Separation of Neutral-to-polaron and Polaron-to-bipolaron Redox Events in Alkoxy Substituted Di-2-thienylphenylene Polymers

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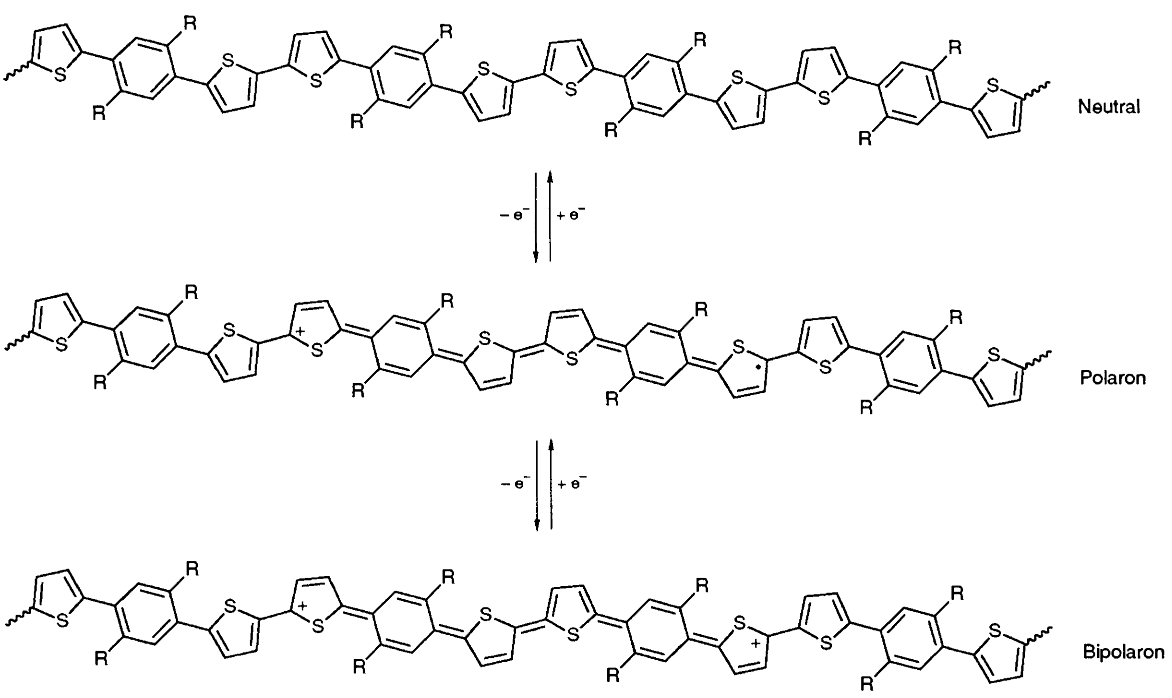
In situ electron paramagnetic resonance (EPR)/electrochemistry methods have been used to elucidate the potential dependence of the presence of polaron and bipolaron charge carriers in poly(di-2-thienyl-2,5-diheptoxyphenylene).

The identification of charge carriers in conjugated conducting polymers has recently received a great amount of attention.[1–6] It is generally accepted that the electrochemical oxidation of polyheterocycles leads to the formation of delocalized radical cations (polarons) and ultimately to delocalized dications (bipolarons).[7] Studies involving the electrochemical oxidation and reduction of conducting polyheterocycle films have suggested that the generation of polarons, and the subsequent formation of bipolarons, occurs at essentially the same potential. The potentials of these redox events appear to be



$R = OC_7H_{15}$

Scheme 1

too close to allow them to be distinguished by voltammetry.[1] *In situ* EPR measurements carried out in an electrochemical cell have verified the presence of spin containing species (polarons) at intermediate doping levels in polypyrrole[1,2,5] and polythiophene.[3,6] The relative stability of the polaron intermediate has still not been fully elucidated; particularly in the case of polythiophene.[1,3] The results for polythiophene vary greatly in both the population of spin species and the potential of maximum spin.[3] Zotti *et al.* have shown that the maximum spin concentration on the cathodic sweep of polythiophene corresponds to a low potential shoulder in the cyclic voltammogram.[3] Variations in the electrolyte medium and temperature also resulted in a low potential shoulder on the anodic scan. Enhanced counterion mobility was therefore thought to lower the potential of the neutral-to-polaron redox event and allow for an observable peak separation from the polaron-to-bipolaron response.

Several polythiophene derivatives containing ether groups at the 3 position have been shown to display two distinct redox couples in their cyclic voltammograms.[8,9] The presence of a relatively sharp initial oxidation of the polymer at a low potential is characteristic of these polymers. The presence of these two separated processes has been attributed to ion transport phenomena where the oxygen atoms of the pendant ether groups increase the mobility of alkali metal ions. To date, no evidence for the formation of polarons at the first couple has been presented.

