Unusually high stability of a poly(alkylquaterthiophene-*alt*-oxadiazole) conjugated copolymer in its n and p-doped states†

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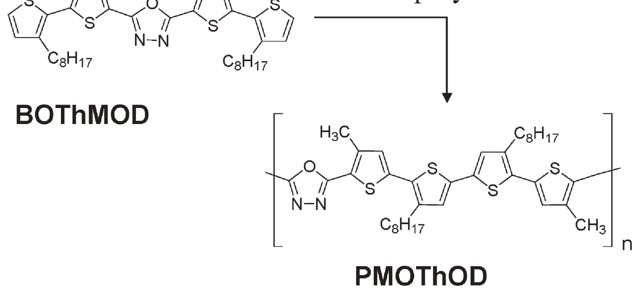
Incorporation of electron accepting units (oxadiazole) into the 2,5-thienylene conjugated chain leads to a significant improvement in the n-doping–undoping redox stability of the resulting polymer.

Electrochemical doping is frequently used to induce changes in the electrical, optical and chemical properties of conjugated polymers. These changes are often exploited for the development of new electrochemical devices, such as different types of electrochemical sensors and actuators, electrochromic windows *etc.*, to name a few.[1] Although relatively high p-doping–undoping cycle stability has been achieved for selected systems,[2] almost all of them suffer from a rather low potential of the degradative oxidation (sometimes termed "overoxidation") which severely limits their utilisation. The electrochemical stability of the polymers in the n-doping region is even more inferior, exhibiting a significant decrease in the Faradaic efficiency when they are cycled in this potential region.[3] There exists, therefore, a strong need for the development of new chemical systems which could be reversibly cycled in the electrochemical n-doping and p-doping regions and whose stability in the doped states could be extended to higher potential ranges and higher doping levels. In this communication we present a conjugated polymer, namely poly(dimethyldioctyl-quaterthiophene-*alt*-oxadiazole), abbreviated further as PMOThOD (see Scheme 1), which exhibits the highest stability ever monitored to date, in the n-doping–undoping redox region. Moreover, we demonstrate that the stability of the p-doping–undoping redox couple of this polymer can also be significantly improved by the selection of an appropriate electrolytic medium, in this case ionic liquids.

In our search for a processable conjugated polymer, that exhibits high stability in its n-doped state, we adopted a "building blocks strategy". It consists of the synthesis of a specially designed macromonomer which contains oligo(alkylthiophene) subunits and oxadiazole subunits,[4] *i.e* 2,5-bis[5-(3′-octylthien-2′-yl)-3-methylthien-2-yl]-1,3,4-oxadiazole, abbreviated further as BOThMOD, (see Scheme 1). Electropolymerization of this pentamer yields a polymer in which tetraalkyl-quaterthiophene blocks, which assure its solution processing, alternate with oxadiazole subunits, the latter modulating the π-electron density in the conjugated macromolecular chain.

Typically, a thin layer of electropolymerized PMOThOD was deposited onto a platinum wire (diameter 0.5 mm, apparent surface area 0.1 cm^2) from an electrolyte consisting of 0.15 M $TBAPF_6$ in a 2 : 3 v/v mixture of methylene chloride and acetonitrile, with 0.005 M of BOThMOD. Galvanostatic polymerization was performed at a current of 0.1 mA over 24 s (polymerization charge 2.4 mC) in a one-compartment T-type cell containing 0.2 ml electrolyte solution with a platinum counter electrode and an Ag/0.1 M $AgClO_4$/acetonitrile reference electrode (the latter was calibrated *versus* a ferrocene redox couple in the same electrolytic solution giving $E = -0.035$ V *vs.* Fc/Fc$^+$). All potentials are quoted with respect to the reversible Ag electrode. The resulting p-doped polymer was then electrochemically reduced down to $E = 0.0$ V to give the neutral (undoped) polymer. The electrode, with the deposited film, was then transferred to a macromonomer free electrolytic solution of the composition 0.15 M $TBAPF_6$ in sulfolane. Fig. 1a shows consecutive cyclic voltammograms, in the potential range characteristic of n-doping, with negative potential limits decreasing from −2.2 V to −2.7 V. Fig. 1b presents the corresponding Faradaic efficiency, together with the doping level, normalized to a polymer repeat unit consisting of 5 rings (see ESI for the calculation of the doping level†).

