

New cation-exchange material based on a sulfonated 3,4-ethylenedioxythiophene monomer

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RÉSUMÉ

L'oxydation électrochimique en milieu aqueux d'un monomère de type 3,4-éthylènedioxythiophène fonctionnalisé par un groupement sulfonate permet d'envisager la synthèse d'un nouveau type de polymère hydrosoluble. Afin d'obtenir électrochimiquement en milieu aqueux, un film de polymère d'épaisseur contrôlée contenant des groupements sulfonates, nous avons envisagé de polymériser ce monomère en présence de son homologue non substitué. En partant d'un mélange équimolaire (0.01 mol/l) des deux monomères et en l'absence d'électrolyte support, nous avons synthétisé un matériau possédant des propriétés d'échange de cations. A titre d'exemple, nous présentons brièvement l'incorporation d'un complexe hexaaminé du ruthénium(III) dans un de ces copolymères.

Mots clés : 3,4-éthylènedioxythiophène, monomère fonctionnalisé, échange d'ions.

ABSTRACT

The electrochemical oxidation, in aqueous medium, of a 3,4-ethylenedioxythiophene monomer functionalized by a sulfonate group exhibiting cation-exchange properties, allows the synthesis of a new type of water-soluble material. In order to synthesize in water, by oxidative electropolymerization, polymer films of controlled thickness containing attached sulfonate groups, we have investigated the polymerization of the functionalized monomer in the presence of the unsubstituted one without supporting electrolyte. Using an equimolar mixture (0.01 mol/l) of both monomers, copolymers exhibiting cation exchange abilities have been synthesized. As an example, the easy incorporation of hexamine-ruthenium(III) into one of these copolymers is briefly reported.

Key words : 3,4-ethylenedioxythiophene, functionalized monomer, ion-exchange.

INTRODUCTION

Among the many conjugated heterocyclic polymers that are now studied, poly(alkylenedioxy-substituted thiophenes), such as poly(3,4-ethylenedioxythiophene) denoted EDT, have emerged as a new class of conducting polymers, due to the improved conductivity and electrochemical stability of the resulting materials when compared to others polyheterocycles such as polypyrrole or unsubstituted polythiophenes [1]. In this field, we have prepared a new EDT monomer functionalized by a sulfonate group, denoted EDTS (see figure 1). As previously reported for sulfonate substituted thiophene [2,3], this substituted monomer is only slightly soluble in organic solvents such as acetonitrile but freely soluble in water allowing the synthesis of a new type of water-soluble polymer. In addition, the cation-exchange properties of the sulfonate group may be used to bind cationic species.

EXPERIMENTAL

All electrochemical experiments were carried out in aqueous solutions, under an argon atmosphere, and run with a conventional three electrodes system. The working electrodes were glassy carbon discs ($\phi = 3$ mm) or SnO₂-coated glass (area 1 cm²). Potentials are reported relative to an aqueous SCE. The synthesis of EDTS has been recently described by us [4].

RESULTS

The cyclic voltammogram of an aqueous solution (water + LiClO₄ 0.1 mol/l + EDTS 0.01 mol/l) shows an irreversible wave at 1.2 V on the first scan. On the subsequent scans there is no evidence for the growth of a polymer layer at the electrode. Nevertheless, one can observe that a dark blue colour is developing at the electrode-solution interface. We have attributed this phenomenon to the diffusion of the electrochemical products away from the electrode and suggested that a water-soluble polymer was generated [4]. As a matter of facts, in water, it is impossible to grow, by oxidative electropolymerization, conducting polymer films from the EDTS monomer alone. On this basis, we have investigated in water, without supporting electrolyte, the electropolymerization of EDTS in the presence of the polymerizable unsubstituted EDT. Indeed, this procedure has been successfully used to synthesize copolymers containing attached sulfonate groups from a mixture of regular pyrrole and 3-(pyrrol-1-yl)sulfonate [5-7].

We first investigate the electropolymerization of an equimolar mixture (0.01 mol/l) of both monomers. Under these conditions, the cyclic voltammogram of the mixture shows a broad irreversible oxidation wave at around 1.15 V attributed to the oxidation

of the EDT moieties [4]. Figure 2 shows the evolution of the cyclic voltammograms during repeated potential scans from -1.4 to 1.2V. As the polymerization proceeds, one can see that the polymer peak current intensities are increasing with the number of successive cycles, indicating that a conductive polymer has been generated at the electrode.

