

# Synthesis and characterization of a new soluble conducting polymer and its electrochromic device

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## Abstract

A mixture of isomers 2,5-di(4-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole, 2-(4-methyl-thiophen-2-yl)-5-(3-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole and 2,5-di(3-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole (Me-SNS(NO<sub>2</sub>)) were synthesized. Resulting monomers were polymerized chemically, producing soluble polymers in common organic solvents. The average molecular weight has been determined by gel permeation chromatography (GPC) as  $M_n = 5.6 \times 10^3$  for the chemically synthesized polymer. The monomers were also electrochemically polymerized in the presence of LiClO<sub>4</sub>, NaClO<sub>4</sub> (1:1) as the supporting electrolyte in acetonitrile solvent. Resulting polymers were characterized via CV, FTIR, NMR, SEM and UV–Vis spectroscopy. Spectroelectrochemistry analysis of polymer revealed  $\Pi$ – $\Pi^*$  transition below 300 nm, with an electronic band gap of 2.18 eV. Switching ability of the polymer was evaluated by kinetic study measuring percent transmittance (%T) at the maximum contrast point, indicating that poly(Me-SNS(NO<sub>2</sub>)) is a suitable material for electrochromic devices.

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**Keywords:** Electrochemical polymerization; Conducting polymers; Electrochromic properties

## 1. Introduction

Polymers of thiophene and pyrrole based compounds are environmentally and thermally stable materials; therefore they can be used as non-linear optical devices [1], polymer light emitting diodes [2], gas sensors [3], organic transistors [4], and electrochromic devices [5]. Electrochromism is a phenomenon where a material shows reversible and visible change in color that is associated with an electrochemically induced oxidation–reduction reaction [6].

Design and synthesis of new conjugated polymers are significant part of the conducting polymer research [7] and has attracted great attention since 1977 [8]. Among conducting polymers, polythiophene and its derivatives have become a subject of considerable interest as electrochromic materials due to their chemical stability, ease of synthesis and structural versatility [9].

One of the most important characteristics exhibited by the polymers from the polythiophene family is their enhanced electrochromism upon application of a small voltage. A variety of conjugated polymers have colors both in the oxidized and reduced states, since the band gap is in the visible region [10]. After oxidation, the intensity of the  $\Pi$ – $\Pi^*$  transition decreases, and two low energy transitions emerge to produce a second color. Therefore, there are many absorption changes in the visible region of the spectrum, making them useful in the construction of electrochromic devices [11].

Insolubility is the major limitation of conducting polymers. Synthesis of soluble conducting polymers enables direct application of these polymers to any substrate using conventional printing techniques [12].

In the present work, new isomers were synthesized. Both chemical and electrochemical polymerization of Me-SNS(NO<sub>2</sub>) were studied. We investigated the optoelectrochemistry and measured the *L*, *a*, *b* values of the polymer coated on ITO via constant potential electrolysis by using LiClO<sub>4</sub> (0.1 M) and NaClO<sub>4</sub> (0.1 M) as the supporting electrolyte. The resultant conducting polymer was characterized by the CV, FTIR, NMR, SEM, and conductivity measurements.

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In recent years there has been a growing interest in application of conducting polymers in electrochromic devices. Thus, in the second part of the study dual type electrochromic device was constructed with poly(Me-SNS(NO<sub>2</sub>)) (anodically coloring polymer) and poly-3,4-ethylenedioxythiophene (PEDOT) (cathodically coloring polymer).

## 2. Experimental

### 2.1. Materials

AlCl<sub>3</sub> (Aldrich), 3-methylthiophene (Aldrich), succinyl chloride (Aldrich), dichloromethane (DCM) (Merck), *p*-toluene sulfonic acid (PTSA) (Sigma), 4-nitroaniline (Sigma), toluene (Sigma), nitromethane (Aldrich), methanol (Merck), ferric(III) chloride (Aldrich), acetonitrile (AN) (Merck), NaOH (Merck), LiClO<sub>4</sub> (Aldrich), NaClO<sub>4</sub> (Aldrich), propylene carbonate (PC) (Aldrich) and poly(methyl methacrylate) (PMMA) (Aldrich) were used without further purification. 3,4-ethylenedioxythiophene (EDOT) (Aldrich) were used as received.

