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Synthesis and Characterization of Thiophene and Thiazole Containing Polymers

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ABSTRACT

In this study, bis(thiophene)-bis(ethylenedioxythiophene)-3,3′-dinonylthiazole (ThEdNBTEdTh) comonomer was obtained by using organometallic polycondensation mediated by organotransition metal complexes. The properties of electrochemically obtained poly[bis(thiophene)-bis(ethylenedioxythiophene)-3,3′-dinonylthiazole] (P[ThEdNBTEdTh]) from this comonomer were characterized by electrochemical techniques such as voltammetry and electrochemical impedance spectroscopy (EIS). Oxidative polymerization of ThEdNBTEdTh was carried out in dichlorometane onto a platinum electrode. Effect of polymerization charge on the redox behaviour of polymer films was investigated and these films were further characterized by ATR-FTIR, UV-Visible and fluorescence spectrophotometric measurements. EIS studies revealed that high capacitance values observed in the lower frequency region and proposed electrical equivalent circuit was applied to the experimental data to correlate the results, obtain the parameter of each element and explain the interface between the Pt/P[ThEdNBTEdTh/Bu_4NPF_6 system. Results showed that polymer has low oxidation potential, low band gap (1.67 eV) and good stability in the oxidized state and it shows p- and n-dopable properties. n-doping was verified experimentally by ex-situ FT-IR spectroelectrochemical measurements. The measured capacitance values are quite promising for supercapacitor applications.

1. Introduction

There are a lot of application areas of conducting polymers from optical information displays to rechargeable batteries. A modification of electrically conducting polymers is a promising line of inquiry, which allows one to expand the range of physicochemical characteristics of polymers and produce polymeric materials with new properties. Organometallic polycondensation reactions are raised great interest for the design of new classes of conjugated materials with enhanced semiconducting properties [1–3]. Donor–acceptor–donor type molecules find different applications in electronic and optical devices [4–9].

Polythiophene (PTh) has rapidly become the subject of considerable interest [10–14]. The high environmental stability of both doped and undoped states of PTh together with its structural versatility has led to multiple developments aimed at applications such as conductors, electrode materials, and organic semiconductors.

After the development of new PTh derivative, poly (3, 4-ethylenedioxythiophene), (PEDOT) during the second half of the 1980s, an exponential increase in the number of publications was observed [15–19]. PEDOT shows high conductivity, lower oxidation potential compared to PTh, high stability at doped state, low band gap and these properties make it attractive for many applications.

Recently thiazole-based conjugated polymers have received great interest [20–30]. Introduction of nitrogen atoms in addition to sulphur in the thiophene (Th) ring improve the properties of resulting polymers which are desirable for applications.

In this study, nonylbithiazole (NBT), 3, 4-ethylenedioxythiophene (EDOT) and Th were chosen to obtain comonomer because of especially π- staking and n-type transporters properties of BTh, superior electrical properties of EDOT and stability at both neutral and oxidized state for PTh. P [ThEdNBTEdTh] is expected to have useful properties for the design of a diode, transistor or capacitor.

2. Experimental

2.1. Equipment and materials

Cyclic voltammetry (CV) experiments, spectroelectrochemistry and electropolymerizations were performed with a Gamry 600 model potentiostat/galvanostat interfaced to a PC. A Pt button electrode (0.022 cm^2), a platinum wire and a silver wire were used as working, counter and pseudo reference electrodes respectively.

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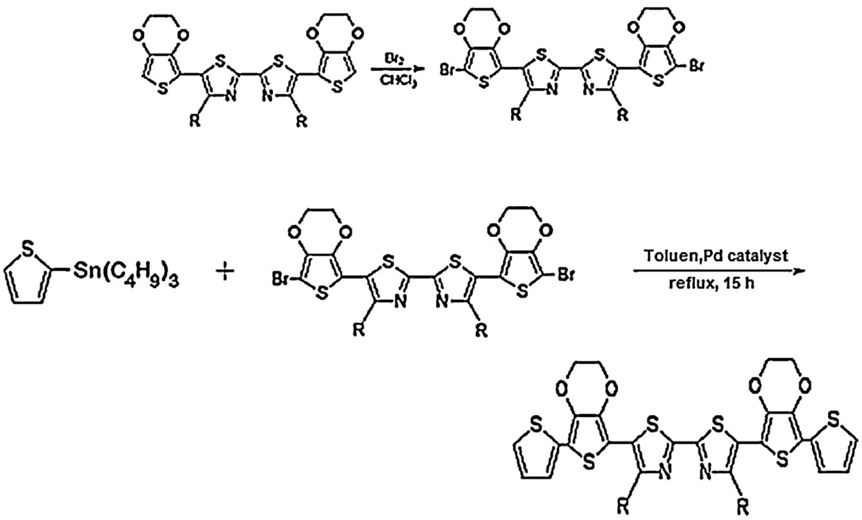


Scheme 1. Synthetic routes for bis (thiophene)-bis (ethylenedioxythiophene)-3,3′-dinonylthiazole (ThEdNBTEdTh).

