



# Alternating copolymers of thiadiazole and quaterthiophenes – Synthesis, electrochemical and spectroelectrochemical characterization



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## ABSTRACT

A series of copolymers consisting of alternating thiadiazole and unsubstituted or alkyl disubstituted quaterthiophene units, were synthesized by electropolymerization of 2,5-bis(2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (polymer **P1**), 2,5-bis(4'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (polymer **P2**), 2,5-bis(3'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (polymer **P3**), 2,5-bis(3-decyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (polymer **P4**). For comparative reasons **P3** was also obtained via Suzuki coupling of 2,5-bis(5-bromo-2-thienyl)-1,3,4-thiadiazole and neopentyl ester of 4,4'-dioctyl-2,2'-dithienyl-5,5'-diboronic acid. As evidenced by cyclic voltammetry studies the presence of electron accepting thiadiazole unit in the main polymer chain results in an increase of the reductive doping potential of the studied compounds as compared to polythiophene or poly(alkylthiophene). Electrochemically determined electron affinities values were found in the range from  $-3.10$  eV to  $-3.14$  eV, showing a negligible effect of the alkyl substituent on this parameter. To the contrary, the oxidation potential of the studied copolymers strongly depended on the presence and the position of the alkyl group. For **P3** the electron donating properties of the substituents were particularly pronounced leading to a decrease of its oxidative doping potential by 210 mV, as compared to the case of the unsubstituted polymer (**P1**), and the corresponding drop of the ionization potentials from  $+5.75$  eV to  $+5.54$  eV. The presence of a characteristic capacitive plateau's following the reductive and oxidative dopings suggests that both redox reactions are true doping reactions and the synthesized polymers can be transformed either in n-type or p-type conductors. For **P3** and **P4** these findings are additionally corroborated by UV-vis-NIR spectroelectrochemical data which unequivocally show the formation of polaronic/bipolaronic bands upon reductive and oxidative dopings. The analysis of the Raman spectroelectrochemical data obtained for **P3**, supported by theoretical calculations of the vibrational model, leads to the conclusion that the mechanism of the electrochemical doping in this polymers is the same as in poly(alkylthiophene) homopolymers and involves the transformation of the benzoid-like structure into quinoid one. As judged from the redox properties of the synthesized copolymers, **P3** seems to be the most promising candidate for application in such organic electronic devices such as p-channel field effect transistors (FETs), photodiodes (PD) or photovoltaic cells (PC), however its use in air operating n-channel and ambipolar FETs seems to be excluded due to relatively high absolute value of electron affinity.

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## 1. Introduction

Alkyl and alkoxy derivatives of polythiophenes constitute an interesting class of electroactive polymers of potential application

in organic electronics. In their undoped (semiconducting) state they can be used as components of active layers in various electronic devices such as thin film field effect transistors [1–3] photovoltaic cells [4] or photodiodes [5] to name a few. In their conducting (doped) state, in blends with conventional polymers, they are frequently applied as components of transparent electrodes. In particular, alkoxy – substituted polythiophenes usually show appropriate ionization potential (IP) to be used in their doped state [6,7]. IP of alkyl derivatives of polythiophene is in turn slightly too low for their applications as semiconductors in active

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layers of some organic electronic devices, although it can be tuned to some extent by changing the type of the polymer regioregularity [8]. However, all these derivatives suffer from a rather low absolute value of electron affinity (EA), which in some cases is disadvantageous and limits their technological utility in various domains of organic electronics such as photovoltaics, to give a typical example. Appropriate chain engineering may help here. For example, introduction of strongly electron accepting groups into a chain of 2,5-linked thienylene mers leads to a simultaneous increase of IP and |EA|, although electron affinity is more affected. In terms of energy bands approach such a modification of the chain constitution results in narrowing of the polymer band gap and makes the polymer more suitable for photovoltaic cells (PCs) [9] or p-channel field effect transistors (FETs) fabrication [8].

Such macromolecular compounds are in reality copolymers consisting of alternating thiophene (or oligothiophene) and electron-acceptor units. They can be prepared from two comonomers by Stille or Suzuki coupling [8] or by recently developed direct heteroarylation [10]. Alternative approach involves the preparation of a macromonomer which contains both constituents of the desired alternating copolymers. Such macromonomers can then be coupled to yield the corresponding macromolecular compounds. This may involve oxidative polymerization (chemical or electrochemical), Yamamoto coupling of dibromo derivatives, transformation of the macromonomer into a Grignard reagent followed by condensation, Suzuki coupling and other reactions [8].

Molecules consisting of an electron-withdrawing central unit, connected on both sides to bithiophene groups, can be regarded as typical macromonomers for preparing alternating copolymers of oligothiophenes with electron acceptors such as fluorenone [11], tetrazine [12,13], oxadiazole [14], thiadiazole [15] and others. In this paper we describe the investigation of polymers obtained from unsubstituted and alkyl-substituted bis(bithiophene)thiadiazoles, namely 2,5-bis-(2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (**M1**), 2,5-bis(4'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (**M2**), 2,5-bis(3'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (**M3**) and 2,5-bis(3'-decyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole (**M4**). We focus on the synthesis as well as electrochemical and spectroelectrochemical properties of the resulting polymers.