First, notice that the new polymer presents significantly attainable higher n-doping levels ($y = 1.85$ per repeat unit or 0.37 per ring) as compared to other thiophene-based polymers.[3] Second, as the film is cycled, the Faradaic efficiency quickly



Scheme 1 Chemical structures of the macromonomer used and the resulting polymer obtained by anodic polymerization.

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† Electronic supplementary information (ESI) available: Method for the calculation of the doping level, EIS curves as a function of potential for n-doping and Faradaic efficiency as a function of potential in both sulfolane and ionic liquid media, determined for p-doping. See DOI: 10.1039/b606320a

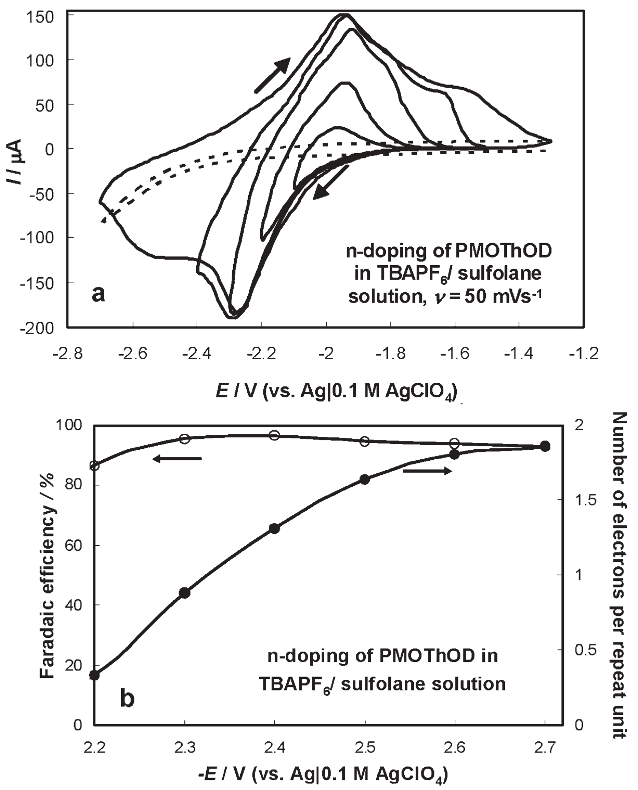

Fig. 1 n-Doping–undoping of PMOThOD. (a) Consecutive cycling voltammograms with the limiting vertex potential decreasing from −2.2 V to −2.7 V (0.15 M TBAPF$_6$–sulfolane; v = 50 mV s^{-1}). (b) Faradaic efficiency and doping level as a function of the electrode potential. Dashed line indicates the background current.

approaches 100%, along with increase in the doping level. No measurable degradation of the polymer is observed even after prolonged cycling. The unusual stability of this redox n-doping–undoping couple enabled us to carry out a complete EIS measurement as a function of potential (see ESI for representative EIS curves†). To the best of our knowledge, this is the first example of a complete EIS characterization of the conjugated polymer n-doping process.

