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Novel conducting polymers based on thieno[3,2-b]indoles: Electrochemical properties and molecular structure ☆

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Abstract

The electropolymerization of thieno[3,2-b]indole (TI), 6-methoxythieno[3,2-b]indole (MeOTI) and *N*-methylthieno[3,2-b]indole (*N*-MeTI) was performed in organic solvents with the aim to prepare new conducting materials. TI and MeOTI anodic oxidation led to the formation on platinum electrodes of electroactive polymer films that were characterized by cyclic voltammetry, quartz microbalance, MALDI-TOF, FT-IR spectroscopy and scanning electron microscopy. MALDI-TOF mass spectrometry indicates that films are mainly constituted of short-chain oligomers. FT-IR studies and molecular orbital calculations show that polymers present coupling occurring on the thiophene and phenyl rings. The great differences observed between the electrochemical and physicochemical properties of the various polymer films were mainly induced by the location and electron-donating effects of substituents in the different monomers. Substitution influenced not only electroactivity, chain length and film morphology, but also the electropolymerization sites.

Keywords: Electrosynthesis; Poly(thieno[3,2-b]indoles); Conducting polymers; Electroactivity properties

1. Introduction

Chemistry and electrochemistry of conducting polymers have considerably developed since Diaz et al. [1] demonstrated in 1979 that electroactive polypyrrole films could be deposited on platinum electrode using monomer electrooxidation. A large number of studies have been devoted to conjugated conducting polymers and oligomers derived from pyrrole, thiophene or aniline and their substituted derivatives because of their potential applications in electronic components, non-linear optics, optical switches, electroluminescent diodes and anticorrosion protection [2–10].

Semiconducting, substituted oligothiophenes have been particularly investigated, due to their aromatic structure, interesting physicochemical properties and air stability [11–13]. Until now, monomers used mostly as precursors for oligothiophene preparation were simple, substituted thiophenes. In contrast, much less studies have concerned conducting polymers obtained by polymerisation of fused heterocycles containing one and more thiophene units or their dimers [12,14–16]. Formation of these polymer films occurred at lower oxidation potentials than polythiophene because of the

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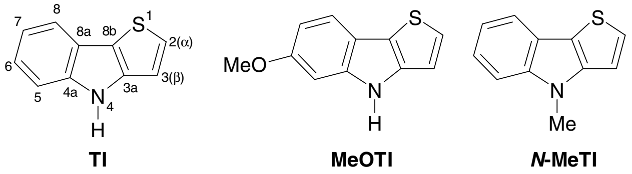

Scheme 1.

increased conjugated character of monomers. Moreover, several interesting applications, outgoing of fused heterocycles-based materials, including thin film transistors [17] and photoluminescent systems [15] have been described.

Recently, we have shown that benzothiophenes and certain diheteropentalenes can be employed as a core for new ferroelectric liquid crystals [18–20] and can also lead to conducting oligomers with interesting electrochemical and luminescent properties [21,22]. For example, it was found that oligomers obtained by thienobenzothiophenes electropolymerization possessed a strong fluorescence occurring in the visible, with dramatic red shifts of the emission maxima ($\Delta\lambda \approx 90$–110 nm) and an important increase of fluorescence intensity relative to the corresponding monomers [21]. These remarks underline the interest of synthesising new polymer films, based on fused benzothiophene derivatives as monomers. In particular, it can be expected that such materials will have important potential applications in the development of luminescent devices.

The aim of our work was to extend the results obtained previously in thienobenzothiophene studies to another type of 1,4-diheteropentalene system. In this article, we describe in detail the electrosynthesis of three new conducting polymers prepared from thieno[3,2-*b*]indole (TI), 6-methoxythieno[3,2-*b*]indole (MeOTI) and *N*-methylthieno[3,2-*b*]indole (*N*-MeTI) (Scheme 1). The electrochemical and physicochemical properties of these polymers were studied and the molecular structure was determined by MALDI-TOF, scanning electron microscopy and FT-IR spectroscopy. In addition, molecular orbital calculations were performed on the basis of a radical-cation electropolymerization mechanism, in order to confirm the interpretation of experimental data.

2. Experimental

2.1. General methods

The electrochemical experiments were carried out in a single compartment three-electrode glass cell at room temperature [22 (±1) °C]. The working electrode was a Pt disc (0.196 cm^2) and the counter-electrode was a Pt grid. The potentials were measured relative to an Ag/AgCl electrode. Electrochemical experiments were realized on a EG&G Princeton Applied Research model 362 potentiostat/galvanostat, and electrochemical curves were recorded on a Kipp&Zonen BD90 *x*–*y* recorder. The supporting background electrolytic solution was either acetonitrile (Prolabo R.P. Normapur™) containing 10^{-1} M lithium perchlorate (Acros) or dichloromethane (Prolabo Rectapur™) containing 10^{-1} M tetrabutylammonium perchlorate (Fluka). Unless otherwise mentioned, polymer characterisation was performed on samples prepared in 10^{-2} M monomer solutions and under optimal polymerisation conditions (see Section 3.2).

Quartz microbalance studies were carried out in a glass cell using an EG&G Seiko QCA917 frequency analyzer and an EG&G Princeton Applied Research model 273A potentiostat/galvanostat, coupled to Ecorr (Corrosion analysis software). The anode was a platinum-coated quartz (area = 0.2 cm^2, 1.12×10^{-9} g Hz^{-1}).

The matrix assisted laser desorption/ionisation-time of flight (MALDI-TOF) mass spectra of polymer films were obtained on a Voyager Elite (Perseptive Biosystems, Framington, MA, USA) mass spectrometer. 2,5-Dihydroxybenzoic acid was used as a matrix.

The scanning electron microscopy (SEM) photos were made on a S 440 model Leica instrument equipped with a tungsten filament, using a four sector detector for secondary and retro-diffused electrons.

All spectra were recorded on a FT-IR Magna 860 spectrometer (Nicolet Instrument Corp. Madison, WI, USA) at 2 cm^{-1} (monomers) and 4 cm^{-1} (polymers) spectral resolution. Transmittance spectra of the monomers were measured in KBr pellets using a standard DTGS detector and collecting 100 scans. Plates of electrodeposited polymers were analysed by IR-Reflexion Absorption Spectroscopy (IR-RAS), using a 80° incidence angle accessory and a high sensitivity Mercury Cadmium Telluride (MCT-A/4000-625 cm^{-1}) detector. All spectra were baseline corrected using OMNIC internal software and were presented in a non-smoothed form.

Molecular orbital calculations were performed for all monomers in the framework of the Density Functional Theory (DFT) method. The geometry of neutral species and radical-cations was optimised without symmetry constraint (convergence criteria = 10^{-4}), using the three-parameter functional of Becke (B3LYP) [23] and the 6-31G(d) basis set [24]. Radical-cations were treated as open shell systems (uB3LYP). All DFT calculations were carried out with the Gaussian 98 suite of programs [25]. The optimised geometries and infrared frequencies were also calculated using BP86 functional program [26,27]. No scaling factor was applied to match the calculated infrared wavenumbers with experimental ones.