Modification of the Structure and Electrochemical Properties of Poly(thiophene) by Ether Groups

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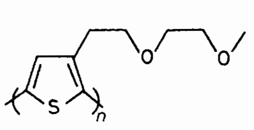
Poly[3-(3,6-dioxaheptyl)thiophene] has been synthesised by electropolymerisation; this highly conducting electroactive polymer exhibits specific interactions with lithium cations.

Whereas the synthesis and the structure of conducting polymers prepared by electropolymerisation of thiophene derivatives are still subject to intense research efforts,[1] the modification of their properties for specific applications in the fields of molecular electronic devices or modified electrodes is attracting increasing interest.[2]

The covalent grafting of polyether chains on the conjugated system of poly(thiophene) represents an interesting approach for the synthesis of conducting polymers showing both electronic and ionic conduction. Such polymers will possess a wide scope of potential applications in ion-selective electrodes and membranes or for interfacing electroactive polymers with ionic conductors such as poly(ethylene oxide) in solid-state batteries.

Poly(thiophenes) which are 3-substituted by ether functions have been described in recent work aiming to improve the solution processibility of poly(thiophene). However, their electrochemical properties have not been reported.[3]

We report here preliminary results on the synthesis and spectroelectrochemical properties of a novel conducting



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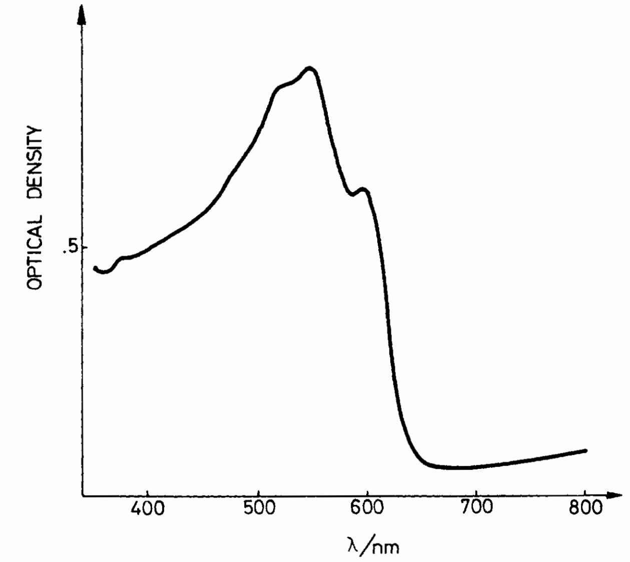

Figure 1. Visible absorption spectrum of an electrochemically undoped film of (**1**) prepared on an ITO electrode using 50 mC cm^{-2}.

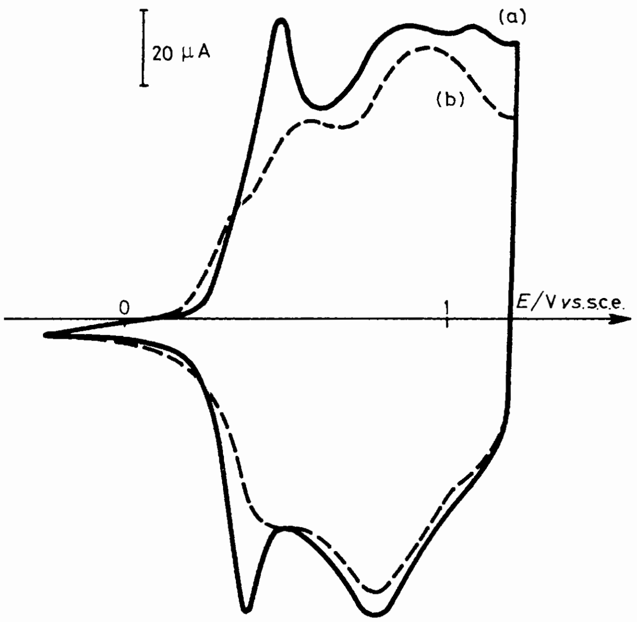

Figure 2. Cyclic voltammograms of (**1**) in MeCN, deposition charge 140 mC cm^{-2} on Pt (0.07 cm^2), scan rate 30 mV s^{-1}, electrolyte concentration 5 × 10^{-1} mol l^{-1}, (a) in LiClO$_4$; (b) in Bu$_4$NClO$_4$.

polymer, poly[3-(3,6-dioxaheptyl)thiophene] (**1**). The structure of this polymer differs from ones already described in respect of the position of the first oxygen atom in the 3-substituent. We show that this structural modification allows the synthesis of a highly conjugated electroactive polymer exhibiting specific interactions with lithium cations.