The silver wire was calibrated externally using a 5 mM solution of ferrocene/ferrocenium (Fc/Fc^+) couple in the electrolyte and the potentials are reported versus Ag/AgCl as suggested in literature [31].

Spectroelectrochemical data were recorded on a Schimadzu 160 A model UV–visible spectrophotometer. A three-electrode cell system was used where the working electrode was a custom cut ITO-coated glass slide (8mm × 50mm × 1.1 mm, 30 mm), counter electrode was a Pt wire and pseudo-reference electrode was Ag wire.

The ATR-FTIR- spectra measurements were performed by using Perkin Elmer Spectrum one model Spectrophotometer.

Voltammetry and EIS were used for electrochemical polymerization and characterization methods. Potentiodynamic polymerizations were done by using 10, 20, 35 and 50 cycles. Q_1 and Q_2 are the polymerization charges obtained in two different potential ranges (0.2-1.0 V and 0.2-1.35 V) respectively by integration of CV curves for 10 ($Q_{1(10)}$ ($Q_{2(10)}$) and 20 (($Q_{1(20)}$and $Q_{2(20)}$) cycles.

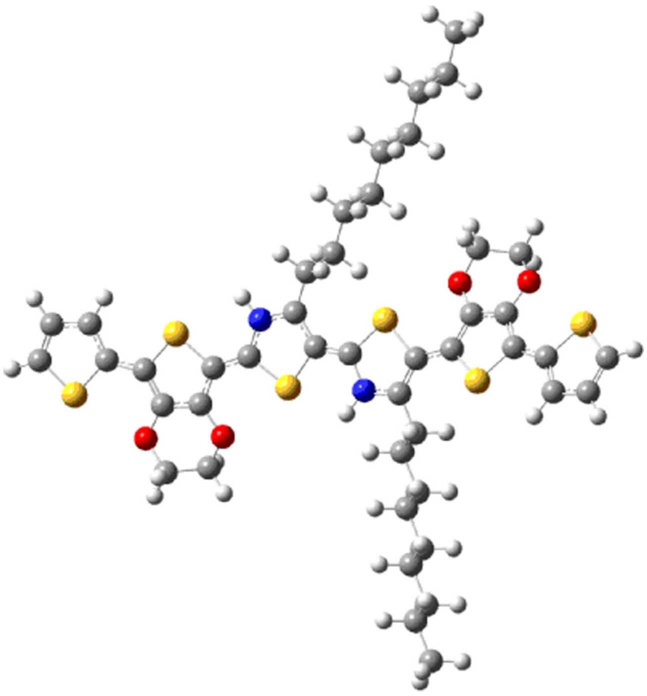
The electrolyte was 0.1 M tetraethylammonium hexafluorophosphate ($TBAPF_6$) obtained from Fluka, dichloromethane (DCM), dimethylformamide (DMF) supplied by Merck. ethylenedioxythiophene (EDOT), thiophene (Th), bromodecanon, dithiooxamide, bromine, trans-dicholorobistriphenylphosphine palladium (II) chloride, butyl lithium, trimetiltinchloride, 2-trimethylstannyl thiophene $MgSO_4$ and ethanol were all analytical grade and used without further purification. During the synthesis of the comonomer, all preparations and reactions were performed under a nitrogen atmosphere; reagent grade solvents were dried and distilled before use. Tetrahydrofuran (THF) and toluene purchased from Carlo-Erba were distilled over sodium.

2.2. *Comonomer Synthesis Methods*

Synthesis of bis (thiophene)–bis (ethylenedioxythiophene) - 3,3′-dinonylthiazole (ThEdNBTEdTh) was synthesized by Stille coupling reaction. Synthesis of the bis (3,4-ethylene-dioxythiophene)-(4,4-dinonyl-2,2-bithiazole) (ENBTE) comonomer and their bromine and trimethylstannyl derivatives are similar to the literature procedures previously described for alkylbithiazole and its derivatives [8]. The mixture of 2′2’dibromoENBTE and 2- trimethylstannyl thiophene was refluxed for 20 h. After cooling to room temperature the reaction mixture was poured into water, and dichloromethane, pentane and chloroform were added. Extracted organic phase was washed with water and dried over $MgSO_4$ and the solvent was rotary evaporated. The final product was re-crystallized in ethanol and obtained as reddish orange solid with the molecular weight of 806 g/mol. Yield was 45%. Synthetic route was given in Scheme 1.

H-NMR spectrum was collected on Agilent VNMRS 500 MHz in $CDCl_3$ and the absence of protons at about 6.3 ppm which belong to EDOT rings and the presence of protons at about 7.2 and 7.4 ppm which belongs to Th shows the coupling and proves the formation of comonomer (Fig. 1).

Optimized geometry of comonomer was obtained by DFT method and given in the Scheme 2.



Scheme 2. Optimized geometry of ThEdNBTEdTh.