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Electrosynthesis of valuable conducting polymers from the anodic coupling of β-substituted oligothiophenes

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Abstract

Electrochemical polymerization of thiophene oligomers ($n = 4$) bearing an hexamethylenic ω-methoxy functionalized side chain at the 3-3‴ position of the thiophene rings, was performed in different solvents and electrode surfaces. The degree of polymerization and the electrochemical behaviour of the different electrosynthetized polymers were compared with a polymer obtained by a chemical method. The polymeric films were characterized using cyclic voltammetry, FT-IR, AFM and SEM microscopy.

Keywords: β-Substituted oligothiophenes; Electrodeposition; Spectroelectrochemistry; Polymer films; Conducting polymers

1. Introduction

In the recent years, oligomers and polymers of substituted thiophenes have received considerable attention owing to potential applications of both scientific and economic value. In addition, oligothiophenes with well-defined structures have been studied not only as model compounds for conducting polythiophenes, but also as a new class of functional π-electron systems. A variety of oligothiophenes have been synthesized and reported in literature [1] and their molecular and crystal structures, electrochemical, photophysical, optical and electrical properties have been studied. Polymerization of substituted thiophenes is usually conducted on monomers bearing an alkyl or alkyl-substituted side chain in the 3-position of the aromatic ring, to improve the solubility and workability of the final material thereby enabling the creation of applications that demand processability [2]. Oligomeric or polymeric thiophenic derivatives should be obtained with regiospecific or regioselective synthesis since the configuration regularity of the polyconjugated main chain is an important factor for the electronic delocalization, an undoubtedly essential parameter to be considered in the obtainement of good conducting materials. In fact, one of the main applications for oligo- and polythiophenes has traditionally been their use as electroactive component in light emitting diodes (LEDs) and organic field-effect transistors (OFETs) [3,4]. Recently, a new class of solution-processable high performance polythiophenes based on oligomeric repeating units, including the poly(3,3‴-dialkylquaterthiophene) (PQT), was reported [5,6]. Compared to other regioregular poly(3-alkylthiophene)s, e.g. the poly(3-hexylthiophene), PQT possess an alternating trans-syn distribution of the side chains along the polymer backbone in the stretched out coplanar conformation. It shows higher air stability, and with appropriate substituents, excellent solution processability, which enabled its fabrication into a high-mobility semiconductor layer via solution deposition under ambient conditions. In addition, PQT can also exhibit a liquid crystal phase in a specified temperature range below its melting point [6].

In this work, we deal with a new thiophene oligomer the 3,3‴-di-(6-methoxyhexyl)-2,2′-5′,2‴-5″,2‴-quaterthiophene (Pr) bearing an hexamethylenic ω-methoxy functionalized side chain at the 3-3‴ position of the thiophene rings (Scheme 1).

Oligoxymethylenic side chains, also with the oxygen directly linked to the thiophenic ring, have been widely employed especially for their benefical effects on polymer solubility. In fact, the –O– group increases the polarity of the side chain without any detrimental effects on its mobility, since the steric require-

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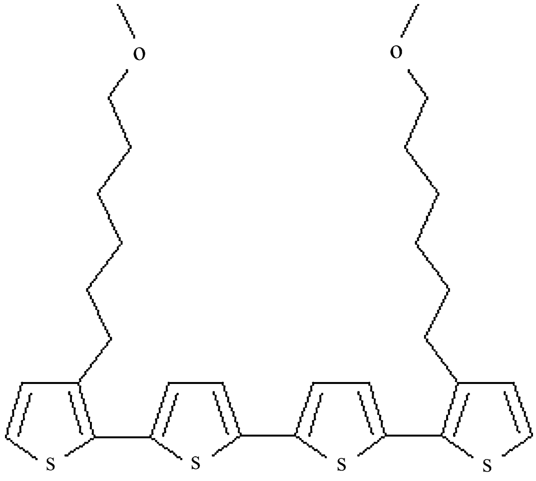


Pr

Scheme 1. Tetramer Pr structure.

ments of the oxygen atom are lower than those of the methylenic groups and the rotation around it is still assured. Generally, polythiophenes functionalized with this kind of chains are soluble in a wide range of solvents and can lead to flexible, thick and homogeneous self-consistent films.