### 2.2. Equipments

NMR spectra of the monomers were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) by using CDCl<sub>3</sub> as the solvent. The FTIR spectrum was recorded on a Nicolet 510 FTIR spectrometer. Mn was measured by gel permeation chromatography (PL220). The surface morphologies of the polymer films were analyzed by using JEOL JSM-6400 scanning electron microscope. Solartron 1285 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and cyclic voltammetry experiments. Varian Cary 5000 UV–Vis spectrophotometer was used in order to perform the spectroelectrochemical studies of polymer and the characterization of the devices. Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

### 2.3. Synthesis of monomers Me-SNS(NO<sub>2</sub>)

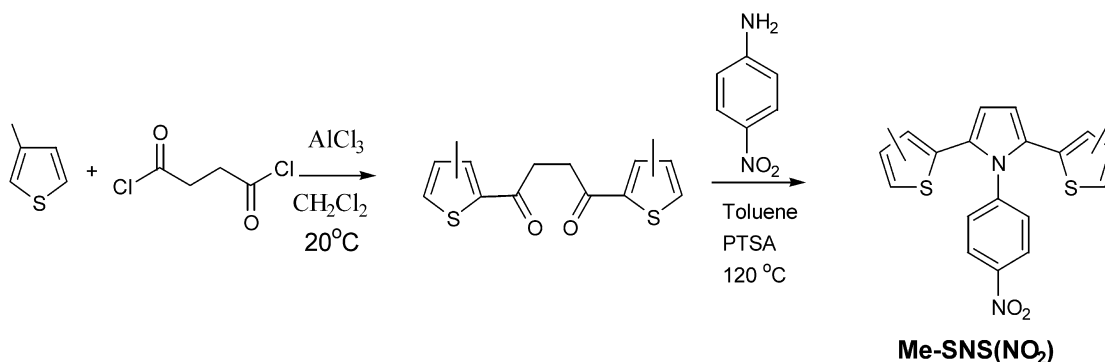
The starting material, 1,4-di(3-methyl-2-thienyl)-1,4-butanedione, 1-(3-methyl-2-thienyl)-4-(4'-methyl-2'-thienyl) butanedione and 1,4-di(4-methyl-2-thienyl)-1,4-butanedione were

synthesized according to procedure in literature [13]. To a suspension of AlCl<sub>3</sub> (16 g, 0.12 mol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml), a solution of 3-methylthiophene (9.61 ml, 0.12 mol) and succinyl chloride (5.51 ml, 0.05 mol) in CH<sub>2</sub>Cl<sub>2</sub> were added dropwise. The red mixture was stirred at room temperature for 4 h. This was then poured into ice and concentrated HCl (5 ml) mixture. The dark colored organic phase was washed with concentrated NaHCO<sub>3</sub> (3 × 25 ml) and brine, and then dried over MgSO<sub>4</sub>. Evaporation of the solvent yielded yellowish solid, which was suspended in ethanol. Filtration and washing with ethanol afforded the desired compound.

The 2,5-di(4-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole, 2-(4-methyl-thiophen-2-yl)-5-(3-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole and 2,5-di(3-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole (Me-SNS(NO<sub>2</sub>)) isomer monomers were synthesized from 1,4-di(3-methyl-2-thienyl)-1,4-butanedione, 1-(3-methyl-2-thienyl)-4-(4'-methyl-2'-thienyl) butanedione, 1,4-di(4-methyl-2-thienyl)-1,4-butanedione isomers (5 mmol, 1.25 g), 0.97 g (7 mmol) 4-nitroaniline, 0.1 g (0.58 mmol) PTSA and 20 ml of toluene were added. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by flash column chromatography (SiO<sub>2</sub> column, elution with dichloromethane:hexane (1:1)) afforded the desired compounds as pale brown powder. The isomers could not be separated into components no matter the type of column or solvent were used. The synthetic route of the monomer is shown in Scheme 1.

### 2.4. Chemical polymerization of Me-SNS(NO<sub>2</sub>) with iron(III) chloride

A typical chemical polymerization of Me-SNS(NO<sub>2</sub>) was fulfilled using iron(III) chloride as the oxidant. To carry out the oxidative polymerization, Me-SNS(NO<sub>2</sub>) (1 × 10<sup>-3</sup> M) was dissolved under a blanket of N<sub>2</sub> in nitromethane (15 mL). A solution of iron(III) chloride (2 × 10<sup>-3</sup> M) in nitromethane (5 mL) was dropwise added to the monomer solution. The reaction was



Scheme 1. The synthetic route of the monomer.

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