We are interested in this class of semiconductors because copolymers containing thiophene and thiadiazole in the main chain are promising materials for applications in organic electronics or electrochemistry [16,17]. For example, soluble poly(quarterthiophene-*alt*-thiadiazole), containing dioctyl solubilizing groups in the cyclopentadithiophene unit joining the inner thiophene rings, was tested as a component of bulk heterojunction solar cells [18]. Transistors based on alternating copolymers of thiophene and thiadiazole were also reported, showing ambipolar behaviour, which is still rare [19].

## 2. Experimental

Detailed description of the synthesis of macromonomers used for electropolymerization as well as reagents used for chemical preparation of poly[2,5-bis-(3'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole] can be found in *Supplementary Information*.

Electropolymerizations were carried out in a one-compartment electrochemical cell using platinum working and counter electrodes and an Ag/Ag<sup>+</sup> reference electrode. The monomer concentration was  $5 \times 10^{-4}$ – $10^{-3}$  M in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> electrolytic solution. Once the polymerization was completed, the deposited polymer was electrochemically reduced to the neutral state and then repeatedly washed with small quantities of acetonitrile. For UV-vis-NIR studies polymer films were electrochemically

deposited on a transparent ITO electrode, the counter and reference electrodes as well as the electrolyte concentration being the same. Chronovoltamperometric and spectroelectrochemical investigations of the deposited polymers were performed in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN using the same working, counter and reference electrodes as in the case of the electropolymerization process.

UV-vis-NIR spectra were recorded on a Varian Cary 5000 spectrometer whereas the Raman spectra – on a FT Raman Bruker RFS 100 spectrometer using the near-IR excitation line (1064 nm).

## 3. Results and discussion

Oxidative polymerization of macromonomers (electrochemical or chemical) seems to be the simplest method of obtaining alternating copolymers of electron acceptors with oligothiophenes. Terthiophenes with alkyl substituents at the β position of the outer rings readily electropolymerize [20]. The corresponding three-ring compounds containing strongly electron withdrawing central unit, such as dithienyl tetrazines [21,22] or dithienyl oxadiazoles [14] do not electropolymerize. This can be rationalized on the basis of the terthiophene polymerization mechanism. The polymerization of this monomer is initiated by the formation of a radical cation through abstraction of an electron from the terthiophene π-electron system. The electrogenerated radical cations can then polymerize forming C<sub>α</sub>–C<sub>α</sub> linkages. The presence of an electron-withdrawing central unit in dithienyl tetrazines or dithienyl oxadiazoles lowers the π-electron density in the adjacent thiophene rings and makes the formation of the radical cation more difficult. As a consequence the oxidation starts at high potentials leading to unstable radical cations which undergo several consecutive degradation reactions at a rate exceeding the desired polymerization *via* C<sub>α</sub>–C<sub>α</sub> coupling. The same phenomenon is observed upon attempts of dithienylthiadiazoles electropolymerization. Compounds with alkyl substituents are resilient towards electropolymerization. However derivatives containing stronger electron-donating substituents like ethylenedioxy – groups, which can compensate the electron-withdrawing effect of the central unit, can be electropolymerized at relatively low potentials [23].

Fortunately, five ring compounds, containing an electron withdrawing central ring such as 2,5-bis(2,2'-bithiophene-5-yl)-1,3,4-thiadiazoles studied in this research or their oxadiazole [14] or tetrazine [13] analogues, can be electropolymerized to give poly(quarterthiophene-*alt*-thiadiazole)s. This is caused by the fact that addition of an extra thiophene ring to the macromonomer molecule makes the polymerization site (terminal C<sub>α</sub>) more remote from the electron-accepting central group and limits its effect on the π-electron density lowering. Alternatively, similar polymers can be prepared from dibromo derivatives of dithienylthiadiazole and stannylated thiophene or bithiophene by Stille coupling [18,24] In our research we have also used the polycondensation method, choosing however the Suzuki coupling pathway (*vide infra*).

The investigated polymers are depicted in [Chart 1](#). In the subsequent text the following abbreviations will be used: **P1** for poly[2,5-bis(2,2'-bithiophene-5-yl)-1,3,4-thiadiazole], **P2** for poly[2,5-bis(4'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole], **P3** for poly[2,5-bis(3'-octyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole]. Since **P3** was prepared by two different methods – electrochemical oxidation and Suzuki-type polycondensation, the electrochemically synthesized polymer will be denoted as **P3E** and the chemically prepared one as **P3C**. Poly[2,5-bis(3'-decyl-2,2'-bithiophene-5-yl)-1,3,4-thiadiazole] (**P4**) differs from **P1–P3** in this respect that it has a different alkyl substituent (decyl instead of octyl) which is attached to the thiophene ring adjacent to the thiadiazole ring.

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