We have previously reported on the synthesis, characterization, and electronic and electrochemical properties of a new class of conducting polymers containing alternating bithiophene and phenylene repeat units.[10–12] The electrochemical and optical properties of these polymers are quite similar to polythiophene, however, the ease of substitution on the phenylene ring allows for greater synthetic flexibility. Substitution at the 2 and 5 positions of the phenylene ring with long chain alkoxy groups results in highly conducting, soluble polymers.[11,12]

Poly(di-2-thienyl-2,5-diheptoxyphenylene) displays two distinct redox processes with anodic peak potentials located at 0.27 and 0.61 V *vs.* Ag/Ag$^+$. Poly(di-2-thienyl-2,5-dimethoxyphenylene) exhibits only a single anodic response with a peak at 0.68 V.[11] It is important to note that the second redox couple observed in the diheptoxy substituted polymer corresponds to approximately the same potential as the single redox couple observed in the dimethoxy substituted polymer. The new anodic peak is observed at a much lower potential and suggests structural influence from the longer alkoxy chain. Each couple has been shown to be independently reversible and chronocoulometry has determined that the same amount of charge is passed for each redox event. Electrogravimetry, carried out using an electrochemical quartz crystal microbalance has demonstrated that equal amounts of mass are also transferred for each couple.

The electrochemistry of this polymer is quite similar to the ether substituted polythiophenes[8,9] whose peak potentials are within 70 mV of those reported above accounting for differences in reference electrodes. In order to assign the redox processes involved in charge carrier formation as outlined in Scheme 1, and the effect of applied potential on the spin concentration in these polymers, we have carried out a series of simultaneous EPR–electrochemistry experiments.

Poly(di-2-thienyl-2,5-diheptoxyphenylene) films, *ca.* 200–300 nm thick, were synthesized by constant potential electropolymerization of 5 mmol dm^{-3} bis(2-thienyl)-2,5-diheptoxybenzene in 0.1 mol dm^{-3} Bu_4NClO_4 in acetonitrile at 0.85 V *vs.* Ag/Ag$^+$. A symmetric derivative EPR signal was observed when the polymer was placed in an EPR cell with a platinum counter electrode and a silver wire reference electrode (-0.27 V *vs.* Ag/Ag$^+$) and cycled between 0 and 1.25 V at 5 mV s^{-1}. The *g* value was determined using a diphenylpicrylhydrazyl standard and found to be close to the free electron value of 2.00232 at 2.0044. The line width of the signal is 2.10 G independent of the oxidation state of the polymer. In order to monitor polaron formation and decay, the magnetic field was held at the maximum of the derivatized signal and the polymer electrode potential scanned. The resulting current response and EPR signal intensity are shown in Fig. 1.

The EPR intensity is inverted during the cathodic scan in order to allow comparison with the current response. The polymer becomes paramagnetic during the first oxidation process as evidenced by the increase in EPR signal intensity at 0.6 to 0.7 V. A maximum in the EPR signal is observed at a

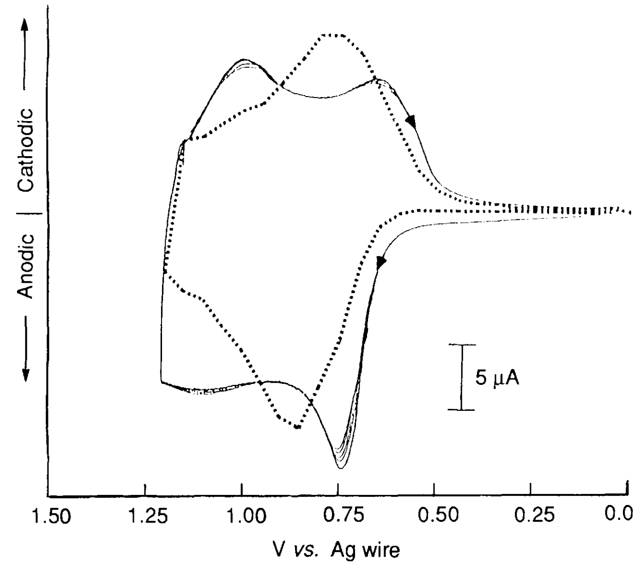


Fig. 1 Current (——) and maximum derivatized EPR signal intensity (------) during a cyclic voltammogram of poly(di-2-thienyl-2,5-diheptoxyphenylene). Scan rate = 5 mV s^{-1}, reference electrode is Ag wire.

potential just beyond the first current response which subsequently decays during the second oxidation process. The potential of maximum EPR signal intensity was verified by carrying out a potential step experiment in which the potential of the electrode was stepped in 25 mV intervals and the current response allowed to equilibrate. Both cathodic and anodic EPR peak potentials remained unchanged from the scanning experiment indicating no scan rate dependence up to 5 mV s^{-1}. This indicates that spin bearing species are formed at the first redox couple and dissipated at the second. The same is true during the reverse scan as the EPR signal reaches a maximum between the two current responses and returns to zero at low potentials where the polymer is in its neutral form. The signal is stable for at least an hour at its maxima indicating no decay of polarons into bipolarons and neutral sites. The polymer is not diamagnetic at 1.2 V which is the highest potential the polymer can be held at without degradation. The EPR signal disappears when the potential is swept to approximately 1.5 V which results in a significant decrease in the electroactivity of the polymer due to over oxidation.[13] These results indicate that the two separate redox processes observed are due to potential controlled polaron and bipolaron formation and are not only an ion transport phenomenon.

Further work will focus on the quantitative effects of substituent length on the spin concentration and the potential of maximum spin concentration.

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