Moreover, for each kind of thiophenic monomer it is important to found the electrical conditions, the solvent system, the kind of electrolyte leading to the polymer with the highest conjugation length and conductivity, that is the best electronic and electrical features. It is in fact well known that the degradation of the polymer may compete with its electrodeposition (polythiophene paradox [7]), especially at high anodic potentials or at low monomer concentrations. In view of the foregoing, a careful investigation of the electrochemical polymerization of the precursor Pr in different solvents, as well as the characterization (electrochemical, spectroelectrochemical and of surface morphology) of the resulting polymers is reported and discussed.

2. Experimental

2.1. Chemicals

The chemical oxidative polymerization of Pr via $FeCl_3$ to the corresponding polymer P* has been conducted as reported elsewhere [8]. Anhydrous acetonitrile (CH_3CN), nitromethane (CH_3NO_2) and dichloromethane (CH_2Cl_2) were from Aldrich, 99.9%/pure, packaged under nitrogen. Chloroform (Fluka, 99.9% pure) was used without further purification. Tetrabutylammonium-hexafluorophosphate ($TBAPF_6$), purchased from Fluka, 99% pure, was dried in a vacuum oven at 50 °C overnight before use.

2.2. Instrumentation

Three-electrode cell geometry was used in all the electrochemical experiments. Different electrodes were used as working electrodes: a Pt disk (0.03 cm^2 geometric area, Goodfellow 99.95% pure), a glassy carbon (GC) disk (0.07 cm^2 geometric area, Goodfellow 99.95% pure) and an indium tin oxide (ITO) coated rectangular glass slide (0.9–2.7 cm). The counter electrode was a Pt wire, the reference electrode was a SCE. All potential values given throughout the paper are referred to this reference. An Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer was used in all the electrochemical measurements. UV–vis spectra were obtained in situ using a Hewlett-Packard 8453 diode array spectrophotometer with a home made electrochemical cell.

Surface roughness and morphology were evaluated by atomic force microscopy (AFM, Scanning Probe Microscope Vista 100, Burleigh Instruments) operating in non-contact mode and by Scanning Electronic Microscopy SEM Zeiss, EVO 50.

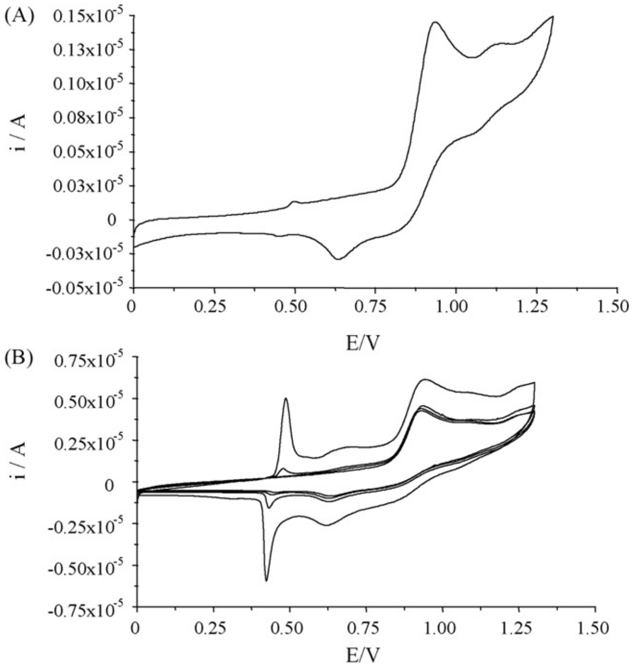
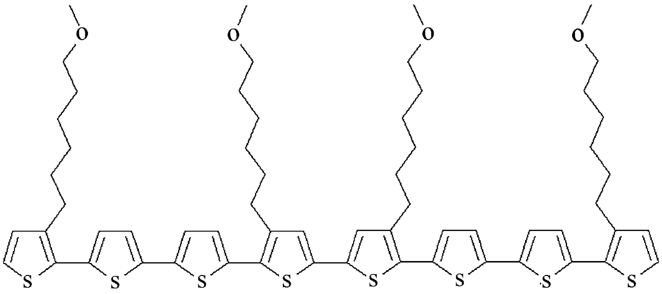


Fig. 1. Cyclic voltammetry on a Pt electrode of a Pr solution ($C^\circ = 0.2$ mM) in CH_3CN (+0.1 M $TBAPF_6$), scan rate = 0.05 V s^{-1}; (A) 1st scan, (B) from 2nd to 25th scans.



2Pr

Scheme 2. Octamer 2Pr structure.