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In situ AFM and conductivity measurements of regioregular oligoalkylthiophenes during electrochemical doping

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Abstract

Electrochemical properties of regioregular oligomers of 3-octylthiophene deposited as a film covering gold or platinum electrode are presented. In situ measurements of conductivity were carried out during oxidation process. These measurements revealed that tetramer is subject of consecutive dimerization reactions whereas hexamer produces a stable cation-radical. AFM in situ observations demonstrate a "life" of the oligomer film driven by phase transitions due to conformational changes of molecules stimulated by applied potential.

Keywords: Polythiophene and derivatives, Electrochemical doping, Conductivity, Self-organization, Atomic force microscopy.

1. Introduction

Substituted oligoalkylthiophenes may be considered as short chain models of regiochemically well defined poly(alkylthiophenes)[1]. Their potential applications in molecular electronics and optoelectronics make them additionally interesting [2]. Electrochemical properties of these compounds not fully recognized yet, may be helpful for explanation of the doping mechanism of polythiophenes. Previous studies were focused on the electrochemical oxidation of thiophene oligomers in homogenous solutions [3] rather than to their electrochemical properties in a solid phase. In the paper we present basic electrochemical properties of monochloro α-substituted regioregular oligooctylthiophenes studied by in situ conductivity measurements, cyclic voltammetry (CV) and electrochemical atomic force microscopy (EC AFM).

2. Experimental

The electrochemical oxidation was carried out in 0.2 M solution of Bu_4NBF_4 in propylene carbonate using Autolab Potentiostat (EcoChemie). Pt wire was used as a counter electrode and Ag/AgCl electrode was a reference electrode. Thiophene oligomers were synthesized according to the procedure described earlier [1]. The solid film of oligothiophenes was deposited by casting from a solution of sexithiophene (ST) in dichloromethane on a microarray electrode for conductivity measurements or on Au foil. NanoScope E (Digital Instruments) with standard electrochemical cell and cantilever of 0.06 N/m spring constant was used in EC AFM measurements.

3. Results

Studies in homogenous solutions have revealed relatively fast consecutive reaction of both, trimer and tetramer after their oxidation to the form of cation radical. This leads to their dimerization in contrast to hexamer which forms a stable cation radical. In the studies presented here we compare the electrochemical properties of quaterothiophene (QT) and ST in solid phase.

3.1. In situ conductivity

Fig. 1 shows the plot of conductivity vs. potential of the electrode taken in situ during two consecutive voltammetric scans recorded for QT film covering a microelectrode. During the first potential cycle the current peak occurs at the potential E_{ox1} = 1.03 V corresponding to the oxidation reaction QT → $QT^{\cdot+}$. Three current peaks are recorded during reverse, reductive scan at E_{red1} = 0.82 V, E_{red2} = 0.6 V and E_{red3} = 0.50 V corresponding respectively to the

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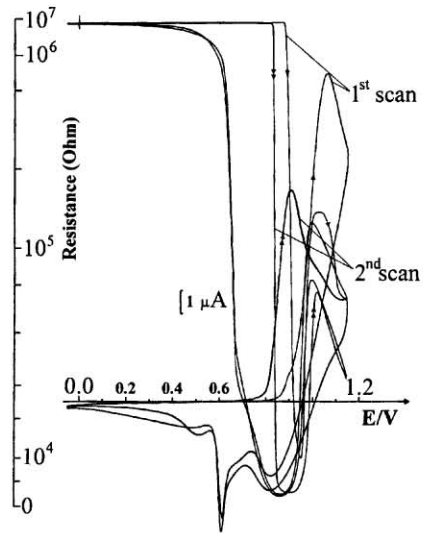

Fig. 1. CV and conductivity of QT film, ν = 10 mV/s

reduction of cation radical, change of the phase structure of the film and deprotonation. As can be seen during the second potential scan, the oxidation of the dimer occurs at lower potential, at E_{ox2} = 0.93 V. The curves of conductivity vs. potential basically reflect the voltammetry and the mechanism of dimerization of QT to octathiophene. Data recorded under the same conditions for ST are shown in Fig.2. There are clear differences in behavior of the QT

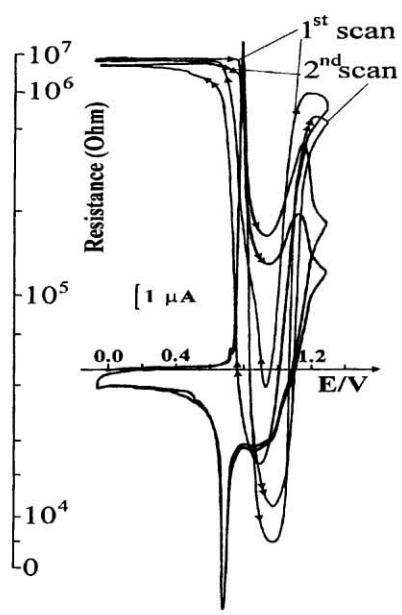

Fig. 2. CV and conductivity of ST film, ν = 10 mV/s

and ST. First, in the time scale of the experiment no dimer is formed as indicated by the equal potentials of the oxidation for the first and the second scan. Also, a very sharp oxidation peak is observed at E_{ox} = 0.83 V with a corresponding reduction peak at E_{red} = 0.64 V. Besides, a conductivity window for the ST film is very narrow. The conductivity line passing through the maximum drops rapidly to very low values, thus the film becomes practically nonconductive. The sharp redox peaks may be a result of drastic changes in a structure of the oligomer film caused by the formation of σ-dimers as observed earlier by Heinze [4]. The loss of conductivity at higher potentials is fully unexpected. From comparison of the conductivity data obtained for ST and QT as well as a regioregular poly(3-alkylthiophene) one could expect of much wider conductivity window than those observed in Fig. 2 or much lower decrease of conductivity.

3.2. AFM results

Formation of σ-dimers or larger molecular assemblies involving stacking, which is stimulated by the applied potential should affect morphology of the film covering the electrode. Fig. 3 shows AFM image taken in the electrolyte solution at potential switched between 0 and 1.2V. It reveals dramatic changes in the ST film structure with corrugations at the level of 1μm. Hills and valleys existing on the surface at positive potential disappear completely at

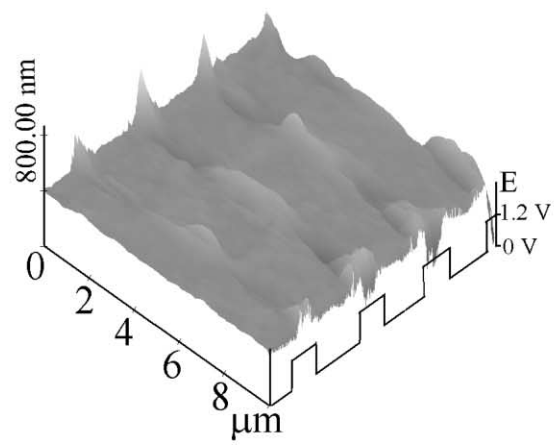

Fig. 3. EC AFM image of ST film at pulsed potential

negative enough electrode polarization. The observed phenomenon of phase transitions due to conformational changes and stacks formation stimulated by applied potential and doping is fully reversible when the film has a sufficient (not less than 1 μm) initial thickness.

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