



Electrochemistry of Secondary Amine Substituted 2,5-di(2-thienyl)pyrrole Derivative and Its Copolymer

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Since the discovery of conductive polymers, one of the most promising innovations in the field of polymer chemistry, these materials have been used in many practical applications. However, new monomers are being designed to overcome some of the disadvantages of conductive polymers, such as their inherent stability, low optical and electrical properties. It is known that minor arrangement on the monomer structure lead to very large changes in the polymer properties. In this study, a thienyl pyrrole monomer, one of the most studied monomers in the field of conductive polymers, has been produced using hydrazine derivatives instead of amines. For this purpose, the model monomer, N-phenyl-2,5-di(thiophen-2-yl)-1H-pyrrol-1-amine, was synthesized and the optical, electrochemical and electrochromic properties of its conductive polymer were investigated. Furthermore, copolymer studies with 3,4-ethylenedioxythiophene (EDOT) have been done to emphasize the importance of copolymerization on electrochromic properties of the conducting polymers. Effects of the feed ratio of the monomers and applied potential for copolymerization on optical and electrochemical properties of the electrochemically synthesized copolymers were investigated in detail.
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Conducting polymers (CP's) are a relatively new class of polymeric materials, and take an interest in academic and industrial researchers over the past two decades because of their electrical, optical, electro-physical and electrochemical properties. These features make them a valuable piece for technologic applications such as light emitting devices,¹ photovoltaic cells,^{2,3} electrochromic devices,^{4,5} biosensor applications⁶⁻⁸ and organic transistors.⁹

Among conducting polymers poly(2,5-dithienylpyrrole)s, PSNS, have received particular interest due to their low oxidation potential and ease in chemical or electrochemical synthesis. Since the first report, various publications on modification of their electronic and optical properties through variation of monomer structure have appeared.¹⁰⁻¹⁴ SNS derivatives are one of the most investigated conducting polymers due to their low oxidation potential, high optical contrast ratio between various redox states, high redox stability and easy chemical/electrochemical polymerization.

Electrochemical copolymerization method can produce an interesting combination which has different properties of homopolymers and make a way to control the electrochromic properties of the conducting polymers.¹⁵ EDOT is a most popular co-monomer choice as a substituted monomer cause of good electrochemical properties such as low bandgap, good conductivity and high stability. It's known that EDOT and its derivatives have eliminate to steric hindrance and thus force the polymer chain to a planarity and this situation leads to a decrease in the bandgap of the polymer.¹⁶

In literature, there are SNS derivatives with having substituted phenyl derivatives,^{17,18} ferrocene,¹⁹ BODIPY²⁰ (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene), azide,²¹ and hydrazide derivatives^{22,23} which have been used and investigated in recent works. However, SNS derivatives which substituted with hydrazine groups have not been reported yet. In this study, a thienyl pyrrole monomer, one of the most studied monomers in the field of conductive polymers, has been produced using hydrazine derivatives instead of amines. For this purpose, the model monomer, N-phenyl-2,5-di(thiophen-2-yl)-1H-pyrrol-1-amine (OG), was synthesized by Paal-Knoor pyrrole synthesis^{24,25} and optical, electrochemical and electrochromic properties of its conductive polymer were investigated.

Copolymers based on OG and EDOT have been successfully obtained with different monomer feed ratios and the effect of various feed ratios of the comonomer on the electrochemical and spectroelectrochemical features of the resultant copolymer films were examined.

Experimental

Instruments.—Three-electrode cell was used in all electrochemical experiments. The indium tin oxide (ITO) coated glass with resistance of 8–12 Ω sq^{-1} and thickness of 0.7 mm were purchased from Delta Technologies Limited, USA, and were used as the working electrodes. Surface area of coated working electrode is set to be 1 cm^2 . Ag wire was used as reference electrode (calibrated against Fc/Fc^+ (0.3 V)), while Pt wire was used as the counter electrode. An ivium potentiostat/galvanostat interfaced computer was used in all electrochemical measurements. Spectroelectrochemical measurements were carried out in a three-electrode quartz cell. The spectra were collected with a Diode Array UV-vis spectrophotometer (Agilent 8453) with a PC interface.

The structure of the monomer was confirmed by NMR analysis. ¹H NMR spectra of the monomer were taken by using a Bruker-instrument NMR spectrometer (DPX-400) with DMSO as the solvent.

Synthesis of monomer N-phenyl-2,5di(thiophen-2-yl)-1H-pyrrol-1-amine (OG).—The monomer; OG was synthesized from 1,4-di(2-thienyl)-1,4-butanedione²⁶ and phenylhydrazin in the presence of p-toluene-sulfonic acid (PTSA). A round bottomed flask equipped and magnetic stirrer was charged with 0.5 g (2 mmol) 1,4-di(2-thienyl)-1,4-butanedione, 200 μL (2 mmol) phenylhydrazin, 35 mg (0.2 mmol) PTSA and 50 mL toluene. The resultant mixture was stirred and refluxed for 96 h. Then, the mixture was cooled to room temperature and the solid product was filtered to give a dark green powder. The product was recrystallized with methanol and dried in air to yield 0.23g 35% (mp: 164°C). Synthetic route of the monomer is shown in Scheme 1. Structure of the monomer was confirmed by ¹H NMR and ¹³C NMR spectral analyses (Figs. 1 and 2).

Electrosynthesis of P(OG) and P(OG-co- EDOT).—Electrochemical polymerization of OG was carried out by potentiodynamically sweeping the potential between –0.1 to 1.7 V at 250 mVs^{-1} in the presence of 0.1 M LiOCl_4 and ACN solvent. (Scheme 1). The system consist of a potentiostat a CV cell with ITO working electrode, platinum wire counter electrode and Ag wire as a pseudo reference electrode. After polymerization, the polymer film was rinsed in ACN to remove monomer residue. EDOT was used as the second monomer for the synthesis of conducting copolymer P(OG-co-EDOT) (Scheme 1). Copolymer films were coated on ITO surface with applied range of potential from –1.5 V to 1.5 V. Copolymer films have been synthesized from OG/EDOT, comonomer feed ratios of (4/1),(3/2),(1/1),(2/3), and (1/4). Short notations of 1, 2, 3, 4 and

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