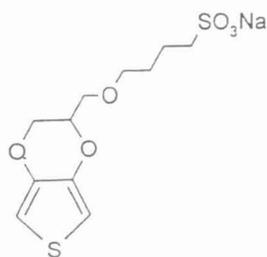


Figure 1 : structure of the sulfonate-substituted monomer (EDTS)

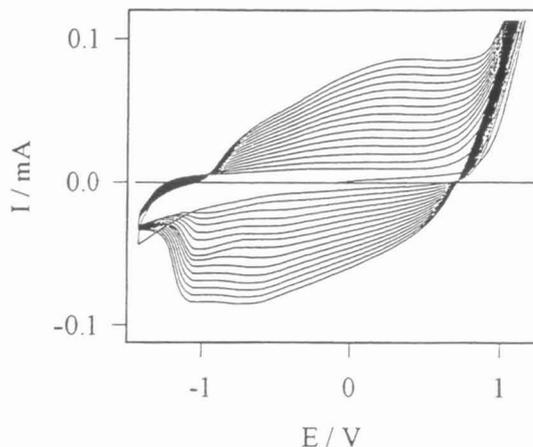


Figure 2 : Electropolymerization of the mixture EDT/EDTS in water at a glassy carbon electrode by repeated scans ; $\gamma = 200 \text{ mV/s}$

A key point is to establish the accurate nature of the deposit. We suggest, as reported for the mixture pyrrole/pyrrole-sulfonate, that the electropolymerization of the EDT/EDTS mixture allows the formation of a copolymer including the two kinds of units. This assumption can be confirmed by investigating the cation-exchange properties of the films. As a rule, if the sulfonate groups are covalently bound to the polymer skeleton, the films should exhibit permanent cation-exchange properties.

In this paper, we will briefly demonstrate that these new materials allow an effective binding of cationic complexes such as hexamine-ruthenium(III). As shown on figure 3, films can be loaded with the ruthenium complex by cycling in a $\text{Ru}(\text{NH}_3)_6^{3+} / \text{KCl-HCl}$ electrolyte. One can see that the amount of trapped ruthenium increases rapidly with the number of scans and reaches a constant level. At that time, the amount of trapped ruthenium can be measured from the charge under the $\text{Ru}^{\text{III/II}}$ wave ($\gamma = 0.02 \text{ V/s}$). For instance, $2.6 \cdot 10^{-9} \text{ mol}$ of metallic complex can be incorporated into a polymer film grown with a polymerization charge of 10 mC. It is noteworthy that this

value is roughly ten times higher than that reported for copolymer of pyrrole and pyrrole-sulfonate synthesized under similar conditions [7]

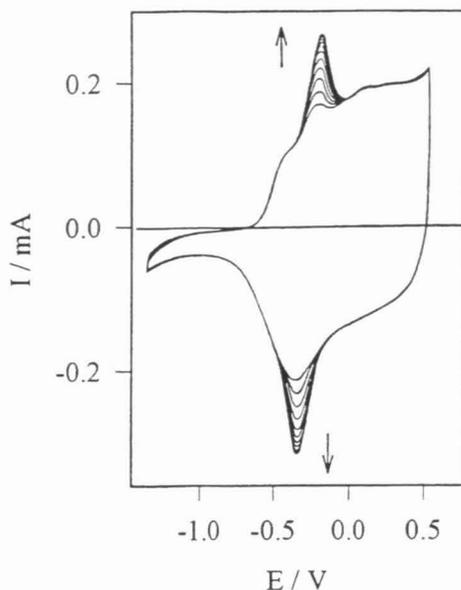


Figure 3 : Loading voltammograms for ruthenium incorporation into a polymer film grown on a glassy carbon electrode ($\phi=3$ mm ; $j=0.5$ mA/cm² ; polymerization charge=25 mC ; $\gamma=200$ mV/s). A 10^{-3} mol/l solution of ruthenium in 0.1 mol/l KCl - 10^{-2} mol/l HCl was used for the experiment.

The present results appears of interest in order to develop new materials able to extract cationic species from aqueous medium. The use of such cation-exchange polymers for analytical applications is currently under investigation.

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