Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 6692–6697
polymer
www.elsevier.com/locate/polymer

Theoretical investigation of the electronic and optical properties of oligothiophenes upon methyl, thiol, and thiomethyl substitutions

Francesca Costanzo [a,b,*], Domenica Tonelli [a], Giovanni Scalmani [c], Jérôme Cornil [b]

[a] Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy
[b] Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires,
Université de Mons-Hainaut, 20 Place du Parc, 7000 Mons, Belgium
[c] Gaussian, Inc. 340 Quinnipiac Street, Building 40, Wallingford, CT 06492, USA

Received 29 April 2006; received in revised form 6 July 2006; accepted 10 July 2006
Available online 9 August 2006

Abstract

The geometric, electronic, and optical properties of oligothiophenes of 2, 4, 6 and 8 units of head-to-head–tail-to-tail (HH–TT) regioselectivity and substituted by methyl, thiol, and thiomethyl groups have been characterized in their neutral and p-doped states with quantum-chemical calculations derived from semiempirical Hartree–Fock approaches and with the nonempirical valence effective Hamiltonian (VEH) method. Such calculations provide a good insight into the electronic properties measured for electropolymerized chains.

Keywords: Conducting polymers; Quantum-chemical calculations; Oligothiophenes

1. Introduction

In the last 20 years, considerable attention has been devoted to organic conducting polymers as a new class of electronic materials [1]. In part, this interest is based on the observation that materials with a wide range of electronic properties could be obtained through tailored synthesis of new polymers. Due to their large increase in electrical conductivity upon doping [2,3], conducting polymers are promising materials for use in electrochromic devices, sensors, smart-windows, artificial muscles, and photonic devices [1,4].

The electrical, optical, and mechanical properties of conjugated chains critically depend on the chemical structure of their building blocks; the reactivity of the monomer units is also an important factor governing the properties of the resulting polymer and is considerably influenced by the steric and electronic properties of the substituents [5,6]. The impact of steric effects on the structural properties of oligomers and polymers is generally well understood whereas the impact on the electronic properties is often more difficult to assess [7].

In this context, theoretical studies prove successful to allow a better understanding of the electropolymerization mechanisms and of the role played by various experimental parameters; calculations are also helpful to relate the variation of a given parameter to the changes expected in the experimental measurements. It is thus of interest to investigate the changes in the geometric, electronic, and optical properties of conjugated systems when going from the neutral to the oxidized states, and especially the way these properties are affected by various substitution patterns.

Polythiophene (PT) and substituted derivatives represent an important class of conducting polymers [1]. The synthesis of polythiophenes is generally achieved by electrochemical or chemical oxidation of suitable monomers [1]. These polymers are characterized by a high processability achieved via the introduction of substituents in the 3 position [8,9] (see Fig. 1). Among the various derivatives, alkyl-substituted polythiophenes are very attractive materials for the development of high-performance solution processible electronic polymers

---

* Corresponding author. Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy. Tel.: +39 051 2093710; fax: +39 051 2093690.
E-mail address: costanzo@ms.fci.unibo.it (F. Costanzo).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.07.016

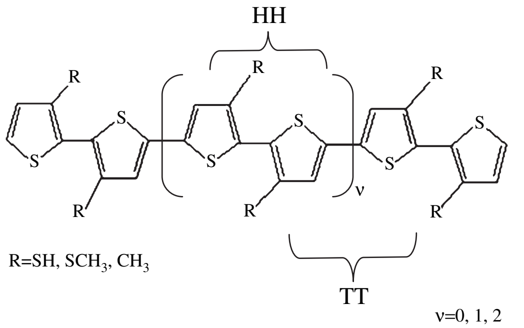

Fig. 1. Molecular structure of the oligothiophenes investigated in this work.

[10,11]. In polyalkylthiophenes, the regiochemistry control is an important factor to be considered since the nature of the coupling controls the structural and electronic properties of the chains. The substituted thiophene rings can be connected via a tail-to-tail (TT) or head-to-head (HH) coupling (see Fig. 1).

