Electrochemical Preparation of Highly Anode-active Poly(3-phenylthiophene)

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The electrochemical preparation of poly(3-phenylthiophene) is described; when doped with cations as well as anions, it exhibits interesting spectroscopic properties.

Electrically conducting polymers have attracted considerable attention, owing to their usefulness in rechargeable batteries, heterojunctions, and electrochromic displays. Electrochemical polymerization has been found to be a convenient technique for obtaining conducting polymers from five-membered heterocycles. Among polyheterocycles, polythiophenes are of increasing interest owing to their enhanced stability in both oxidized and neutral states. Many kinds of polythiophenes have been prepared by electrochemical polymerization and have shown various interesting properties. Phenyl derivatives of polythiophenes are of current interest: poly(benzo[*c*]thiophene) has a very small band gap,[1] poly(1,4-di-2-thienylbenzene) is a novel type of conducting polymer,[2] and poly(1,3-dithienylbenzene) and poly(4,4'-di-2-thienylbiphenyl) exhibit green-yellow electrochromism.[3] Here we report the electrochemical preparation of highly anode-active poly(3-phenylthiophene) (PPT).

3-Phenylthiophene was obtained by coupling of phenylmagnesium bromide with 3-bromothiophene in the presence of a nickel catalyst (m.p. 92.3—93.6 °C; lit.[4] 92 °C). The structure was confirmed by n.m.r. and i.r. spectroscopy. The electrochemical vessel consisted of a one-compartment cell equipped

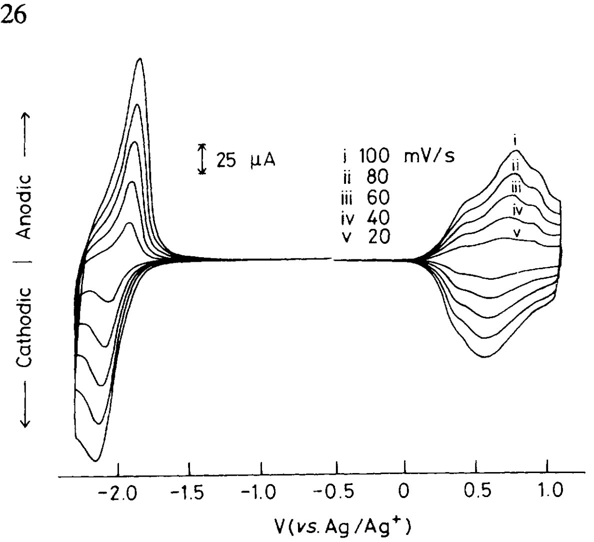

Figure 1. Cyclic voltammograms of PPT, film 720 nm thick, acetonitrile solution containing 0.1 M Et_4NPF_6.

with a platinum plate as the cathode and an indium–tin oxide conducting glass plate for spectroscopic measurements or a polished platinum disk electrode (s = 0.024 cm^2) for cyclic voltammetry as the anode. The electrochemical polymerization was performed at a constant current density of 1 mA cm^{-2} at 5 °C under an argon atmosphere and continued until the charge reached 1.8 C cm^{-2}. Propylene carbonate was used as solvent. The concentrations of the monomer and electrolyte (Et_4NPF_6) were 0.1 and 0.03 mol dm^{-3}, respectively.[5] The conductivity of a free-standing film was 100 S cm^{-1}. Analysis for sulphur and phosphorus indicated that an as-grown film contained 0.19 unit of dopant per monomer unit. A neutral film was obtained by the electrochemical reduction of an as-grown film and its i.r. spectrum was consistent with the regular structure denoted as poly(3-phenylthiophene-2,5-diyl).

The cyclic voltammograms were measured in an acetonitrile solution containing 0.1 M Et_4NPF_6 for a PPT film electrosynthesized in propylene carbonate with charge of 0.24 C cm^{-2} and rinsed thoroughly with acetonitrile. Figure 1 shows the cyclic voltammograms of a PPT film on a platinum disk in the potential ranges of −0.5 to +1.1 and −0.5 to −2.3 V *vs.* Ag/Ag$^+$. In the range of −0.5 to +1.1 V, the anodic and cathodic peaks were ascribed to the doping and undoping of PF_6^-, respectively. The oxidized film was blue in colour and the neutral one, red–purple. The amount of charge, Q, reversibly exchanged during the redox cycles was 0.78 electron per monomer unit. Q was obtained by integrating the absolute value of the current in Figure 1 with respect to time. In the range of −0.5 to −2.3 V, the cathodic and anodic peaks may be ascribed to the doping and undoping of Et_4N^+, respectively. The reduced film was blue–purple in colour. The Q value for cation doping and undoping was 0.72 electron per monomer unit. These cyclic voltammograms are somewhat similar to those of a thin Prussian blue film which is reduced to Everitt's salt or oxidized to Berlin green.[6]

Figure 2 shows the cyclic voltammograms of polythiophene in the potential ranges of −0.5 to +1.15 and −0.5 to −2.4 V.[7,8] The Q values[†] for anion and cation doping were

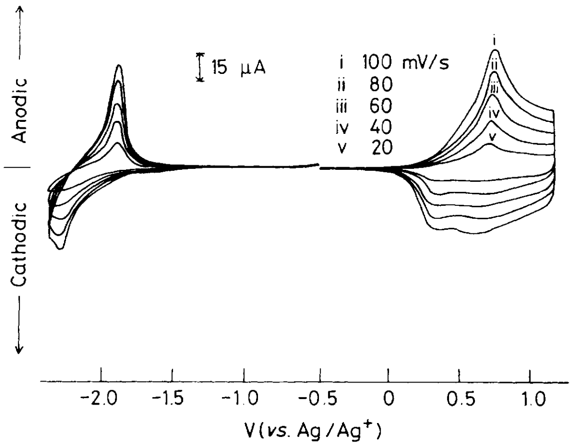

Figure 2. Cyclic voltammograms of polythiophene, film 250 nm thick, acetonitrile solution containing 0.1 M Et_4NPF_6.

estimated to be 0.69 and 0.24 electron per monomer unit, respectively. It is clear that the phenyl group has a favourable effect on the cation doping of polythiophene.

The changes in visible–near i.r. spectra of a PPT film during electrochemical doping were measured. In neutral states, the absorption onset corresponding to the transition between the valence and conduction bands was observed at 1.74 eV. The absorption peak was at 2.21 eV. These values were the smallest among poly(3-substituted thiophenes).[9] At low levels of anion doping, three additional peaks appeared at 1.48, 1.21, and <0.6 eV within the gap region. The peak at 1.21 eV may be associated with the transition between the two polaron bands which had not hitherto been observed explicitly in the spectra of polythiophenes. At higher doping levels, two peaks due to bipolaron bands were observed at 1.43 and < 0.6 eV. When a PPT film was electrochemically cation-doped, two peaks at *ca.* 1.5 and 0.7 eV appeared in addition to the band-to-band transition peak at 2.21 eV.

A p–n junction thin film was fabricated by sequential electrochemical polymerization of pyrrole and thiophene.[10] PPT would be more suitable for such a p–n junction diode than polythiophene.

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[†] The charge for doping and undoping was determined by integrating the absolute value of the current in Figure 1 with respect to sweep time. The charge Q was obtained by dividing the charge by polymer weight on the electrode.