



Synthesis and electrochemical and optical characterization of poly(3-octadecylthiophene)

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ABSTRACT

The 3-octadecylthiophene has been synthesized and characterized by FTIR, UV–vis and ¹H and ¹³C NMR. The correspondent polymer, the poly(3-octadecylthiophene) (PODT) has been chemically and electrochemically synthesized. The obtained polymer is soluble in common organic solvents, such as chloroform, tetrahydrofuran and toluene. IR and NMR spectra analysis confirm its regio-regularity. The electrochemical properties studied by cyclic voltammetry of PODT electrochemically synthesized were characterized by a semi-reversible behavior with one anodic peak at 0.96 V and one cathodic peak at 0.77 V vs. Ag/AgNO₃. Spectroelectrochemistry and optical properties, such as optical absorption and photoluminescence (PL) were studied at different temperatures for the PODT chemically synthesized. Spectroelectrochemical results clearly indicate the polaron formation. The results obtained from the analysis of the dependence on temperature of the optical properties of the PODT casting film corroborate the high regio-regular structure of the chains.

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1. Introduction

Conducting polymers are an interesting class of materials which may find application in a variety of important technological sectors. Organic semiconductors, as these materials are also known due to the fact that they have been the subject of active research by their conducting properties for over last two decades. Some of them are emerging as light-emitting displays and printable electronic circuits [1a]. Exciting results have been already obtained with both polymer-based light-emitting diodes and organic transistors [1b]. The particular advantages of these polymeric systems: are that they are cheapness, easy synthesis and manipulation for incorporation into several devices [1b]. Another important advantage of these organic materials is the possibility of ordering their thin semi-crystalline layers, which support the mobile high charge-carrier (electron and hole) that are essential to guarantee its electronic performance.

Photophysics of conjugated polymers strongly depends on chain packing, but the nature of inter-chain excited states is still under debate and their electronic properties are poorly understood [2].

Polythiophenes are important materials for electronics devices and non-linear optical applications [2], showing attractive performance in optoelectronic devices such, e.g. micro-cavity laser devices and plastic solar cell. The relatively high stability and the possibility of tuning the properties by molecular engineering make the polythiophenes one of the most versatile classes of conjugated polymers [3]. Since poly(3-alkylthiophenes) were first reported to be soluble and conducting, soluble polythiophenes with flexible side chains have attracted considerable attention [4].

This work is dedicated to the chemical synthesis of the monomer 3-octadecylthiophene (ODT), the chemical and electrochemical synthesis of poly(3-octadecylthiophene) (PODT) and the study of spectroelectrochemical and optical properties of poly(3-octadecylthiophene) films, in particular, the spectroelectrochemical properties as a function of the imposed potential and the UV–vis absorption and photoluminescence (PL) as a function of the temperature.

2. Experimental details

2.1. General methods—synthesis

¹H and ¹³C NMR spectroscopy was performed at 200 MHz on a Brücker DPX 200 advance spectrometer, using solvents as internal references. Chemical shifts (δ) are reported in ppm down-

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¹ “In memoriam”.

field from tetramethylsilane (TMS) or CDCl_3 (7.24 ppm; solvent unless otherwise indicated) for ^1H and CDCl_3 (77.0 ppm) for ^{13}C NMR spectra unless otherwise noted. Reactions were monitored by thin layer chromatography using commercial precoated aluminum sheets (0.2 mm layer thickness, 20 cm \times 20 cm, silica gel 60 F254(Merck®)).

The infrared spectra were obtained in a spectrophotometer Mattson Galaxy FTIR 3000, with HP Color Pro Register. Films of samples were formed on KBr window support. The monomer were deposited directly on KBr window, and the polymer were deposited by solvent casting or solution (>0.5 mg in 0.5 mL CHCl_3) and quickly dried at room temperature. All reagents were obtained from commercial (Aldrich®) and used as received unless otherwise noted. All solvents were dried and distilled before used.

2.2. Chemical synthesis

In a flask fitted with reflux condenser, 4.0 g of magnesium (0.16 mol L^{-1} ; 15% of excess) and 50 mL of dry ethyl ether were added under nitrogen atmosphere. 20 mL of *n*-octadecylbromide (0.14 mol L^{-1}) in 20 mL of dry ethyl ether were added dropwise about 3 h under stirring and also under nitrogen. The intermediate alkylmagnesium bromide was stirred for 4 h. In a second flask fitted to reflux condenser (under nitrogen atmosphere too), 0.116 g of $\text{NiCl}_2(\text{dppp})$ (21.3 mmol), 90 mL of dry ethyl ether and 13.3 mL of 3-bromthiophene (0.14 mol L^{-1}) were then added under. Alkylmagnesium bromide previously prepared was added dropwise, under stirring. The final solution was stirred about 18 h at room temperature. After the end of the reaction an aqueous saturated solution of NH_4Cl was added. The aqueous phase was extracted with ethyl ether, the organic phase was neutralized with an aqueous saturated solution of NaHCO_3 , dried with anhydrous K_2CO_3 and the solvent was removed under low pressure.

The polymerization to obtain the PODT was carried out by procedures described elsewhere [5]. The monomer 3-octadecylthiophene (0.05 mol L^{-1}) was dissolved in chloroform. A suspension of FeCl_3 (0.2 mol L^{-1}) also in chloroform was added with magnetic stirring at room temperature under a nitrogen atmosphere to the monomer solution for 8 h. When the addition was complete, the mixture was stirred for 16 h. The reaction mixture was poured into methanol; the solid was filtered off and washed with more methanol. The purification was carried out by Soxhlet extraction with methanol. The yield of polymer was 82%, and the molecular weight was determined by GPC with tetrahydrofuran (THF) as solvent and using polystyrene standards resulting $\text{Mw} = 52.700 \text{ g mol}^{-1}$, with a dispersion index of 1.9.

