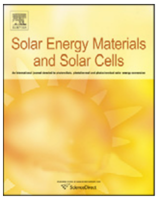
Solar Energy Materials & Solar Cells 99 (2012) 101–108

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Role played by chain length and polarity of n-substitutents in electrochromic polymers from the tri-heterocyclic monomer pyrrole-thiophene-pyrrole

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ARTICLE INFO

Available online 16 August 2011

Keywords:
Electropolymerization
Charge trapping
Electrochromism
Side chains

ABSTRACT

Conjugated polymers play an increasingly relevant role in a large number of technological applications (organic solar cells, electrochromic devices, OLEDs). Such preeminence is as much a consequence of their peculiar optoelectronic properties as it is of the possibility to be solution processed. In fact, although unfunctionalized conjugated polymers are almost insoluble, an extensive functionalization with suitable solubilizing chains conveys the required solution processability as well as good adhesion properties with respect to a number of different substrates. The chemical nature (polar, nonpolar) length and branching of the chains do not sizably influence the electronic properties of the polymer, but plays a major role in the solid-state morphology. We here present a systematic study on the role of the solubilizing chains in the overall performances of a series of electropolymerized 2,2′-{thiene-2,5-diylbis[(*E*)ethene-2,1-diyl]}bis(1*H*-pyrrole) derivatives. In particular, we show how the nature and length of the chain play a relevant role on the electrochemical behavior of the polymers. Our results can be rationalized in terms of lateral chain induced noncovalent interactions. Finally, the spectroelectrochemical properties of some of these polymers could be of interest for NIR-operating variable optical attenuators.

1. Introduction

Intrinsically conducting polymers (ICP) play a key role in most of the leading technological applications of organic materials. To name but a few research areas, ICP are currently successfully employed in commercially available organic light emitting diodes (OLEDs) [1–3], electrochromic devices (ECDs) [4–6], organic photovoltaics (OPVs) [7–10] and organic field effect transistors (OFETs) [11–14]. This remarkable success is the consequence of a few ICP distinctive characteristics: wide tuning of spectroelectrochemical properties, low cost, compatibility with plastic substrates and favorable mechanical properties. One of the most attractive ICP characteristics is the possibility to be processed from solution either by spin coating (in the case of batch processes) or by blade coating (thus enabling roll to roll continuous deposition). Solution processing holds promises for dramatic cost reduction and very often counter balances some on the ICP weaknesses such as a limited stability [15]. The vast majority of unfunctionalized ICP (such as polypyrrole, polythiophene, polyparaphenylene vinylene) are almost completely insoluble in common organic solvents [16]. The aforementioned solution processability is the result of an extensive functionalization process aimed at the introduction of at least one, but often more, solubilizing chains per repeating unit. The literature reports a wide variety of such chains, differing in terms of length and branching and/or by the presence of polar groups (most frequently ethers or esters groups) [4]. The increase in solubility is not the exclusive outcome of the functionalization process. In fact, although the optoelectronic properties of the functionalized polymers do not significantly differ from those of their parent pristine derivatives, the solubilizing chains play a major role in the solid-state morphology. This holds true not only for single component films but also for blends (as in the case of organic photovoltaics), as the number, nature and length of the lateral chains influence interfaces as well as interphases [17,18].

On this respect, polymeric electrochromic materials [19,20] are particularly instructive as the final device performances critically depend upon the functionalization process. In this case in fact the conjugated material, deposited as a thin solid film, undergoes a redox reaction, which is connected with a major variation of volume. This effect is both the consequences of the

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doi:10.1016/j.solmat.2011.07.024

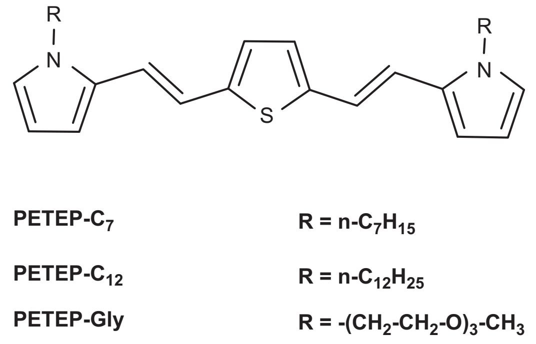

Fig. 1. Structures of 2,2′-{thiene-2,5-diylbis[(*E*)ethene-2,1-diyl]}bis(1-heptyl-1*H*-pyrrole) (**PETEP-C$_7$**), 2,2′-{thiene-2,5-diylbis[(*E*)ethene-2,1-diyl]}bis(1-dodecyl-1*H*-pyrrole) (**PETEP-C$_{12}$**), 2,2′-{thiene-2,5-diylbis[(*E*)ethene- 2,1-diyl]}bis(1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-1*H*-pyrrole) (**PETEP-Gly**).

alteration (quinoidal distortion) in the conjugated structure of the polymer and of the introduction/removal of counterions upon oxidation/reduction. The role of the solubilizing chains is thus critical on at least three respects: (a) the adhesion towards the substrate (usually a transparent conductive oxide such as indium tin oxide ITO or fluorine doped tin oxide FTO); (b) the morphology obtained after deposition (either chemical or electrochemical); (c) the interaction with the counterions balancing the charge in the oxidized form. The chains will also play a role during the polymerization process. The monomer reactivity will in fact also depend on the size/nature of the solubilizing residues.

