A Conducting Polymer Formed from the Anodic Oxidation of Toluene in Acetonitrile

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As opposed to the much harsher conditions demanded in homogeneous solutions, a conducting polymer of toluene is readily formed by anodic oxidation of acetonitrile solutions containing the precursor.

The fabrication of new conductive polymers is of interest owing to the potential practical applications of these materials. We report here the electrochemical formation of a conducting polymer from toluene precursor. Anodic oxidation of concentrated solutions (0.5 M) of toluene in anhydrous acetonitrile containing ($Bu_4N^+BF_4^-$, 0.15 M) leads to the formation of a highly conductive poly(methylphenylene) polymer film on the surface of a platinum mirror electrode (bulk metal). The polymer can also be formed in solutions of lower toluene concentrations (1—10 mM), but only after successive pulsing or sweeping techniques at high positive potentials (>1.8 V vs. Ag/Ag^+) for long periods of time.

Preliminary electrochemical experiments on the formation and characterization of the film were carried out in dry acetonitrile (nominal water content <0.005%) with Bu_4NBF_4 electrolyte, which had been freshly recrystallized twice from methylene chloride–diethyl ether and dried in vacuo at 75 °C for 24 h. Solutions were degassed with and carried out under Ar. Films were formed in the range of thicknesses 0.5—5 microns.
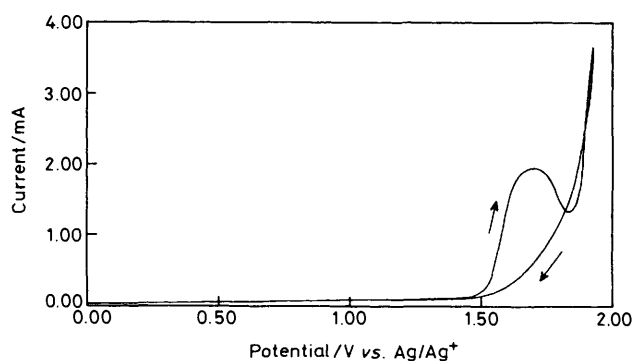
Figure 1. Voltammogram of toluene (0.5 M) in acetonitrile containing tetra n-butylammonium tetrafluoroborate (0.15 M) at a platinum mirror disk electrode. Sweep rate is 50 mV s^{-1}.
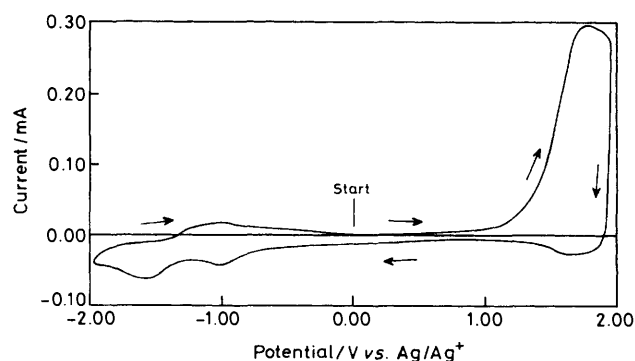
Figure 3. Voltammogram of an approximately 1 micron thick polymer film electrode in the pure electrolyte solution. Sweep rate is 100 mV s^{-1}.
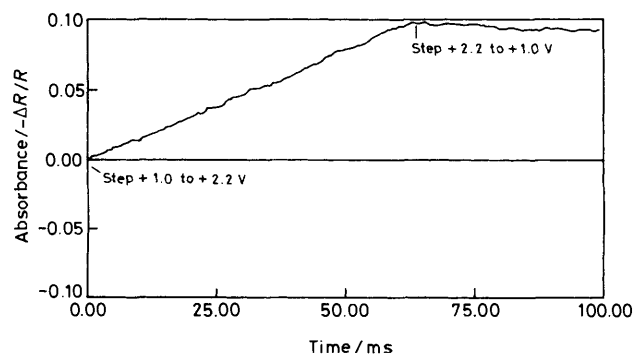
Figure 2. Absorbance transient at 430 nm following a potential step from +1.0 to +2.2 V on the system described in Figure 1. The transient is the average of 10 experiments.
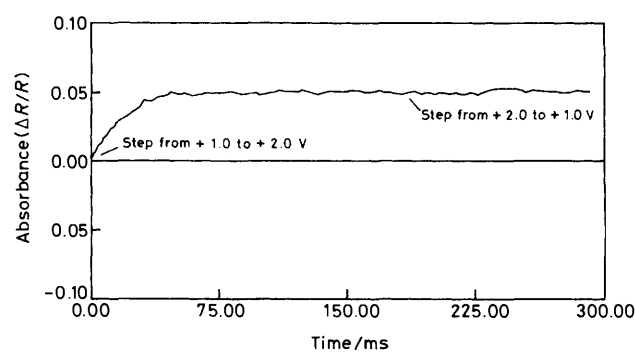
Figure 4. Absorbance transient at 420 nm following a potential step from +1.0 to +2.0 V on a polymer film formed from the system described in Figure 1. The transient is a single scan.