2.3. Electrochemical growth experiments

The electrochemical experiments were carried out in a typical three electrode cell, a disk platinum electrode ($a = 8 \times 10^{-3} \text{ cm}^2$) was used as the working electrode, a platinum wire as the counter electrode and a Ag/AgNO_3 as the reference electrode. The electrochemical experiments were conducted using an AUTOLAB (PGSTAT30) potentiostat-galvanostat controlled by GPES 4.9.

Initially the redox profile of the monomer was studied in nitrobenzene solution containing $1 \times 10^{-2} \text{ mol L}^{-1}$ of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) at 5°C , under nitrogen atmosphere. Cyclic voltammeter were recorded at high scan rate (100 mVs^{-1}), and low monomer concentration ($2 \times 10^{-2} \text{ mmol L}^{-1}$) in order to avoid polymer formation. Polymeric films were galvanostatically (2 mA cm^{-2} , 60 s) obtained using the same solution for the monomer at low temperature. After the polymerization were obtained films with thickness (L) proximally equal to 0.3 μm . The thickness were estimated employing the rela-

tion $L = Q_p \times F$, where Q_p (mC cm^{-2}) is the deposition charge and $F = 2 \times 10^{-4} \text{ (cm}^3 \text{ mC}^{-1})$ [6]. After polymerization, the films were rinsed with acetonitrile (CH_3CN) and transferred to one cell containing $1 \times 10^{-1} \text{ mol L}^{-1}$ $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ where the redox profile of polymeric films was recorded.

2.4. Spectroelectrochemical characterization

The PODT films were obtained, upon ITO coated glass (Hoya, MERCK) (0.5 cm \times 4.0 cm), by two ways: prepared by solvent casting from the chemically synthesized PODT (30 mg into 3 mL of toluene) and by galvanostatic deposition (2 mA cm^{-2} , 300 s). After the deposition, the films were rinsed with CH_3CN , dried, and insert in electrochemical cell.

The electrochemical cell was assembled in a standard quartz cuvette (1 cm \times 1 cm) using ITO as working electrode, a Pt wire was used as counter electrode and an Ag wire as a quasi-reference (Ag/Ag^+). The cuvette was filled with the supporting electrolyte solution ($10^{-2} \text{ mol L}^{-1}$ of Bu_4NBF_4 in CH_3CN).

Spectroelectrochemical experiments were performed on electrochemical cell that was inserted in the spectrophotometer UV SOLUTION 2010 HITACHI and connected to a FAC-200 A potentiostat/galvanostat HITACHI.

The films were stabilized between -1.2 and $+1.2 \text{ V}$ at increasingly positive potentials for 2 min, after each stabilization of the current signal one absorption spectra was recorded. All experiments were performed at room temperature and one quartz cuvette containing the same solution and the uncoated ITO electrode was placed as the reference beam.

2.5. Optical experiments

Polymer solution was prepared by dissolving 30 mg of PODT into 3 mL of toluene solvent and stirred during more than 4 h. Solvent cast polymer films were formed on glass and dried at room temperature. Photoluminescence spectra of PODT film were measured at different temperatures with the sample inside an immersion cryostat under vacuum, in order to avoid any photo-oxidation effect. A CW Ar-ion laser emitting at 514 nm was used as the excitation source and the laser power was 660 μW . The PL emission was collected in a backscattering configuration, focused into a SPEX 0.75 m monochromator, and detected by a Gallium Arsenide (GaAs) photomultiplier tube.

3. Results and discussions

3.1. Physical-chemistry characterization

The 3-octadecylthiophene, is a white solid and was distilled at 209°C (10 mmHg). The chromatography analysis showed 83.2% of purity. The ^1H NMR spectra ($\delta_{\text{relative TMS}}$, CDCl_3) shows signals in the following ranges: 7.24–7.21 ppm (1H, m, $\text{H}\beta'$); 6.94–6.90 ppm (2H, m, $\text{H}\alpha$, $\text{H}\alpha'$), 2.65–2.57 ppm (2H, t, CH_2 α -thiophene, $J = 7.6 \text{ Hz}$); 1.65–1.52 ppm (2H, m, CH_2 β -thiophene, $J = 7.3 \text{ Hz}$); 1.25 ppm (30H, CH_2); 0.90–0.84 ppm (3H, CH_3 , $J = 6.4 \text{ Hz}$), and the ^{13}C NMR spectra ($\delta_{\text{relative TMS}}$, CDCl_3) show signals in 183.00 ppm ($\text{C}\beta$); 143.26 ppm ($\text{C}\beta'$); 128.28 ppm ($\text{C}\alpha$); 125.86 ppm ($\text{C}\alpha'$); 124.99 ppm (CH_2 , 1); 119.73 ppm (CH_2 , 2); 31.93 ppm (CH_2 , 3); 30.57 ppm (CH_2 , 4); 29.70 ppm (CH_2 , 17); 29.61 ppm (CH_2 , 5–16); 14.11 ppm (CH_3 , 18). The UV-vis region in CHCl_3 solution showed an absorption band at 231 nm (5.37 eV). The infrared spectra of the ODT (Fig. 1) showed absorptions at 3500 cm^{-1} $\nu(\text{-OH})$; 3100 cm^{-1} $\nu(\text{=C}\alpha\text{-H-})$; $2850\text{--}2900 \text{ cm}^{-1}$ $\nu_{\text{as}}(\text{-C-S})$ and $\nu(\text{-CH})$ aliphatic; 1400, 1070 and 950 cm^{-1} ; $\delta_{\text{out of plane}}(\text{-C-H})$ aromatic, 1450, 1500 and 1550,

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