Synthesis, Characterization and Properties of Polythiophenes Modified with Mesogenic Group Spacers with Different Chain Lengths

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Received: 30 January 2005 / Revised version: 18 March 2005 / Accepted: 24 March 2005
Published online: 13 April 2005 – © Springer-Verlag 2005

Summary

A new family of conjugated polymers formed by 3-alkyloximethylthiophenes substituted with a biphenylcarbonitril group was synthesized by a route involving first the coupling of a functionalized alkyl chain, from 6 to 12 carbon atoms, to 3-methanolthiophene, and then the attachment of the mesogenic group. The monomeric units were characterized by conventional techniques. Thermal studies were also carried out. The polymerization of these monomers was accomplished by chemical oxidation with FeCl3, and the resulting polymers were characterized by FT-IR spectroscopy, elemental microanalysis, and XPS. Subsequently, these materials were doped with I2 and characterized by the same above-mentioned techniques. Conductivity measurements indicate that the polymers lie within the semiconductor range. Electrochemical polymerization of these monomers was also performed. XPS analysis and theoretical calculations revealed that both the biphenyl group and the thiophene ring are simultaneously oxidized during the electrochemical synthesis of the product, giving rise to an overoxidized material.

Introduction

For over a decade extensive work has been accomplished to synthesize and analyze new organic materials useful in the preparation of numerous electric and/or electronic devices, such as diodes, photoluminescent cells, sensors, etc. Among these materials, conducting polymers have aroused considerable interest due to their outstanding properties. Following this trend, the latest contributions in this field have been aimed to synthesize compounds whose main polymeric chain presents a lateral functionalization, that confers them new properties, such as higher solubility and reactivity, disclosing new and exciting possibilities of applications.

Amidst these new materials, polythiophene has been extensively studied because the polymer possesses high conductivity and good stability, which accounts for its wide range of applications [1,2]. Inconvenience of working with such units is the incompatibility of its synthesis with the insertion of functional groups, because most
of the reactions involved are of the Kumada-type, being the formation of Grignard’s reagent the main limitation for the diversification of the structures and, therefore, of the possible materials that can be formed [3].

The main innovation in this context is functionalization with groups that are capable of modifying the electronic density of the side chain, the attachment of alkyl groups in the positions 3 and 4 of the thiophene ring, or then, ether-like groups that increase the solubility of these materials. Their low solubility is the greatest disadvantage of working with these compounds [4, 5].

A compound of thiophene with a mesogen group in position 3 of the ring (4’-(8-thiophen-3-yl-octyloxy)biphenyl-4-carbonitrile) has been recently reported wherein some mesophases could be identified. Electropolymerization was also attempted, but difficulties in the characterization of the polymeric material were found because the biphenyl group is also electroactive [6].

In this paper a novel synthetic route is reported for the preparation of thiophene units functionalized in position 3, Scheme 1. The properties of the polymers and the way these properties are affected by the length of the alkyl chain are discussed.

Experimental

3-thiophenemethanol, 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, 1,12-dibromododecan, 4’-hydroxy-4-biphenyl-carbonitrile, and anhydrous FeCl₃ were supplied by Aldrich and used as received.

A BRUKER, ACP200, NMR Spectrometer, with Superconductor Magnet and Fourier Transform, was utilized to obtain ¹H-NMR spectra. FTIR spectra were measured at KBr pellets in a BRUKER, Vector 22 Spectrophotometer. XPS analyses were recorded with a Leybold LHS-12 Spectrometer at Nantes-CNRS University, Nantes, France. Elemental analysis was carried out on a CE Instruments, Model EA 1108 Elemental Analyzer, configured to perform the simultaneous determination of carbon, hydrogen, nitrogen and sulfur percentages. A DSC822 Star High Performance Differential Scanning Calorimeter, Mettler Toledo Star System within the range 25-200 °C, scanning rate 5 °C/min, was used for the calorimetric measurements. Conductivity measurements were carried out at room temperature, on polymer-powder pressed pellets, by the four-probe method in an Elchema Electrometer CM 508.

The electrochemical work was accomplished using a conventional three-compartment cell. Polycrystalline platinum (0.07 cm² geometric area), was used as working electrode. All potentials quoted in this work are referred to Ag/AgCl electrode in tetramethylammonium chloride to match the potential of a SCE at room temperature [7]. The auxiliary electrode was a helical platinum wire of large area.