The synthesis of the monomer has been described elsewhere.[4] The polymer was prepared in a one-compartment cell containing 2 × 10^{-1} mol l^{-1} monomer and 2 × 10^{-2} mol l^{-1} Bu$_4$NPF$_6$ in nitrobenzene according to previously reported procedures.[1c,5b] Electropolymerisations were performed under galvanostatic conditions (3 mA cm^{-2}) at ambient temperature. Films for visible absorption spectroscopy and conductivity measurements were grown respectively on indium–tin oxide (ITO) and platinum electrodes. Cyclic voltammetry was performed in dry acetonitrile containing LiClO$_4$ or Bu$_4$NClO$_4$, on films deposited on 0.07 or 0.7 cm^2 Pt disk electrodes; all potentials refer to the saturated calomel electrode (s.c.e.). Conductivities were determined by a standard four-probe technique.

Figure 1 shows the absorption spectrum of the undoped polymer. In contrast to the broad absorption band generally observed in the 450—540 nm region with poly(3-alkylthiophenes)[5] (PATs), the spectrum of (**1**) presents several well resolved structures including a maximum at 552 nm and two well defined shoulders at 510 and 600 nm. Absorption bands corresponding to these maxima have already been observed at low temperature, in studies of the thermochromic effects in PATs.[6] These absorption features were interpreted in terms of thermally induced conformational changes leading to longer effective mean conjugation lengths. The similarity between these spectra and that of (**1**) suggests that the ether groups contribute to stabilising preferential conformations corresponding to longer effective mean conjugation lengths. Furthermore, the 57 nm bathochromic shift of the absorption maximum of (**1**) compared to its alkyl homologue poly(3-heptylthiophene)[5b] confirms the highly conjugated structure of (**1**).

Larger scale electrosynthesis led to free standing films with a shiny blue metallic aspect and a conductivity of 100 S cm^{-1} for a 5 μm thick film prepared using 1 C cm^{-2}. Limiting the film thickness to 500 nm raises the conductivity up to 250 S cm^{-1}, in agreement with our recent analysis of the effects of thickness on the conductivity of poly(thiophenes).[7] This high conductivity appears consistent with the highly conjugated structure indicated by the absorption spectrum of (**1**).

The cyclic voltammogram of (**1**) in Bu$_4$NClO$_4$ and LiClO$_4$ (Figure 2) is quite unusual for a poly(thiophene) derivative and displays two distinct components which include a first pair of voltammetric waves at 0.5 V and a main redox system at 0.8 V. These successive redox systems can be related to the presence of several bands in the absorption spectrum and suggest an electrochemical doping of polymer chains of different mean conjugation lengths. Replacing Bu$_4$N$^+$ by Li$^+$ leads to important modifications of the voltammogram, namely an increase in the intensity of the first system and a shift of both anodic waves toward less anodic potentials. Furthermore, whereas in Bu$_4$N$^+$ the CV response is independent of the electrolyte concentration, increasing the concentration of Li$^+$ produces a further decrease of the peak potentials and a narrowing of the voltammetric waves. Various interpretations can be proposed to account for these results; (i), an increase of the ionic conductivity of the polymer assisting the doping process which is limited by the insulating character of the undoped polymer, or (ii), conformational changes of the conjugated backbone induced by the complexation of Li$^+$ by the ether groups. The cation dependence of the *in situ* absorption spectra recorded in the presence of both cations appears consistent with the second hypothesis, although changes in the ionic conductivity of the polymer cannot be neglected.[8]