Figure 1 shows the cyclic voltammogram of a typical solution. The irrerversible wave is similar to those observed in the anodic oxidation of pyrrole to polypyrrole,[1] or biphenyl to poly(p-phenylene)[2] in similar electrolytes. At high potentials, a brassy film is rapidly formed on the surface of the electrode, and streaming of unprecipitated solid product away from the surface is observed. Continued growth of the film is observed on subsequent potential scans as evidenced by the behaviour of the current on the anodic excursion and darkening of the surface film. Slight attenuation of the current after several scans is similar to that observed in polypyrrole formation.[2] As has been observed and reported previously, these films are doped during the oxidation with the BF$_4^-$ anion;[2—4] i.r. spectra confirm the presence of the electrolyte within the film.

Figure 2 shows the transient spectroelectrochemistry at 420 nm for the formation of the polymer film at a platinum mirror electrode upon application of a +2.2 V ($vs.$ Ag/Ag$^+$) potential step from 1.0 V. We note that the shape of the forward transient is linear with time. If the potential is then returned to 0.0 V, the absorbance falls only slowly. This is typical behaviour for an irreversibly formed adherent polymer film at a surface. At high concentrations of the precursor, the reaction is virtually first order with respect to the coupling of the hydrocarbon free radicals, and the total amount of product formed is linear over this time interval. An increase in the oxidity of the solution, as evidenced by the appearance of a proton reduction wave at −0.2 V, is direct evidence for the formation of the toluene free radical species from the initially formed toluene cation radical.[5,6]

Figure 3 shows the voltammogram of a typical polymer film electrode which has been removed from the synthetic cell to a cell containing only the electrolyte solution. Again, the film behaves similarly to other conducting polymer films.[4,7,8] In the present case, the film is oxidized at about +1.8 V, and a significant capacitative component to the current is observed (there is a sudden decrease in current at the positive potential switching potential). The oxidation of the film also results in the coupled chemical formation of other insoluble polymeric forms in the matrix; continued proton loss from the initially formed polymer film is observed at potentials where the film is oxidized. This indicates that the polymer anions formed under these conditions are still unstable with respect to further cross-linking or to the formation of multiply π-bonded polymer products. The voltammetric behaviour of the film changes only slowly over continued scanning, indicating the sluggishness of the oxidation of the total film. The film is reduced at about −1.0 V, and breaks down rapidly after sweeps to higher negative potentials. Preliminary measurements of the conductivity give a value of approximately 0.1 S cm^{-1}.

The film exhibits an electrochromic effect. Figure 4 shows the change in absorbance at 420 nm of the film upon anodic oxidation. Unlike poly(p-phenylene) the effect is irreversible (note the constant value of the absorbance when the potential is switched back to 0.0 V). This corroborates the assumption of chemical irreversibility of the film oxidation under these conditions. This result, together with the voltammetric results and the previous spectroelectrochemical results (Figure 2), indicates that the product of the oxidation is also conductive, and that electron transfer to the outer layers of the initially formed film is slow.

Raman scattering studies from the film show bands at 1338,

1362, 1395, and 1610 cm^{-1}; strong fluorescence from the film may obscure other bands. The Raman shifts are similar to those observed for poly(phenylene).[9] The conductivity of the polymer film is lower than that of poly(p-phenylene); conductivity values as a function of type of electrolyte dopant and a full characterization of the system will be reported elsewhere. It may be that poly(o-phenylene) type products are formed; these types of polymers are the primary products in the homogeneous solution oxidation of toluene.[10]

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