Aim of the present paper is the evaluation of the role of the solubilizing chains in the overall electrochromic performances of a series of electropolymerized 2,2′-{thiene-2,5-diylbis[(*E*)ethene-2,1-diyl]}bis(1*H*-pyrrole) derivatives (Fig. 1).

We chose the electropolymerization as the preferred deposition process because this technique enables a higher degree of control in terms of film thickness and homogeneity. Some of us introduced the 2,2′-{thiene-2,5- diylbis[(*E*)ethene-2,1-diyl]}bis(1*H*-pyrrole) structure in the past [21,22] aiming at the characterization of its oxidized state conductivity. So far we only employed methyl substituted pyrrole rings and we did not characterize the polymer electrochromism. Obviously, the polymer we previously obtained was completely insoluble in common organic solvents [23]. We now describe the functionalization with two alkyl chains of different length, one with an odd number of carbon atoms and the other with an even number: n-heptyl and n-dodecyl. As a polar chain, we will exploit a *ter*-glycolic residue.

We will discuss how the nature (polar, nonpolar) and length of the chain has a major influence on the electrochemical behavior of the polymers. We will rationalize our results in terms of the different noncovalent interactions induced by the lateral chain depending upon their chemical structure. Finally, we will show how the electrochromism of some of the polymers we obtained could be exploited in the preparation of NIR-operating fast variable optical attenuator (VOA) [24,25], devices that are commonly used to compensate power variations in the signal caused by other components of photonic circuits.

2. Experimental details

2.1. Materials

The starting materials were purchased from Aldrich and used without further purification unless otherwise stated. All reactions were carried out under a nitrogen atmosphere. NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 MHz for ^{1}H.

2.2. Electrochemical polymerization, electrochemical and spectroelectrochemical characterization

Tetrabutylammonium perchlorate and acetonitrile, both anhydrous, were purchased at Aldrich Chemicals and stored in a glove box fed with Ar gas. The electrolyte solution (TBAClO$_4$ 0.1 M in MeCN, from now on TCAN01), monomer solutions (0.01 M in TCAN01), and calibration solution (Ferrocene 0.001 M in TCAN01), were prepared and stored in the glove box. The experiments were performed in a three-electrode (one compartment) glass cell using a 1×2 cm^2 FTO-glass (15 Ωsq) as working electrode (WE, working area ~1 cm^2), a platinum foil/mesh/wire as counter electrode (CE), and Ag/AgCl as the quasi reference electrode (QRE). During polymerization we worked also with a three electrodes (two compartments) cell with separated counter electrode. QRE was calibrated (cyclic voltammetry 0.8–0.1 V 50 mV/s) before all analysis in a three electrodes cone cell (WE Au pin, CE Pt foil) filled with calibration solution. All electrochemical measures are reported vs. Fc/Fc$^+$ potential and cathodic current was considered negative. Working electrode FTO-glass substrates were cleaned before using by sonication in detergent, sonication in acetone, rinsing in EtOH, rinsing in pure water and finally drying in air. Electrochemical deposition and analysis were performed with a EG&G Princeton Applied 2273 potentiostat/galvanostat, all the deposition and the electrochemical characterization were performed in glove box.

HOMO and LUMO values were calculated from the onset of oxidative and reductive CV waves, respectively. The potential values of 4.6 ± 0.2 eV for NHE vs. vacuum [26] and of 0.63 eV for Fc/Fc$^+$ vs. NHE [27] were used in potential/energy conversions.

The spectroelectrochemical measurements were performed using the same cell arrangement used for electrochemical characterization assembled in a sealed optical cuvette. A Jasco V-570 UV–vis-near IR, coupled with a EG&G Princeton Applied model 273 potentiostat/galvanostat, was used as spectrophotometer in the NIR/visible spectra ($1100\geq\lambda\geq340$ nm) under several applied potentials. The potential was applied before the spectrum acquisition for a time long enough to drive the system to a stationary state and it was maintained during the measurements.

2.3. Synthesis

2.3.1. General procedure

A solution of pyrrole derivative and 2,5-thienediyildi(methylene)bis(diethylphosphine)dioxide [28] in anhydrous THF was stirred under nitrogen at room temperature for 20 min. *t*-BuOK was added portion wise and the solution was stirred overnight at the same temperature. The reaction mixture was poured into water and extracted with CH$_2$Cl$_2$. The organic phase was dried over Na$_2$SO$_4$ then vacuum evaporated to obtain an orange oil that was purified by column chromatography (CC).

2,2′–{thiene-2,5-diylbis[(*E*)ethene-2,1-diyl]}bis(1-heptyl -1*H*-pyrrole)-PETEP-C$_7$.

Using general procedure, **2a** [29a] (1.00 g, 5.58 mmol), [2,5]-thienediyildi(methylene)bis(diethylphosphine)dioxide (1.07 g, 2.79 mmol) and *t*-BuOK (0.674 g, 6 mmol) were stirred in THF (30 mL) overnight. CC (Silica Gel, Hex/EtOAc 9:1) afforded **PETEP-C$_7$** as a yellow oil (625 mg, 48%).

^{1}H NMR (CDCl$_3$) δ: 7.04 (d, J=15.65, 2H), 7.02 (d, J=14.10, 2H), 6.78 (m, 4H), 6.48 (m, 2H), 6.08 (m, 2H), 4.05 (t, J=7.05, 15 Hz, 4H), 1.71 (m, 4H), 1.32 (m, 12H) and 0.89 (m, 6H).