-methylthiophene) films made electrochemically inactive by overoxidation in the presence of Cl^- can be reactivated both electrochemically and chemically to produce a partially chlorinated conducting polymer.

The degradation of electronic properties by overoxidation is a ubiquitous problem in the field of conducting polymers. In the cases of polypyrroles and polythiophenes it generally results from nucleophilic attack of water on the dication (bipolaron) charge carriers,[1-3] and can be avoided by use of extremely dry non-nucleophilic electrolyte solutions.[4]

We have found that oxidative degradation of poly(3-methylthiophene) is promoted by the presence of Cl^- (Fig. 1) providing further evidence for the nucleophilic attack mechanism. The polymer becomes electrochemically inactive after a single cycle of the potential to +1.3 V in a Cl^- solution
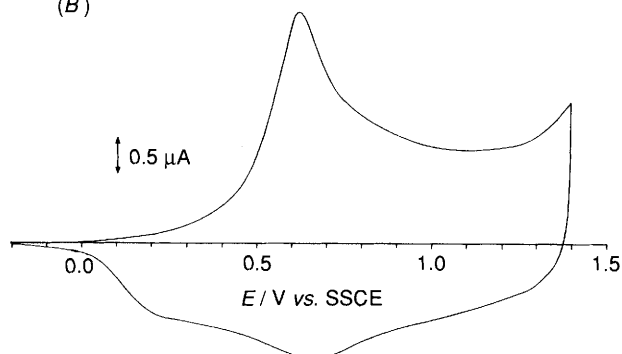

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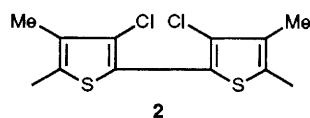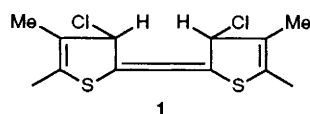
(*A*)
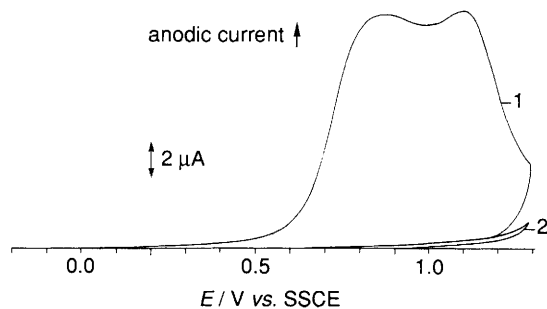
(*B*)

Fig. 1 Cyclic voltammograms for poly(3-methylthiophene)-coated Pt electrodes in acetonitrile containing (*A*) 0.1 mol dm^{-3} Et_4NCl (scan numbers indicated), and (*B*) 0.1 mol dm^{-3} Et_4NClO_4. The polymer films were prepared at a constant current of 1.0 mA cm^{-2} from 0.1 mol dm^{-3} 3-methylthiophene in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4 and were approximately 0.1 μm thick. Scan speed = 50 mV s^{-1}. Electrode area = 0.005 cm^2 (SSCE = saturated sodium chloride calomel electrode).

[Fig. 1(*A*)], while in the absence of chloride it is stable to potentials as high as 1.4 V [Fig. 1(*B*)]. *In situ* conductivity measurements reveal that deactivation in the Cl^- solution results in an approximately 100 fold drop in conductivity at 0.6 V, while X-ray emission analysis[5] has shown that Cl becomes covalently bound to approximately every second thiophene ring of the polymer. Based on this evidence we propose that approximately half of the thiophenes in each chain are converted to structures like **1** during deactivation. The deactivated rings need not occur in adjacent pairs but have been represented that way for simplicity. The lack of conjugation in these structures is responsible for the loss of electroactivity and the decrease in conductivity. The decrease in conductivity is surprisingly small in view of the change in electroactivity and suggests that a significant concentration of charge carriers remain in the deactivated polymer.

It is clear from structure **1** that it should be possible to restore the conjugation of the polymer and therefore reactivate it by elimination of H to give structure **2**. Electrochemical, chemical and thermal routes were tested, the first two succeeding.