Hadziioannou and co-workers synthesized a number of alkylated polythiophenes and showed photoluminescence and electroluminescence color tuning through the variation of the length of the HT sequences between HH connections [12]. They reported blue shifts in absorption larger than 100 nm when increasing the steric hindrance in the polymer backbone. The energies of the absorption and emission maxima were found to scale linearly as a function of the inverse number of thiophene units ($1/n$) between two consecutive HH links. These results clearly demonstrate that the effective conjugation length is limited by the HH links along the polymer backbone. The presence of HH coupling in PTs induces an increase in the torsion angle between the thiophene rings due to steric effects and a loss of conjugation that leads to an increased bandgap (i.e., a blue shift in the absorption and emission spectra) and a reduced electrical conductivity. Regioregularity can thus be exploited as a tool to tune the luminescence properties of PT-based light-emitting diodes [13].

In electropolymerization, the stability of the radical cations generated upon monomer oxidation plays a crucial role in conditioning the degree of polymerization, and hence the length of the π-conjugated backbone. The polymerization can be hampered by: (i) the high reactivity of the radical cations which may undergo rapid reactions with solvent or electrolyte species to yield low molecular weight products rather than to polymerize in chain propagation reactions [14]; and (ii) the high stability of the reacted species which can diffuse away from the electrode to form oligomers in solution.

Unsubstituted thiophene and 3-alkylthiophene yield sufficiently reactive radical cations to form highly conjugated polymers; the synthesis should be further facilitated by the introduction of π-electron donating groups such as alkoxy and thioalkyl substituents that decrease the oxidation potential of the monomer units, thus increasing the energy of their highest occupied molecular orbital (HOMO) level. However, alkoxy and thioalkyl-substituted thiophenes cannot be easily electropolymerized and are usually obtained by chemical polymerization [15]. High-quality polymers were obtained only when 4-4′-dialkoxy-2-2′-bithiophene or 4-4′-dimethylthio-2-2′-bithiophene were used as starting monomers [16]. In a previous paper, we have reported the successful synthesis of poly[4-4′-bis(butylsulphanil)-2-2′-bithiophene] starting from a dimer unit both by chemical and electrochemical methods [17,18] (see the chemical structure in Fig. 1). In addition to the thermochromic, solvatochromic, and electrical properties [18], the electrochemical properties of the electrogenerated polymers were investigated in depth, with a particular attention paid to the charge–discharge processes and to p- and n-doped states via spectroelectrochemistry [17].

According to the generally accepted model, charges injected in conjugated polymers with a nondegenerate ground state relax under the form of self-localized polarons, which may couple to yield spinless bipolarons [19,20]. The terminology of polarons and bipolarons used in solid-state physics corresponds in chemical terms to radical cations and dications, respectively; they can be generated upon chemical [21,22], photochemical [23], and electrochemical oxidation/reduction [24] of the neutral molecules. The properties of long conjugated chains can be derived in the very first approximation from linear extrapolation to infinite chain length of the data obtained for the corresponding oligomers [25]. The formation of charged defects (polarons and bipolarons) in nondegenerate ground-state polymers deeply modifies their one-electron structure; electronic levels move inside the forbidden gap and induce the appearance of new subgap absorption features in the optical absorption spectra. Two subgap transitions are observed for isolated polarons while a single peak prevails in the presence of isolated bipolarons [26].

As a follow-up of the electrochemical study previously performed [17], the present work aims at investigating at the theoretical level the modifications upon p-doping in the geometric and optical properties of oligothiophenes built by repeating from 2 to 4 bithiophene units in an HH configuration (see Fig. 1). The impact of substitution by thiol and thiomethyl groups has been also investigated in comparison to methyl substituents.

2. Theoretical methodology

The geometries of neutral and charged oligomers containing 4, 6, and 8 rings have been optimized with the semiempirical Hartree–Fock Austin Model 1 (AM1) method [27], which is parameterized to reproduce the geometry and heat of formation of organic molecules in their ground state. The AM1 approach has also been shown to provide a good description of the torsional potential energy curve in bithiophene compared to that obtained with sophisticated *ab initio* calculations [28,29]. The geometry optimizations are performed on isolated molecules, thus neglecting the effect of counter-ions for charged oligomers (both singly and doubly oxidized molecules). The restricted open shell Hartree–Fock (ROHF) formalism has been adopted in the case of singly charged oligomers, as in earlier works [30,31]. The calculations have been carried out on oligothiophenes containing 4, 6, and 8 rings (denoted as 4T, 6T, and 8T in the following) substituted