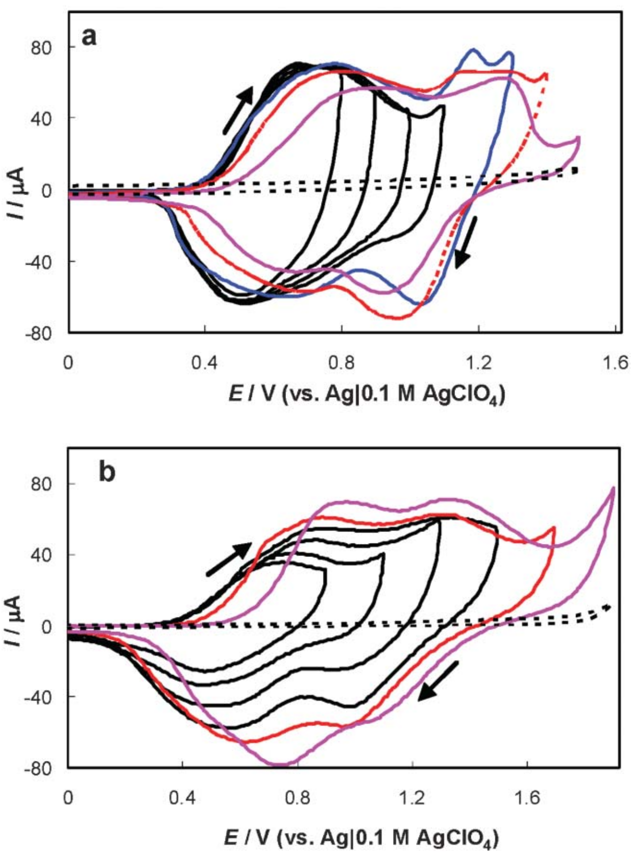

Fig. 2 p-Doping–undoping of PMOThOD. (a) Consecutive cycling voltammograms with the limiting vertex potential increasing from 0.8 V to 1.5 V, obtained in the sulfolane-based electrolyte (0.15 M TBAPF$_6$–sulfolane; v = 50 mV s^{-1}). (b) Consecutive cycling voltammograms with the limiting vertex potential increasing from 0.8 V to 1.9 V, obtained in the ionic liquid-based electrolyte (BMIMPF$_6$; v = 50 mV s^{-1}). Dashed lines indicate the background current.

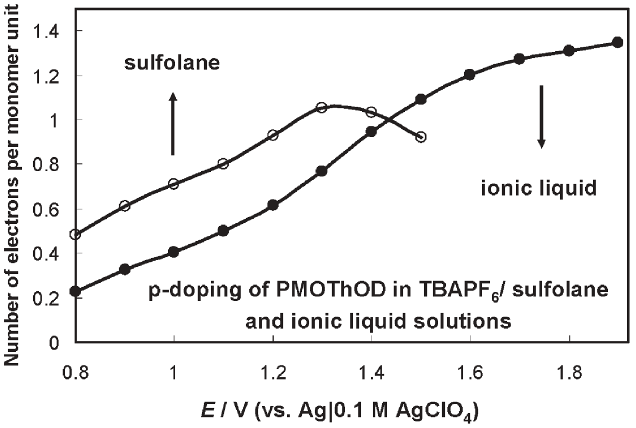

Fig. 3 Doping level as a function of the electrode potential for the PMOThOD p-doped in the sulfolane and ionic liquid-based electrolytes.

The p-doping–undoping process of the new polymer in TBAPF$_6$–sulfolane electrolyte, carried out in a similar manner to the n-doping, *i.e.* by consecutive cycling with the consecutively increasing anodic potential limits from 0.8 to 1.5 V, is shown in Fig. 2a. In Fig. 3 the relationship between the charge introduced during doping and the electrode potential is presented. The maximum doping level (y = 1.05 per repeat unit or 0.21 per ring) is obtained for E = 1.3 V and then it decreases. This value is significantly lower than the maximum n-doping level. Inspired by recent reports on ionic liquids as electrolytes for electropolymerization and electrochemical doping of polyconjugated systems[1,5] we carried out p-doping–undoping studies in an ionic liquid composed of the 1-butyl-3-methyl imidazolium cation and the PF$_6^-$ anion (BMIMPF$_6$). We expected that the extended electrochemical anodic window of this electrolyte would improve the stability of the polymer in the p-doping region. Indeed, this was found to be the case. In Fig. 2b and 3 the consecutive cyclic voltammograms, obtained in the ionic liquid, and the doping charge as a function of the electrode potential are shown, respectively. Note that the doping level steadily increases with increasing the positive potential limit, reaching y = 1.35 per repeat unit or 0.27 per ring for E = 1.9 V. For low p-doping levels (y = 0.20 per repeat unit or 0.04 per ring) the Faradaic efficiency is essentially 100%. It decreases continuously with increasing doping level, being however >90% for $y = 1.25$ per repeat unit or 0.25 per ring (see ESI†).

To summarize, we have demonstrated that the incorporation of π-conjugated electron accepting units (oxadiazole) into the polythiophene backbone leads to a significant improvement of the n-doping–undoping redox stability of the resulting polymer. In effect, we have obtained the most stable, in its n-doped state, polymer reported to date. Moreover, by selecting an appropriate electrolytic medium (an ionic liquid) we have improved the stability of the polymer in its p-doped state. The presented study can be considered as an instructive example of a strategy for the preparation of a stable doped polymer with exceptional doping levels.

Notes and references

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