Fig. 2 shows cyclic voltammograms for a deactivated film in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4. The current is negligible at potentials below +0.9 V during the first anodic scan, confirming that the film has been deactivated. However, a sharp irreversible anodic peak is observed at +1.3 V, and scanning the potential of the polymer through this peak restores its electroactivity at lower potentials. The conductivity of the polymer was also restored by this electrochemical
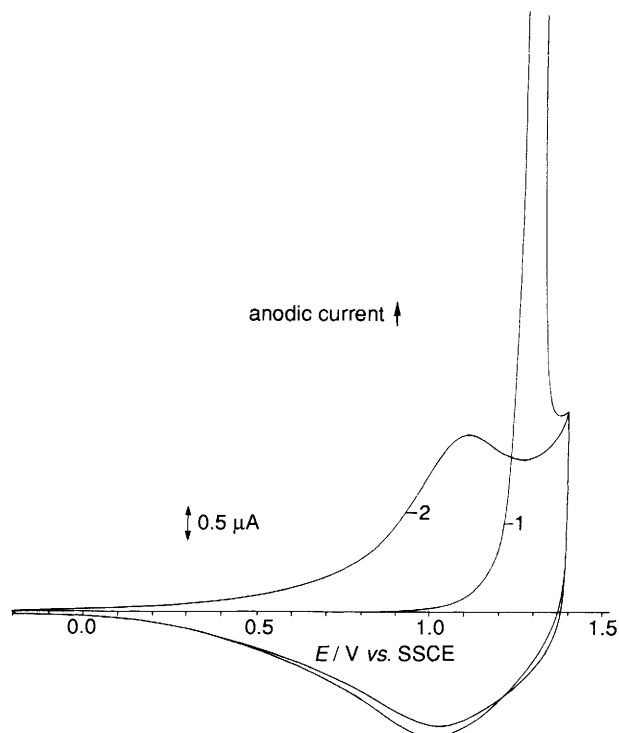

Fig. 2 Cyclic voltammograms for a deactivated [as in Fig. 1(*A*)] poly(3-methylthiophene) film in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4. Scan numbers are indicated; subsequent scans were similar to 2.

reactivation: to approximately 20% of the virgin polymer value at 0.6 V and to approximately 50% of the original value at 1.0 V. The redox potential of the reactivated polymer is about 0.5 V more positive than that of the virgin polymer, consistent with a net halogenation.[6] X-Ray emission analysis confirmed that the covalently bound chlorine introduced during deactivation was retained in reactivated films. The sharp peak at +1.3 V in Fig. 2 must therefore be due to the process in eqn. (1). Consistent with this interpretation, the

$$1 \rightarrow 2 + 2H^+ + 2e^- \qquad (1)$$
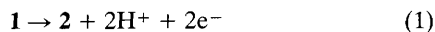
deactivated polymer can also be reactivated with the dehydrogenation reagent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 5 min at reflux in toluene containing 0.05 mol dm^{-3} DDQ and 0.05 mol dm^{-3} toluene-p-sulfonic acid or HCl).

The net electrochemical halogenation observed with Cl$^-$ also occurs for Br$^-$, although a deactivated intermediate analogous to 1 has not been observed. Thus, after potential cycling between 0 and 1.4 V in acetonitrile containing 0.1 mol dm^{-3} Bu$_4$NBr, a poly(3-methylthiophene) film was found to contain approximately 0.4 covalently bound Br atoms per thiophene ring. However, films treated in this way still exhibited reversible electrochemistry when examined in acetonitrile containing Et$_4$NClO$_4$. Presumably both deactivation and reactivation occurred during potential cycling in the Br$^-$ solution. Electrochemical bromination has been reported to occur during the polymerization of pyrrole[7] and the oxidative deactivation of polypyrrole[1] and thiophene,[8] in the presence of Br$^-$.

The reactivation of poly(3-methylthiophene) described here provides important new insight into the reactions accompanying overoxidation of conducting polymers. Although we have not solved the overoxidation problem, we have shown for the first time that an overoxidized polymer can be reactivated. We have also demonstrated a potentially useful method for the introduction of a functional group into a preformed conducting polymer. The halogens introduced here can provide a pathway for further functionalization. Alternatively, it may be possible directly to introduce other functional groups by electrochemical nucelophilic substitution.

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