Interestingly, (**1**) can also undergo an electrochemical n-type doping process as shown by the cyclic voltammograms of Figure 3. The voltammogram recorded in the presence of Bu$_4$N$^+$ (Figure 3a) is similar to those obtained on poly-

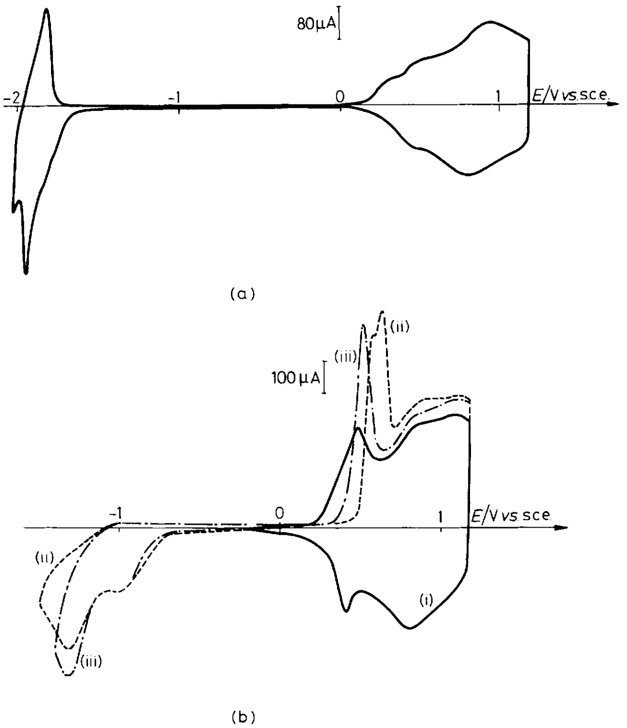

Figure 3. Cyclic voltammograms of (**1**) in MeCN, deposition charge 140 mC cm^{-2} on Pt (0.7 cm^2): (a) 5×10^{-1} mol l^{-1} Bu_4NPF_6, scan rate 20 mV s^{-1}; (b) 5×10^{-1} mol l^{-1} $LiClO_4$, scan rate 30 mV s^{-1}; (i) initial curve; (ii) after one scan up to −1.4 V; (iii) after one scan up to −1.5 V.

thiophene and shows a quasi-reversible system at *ca.* −2 V.[9] In contrast, in the presence of Li^+ (Figure 3b), the threshold corresponding to n-doping occurs at a potential which is 1 V less cathodic. Cathodic waves are observed at −1 and −1.3 V, while the undoping process occurs in the anodic potential region and corresponds to the intense first anodic peak observed at 0.55 V during the reverse scan, as confirmed by coulometric measurements and by the slight decrease of the absorbance at 552 nm. Similar to p-doping, the n-doping process exhibits a strong dependence on the Li^+ concentration and increases from 6 to 12 mol % from 10^{-1} to 1 mol l^{-1} Li^+. Increasing the cathodic potential from −1.3 to −1.5 V leads to a shift from 0.55 to 0.65 V of the anodic peak corresponding to the n-undoping process. These results, together with the very large ΔE_p between the n-doping and n-undoping process, suggest a stabilisation of the Li^+ n-doped polymer compared to Bu_4N^+. The fact that the voltammograms of poly(thiophene) or PATs analysed in the presence of Li^+ are flat down to −2.5 V suggests that the presence of the ether groups in the alkyl chain is responsible for the stabilisation of the n-doped polymer. As already observed in the case of poly(3-alkoxy-2,5-thienylene vinylene) n-doped with Na^+,[10] the stability of the polymer upon cycling on the n-redox system is much more limited than in the case of the p-system. Thus the application of potentials more cathodic than −1.5 V results in the degradation of the film.

Although the detailed understanding of the effects of the ether groups on the structure and properties of the polymer still requires further work, these results show that the introduction of ether groups at appropriate positions in the alkyl substituent leads to a highly conjugated and conducting polymer presenting a specific electroactivity in the presence of lithium cations.

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