

Electrochemical synthesis of polymer based on 4-(2-thienyl)benzenamine in aqueous solutions: Electrochemical properties, characterization and application



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ABSTRACT

4-(2-Thienyl)benzenamine (TBA) was successfully synthesized by a simple method including substitution of thiophene on *p*-nitroaniline followed by reduction of nitro group. Structure of the synthesized monomer was verified using IR, ¹H NMR, GC–MS and elemental analysis techniques. Corresponding poly 4-(2-thienyl)benzenamine (PTBA) was electrochemically synthesized in acidic aqueous solution by cyclic potential sweep method for the first time. Characterization of the resulting polymer was performed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), UV–vis and IR spectroscopies, and scanning electron microscopy (SEM). Effects of pH and temperature on the electroactivity of the polymer modified electrode were investigated. The corrosion behavior of PTBA in 3.5 wt% NaCl solution was studied by potentiodynamic polarization test and electrochemical impedance spectroscopy. The PTBA was found to exhibit enhanced corrosion protection effect on stainless steel electrode in comparison with polyaniline (PANI) and polythiophene (PTH) homopolymers.

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1. Introduction

The need for new conducting polymers comprising a collection of properties (processability, conductivity, stability . . .) has led to the various strategies in order to overcome the limitation due to the rarity of monomers [1–7]. Aniline–thiophene copolymers are interesting because their oxidized form is more stable even at high electrode potentials so the consecutive switching the potential can be performed without considerable change in conductivity of the copolymer [8–12]. Then it is interesting to obtain conjugated polymers that include thiophene and aniline simultaneously. This can be achieved in three ways: preparation of thiophene and aniline copolymers from a mixture of the corresponding monomers [8–12], copolymerization of thiophene and bi- or α -terthiophenes [13], and synthesis and further polymerization of substituted monomers incorporating both thiophene and aniline moieties in their structure [14–17].

The effect of thiophene on the electropreparation and properties of PANI was investigated by Yildiz et al. [8]. They found that in

acidic/acetonitrile solutions containing high thiophene to aniline concentration ratios and at oxidation potential of 1.7 V vs. Ag/AgCl reference electrode, thiophene enters into the structure of the polymer and a copolymer is formed. The copolymerization of aniline and thiophene with varying concentration ratios was studied in acetonitrile by Holze et al. [9,10]. Since of the oxidation potential of the thiophene is 1.7 V, the electropolymerization potential of at least 1.7 V vs. Ag/AgCl reference electrode was selected [9,10]. Holze et al. showed that the presence of thiophene in acetonitrile solution of aniline accelerates the formation of polymer [9,10]. The important point was that no degradation of copolymers took place at high over potentials in aprotic solvent so the range of stability of copolymer was considerably extended compared to corresponding homopolymers for which a complete loss of conductivity occurs during potential excursions to 1.9 V versus Ag/AgCl [9]. The reversible doping/undoping behavior of PANI up to this potential limit was also observed in this copolymer, albeit with much lower overall conductivities [9]. Nevertheless, electrocopolymerization of aniline and thiophene has been found to be difficult because of a large difference in their oxidation potentials. This problem can be solved by synthesis of a monomer containing both moieties (aniline and thiophene). Preliminary findings were reported on the PTBA which can be viewed as a copolymer with alternating aniline and thiophene repeating unit

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[14]. Synthesis of the monomer was accomplished in four steps using Grignard reagent. Chemical polymerization was performed using FeCl_3 oxidizing agent in chloroform solution. From IR spectra (absence of the absorption band at 682 cm^{-1} corresponding to C–H α deformation) it was recognized that the polymerization is occurred predominantly through the α -position of the thiophene moiety [14]. A series of alternating block copolymers incorporating 3-alkyl substituted thiophene and aniline repeat units were synthesized via chemical oxidative polymerization using ferric chloride as oxidant [15]. It was indicated that apart from being conductive, these polymers also depicted fluorescence characteristic which were more akin to PTh than PANI. Copoly(thiophenediyl-1,4-diaminophenylene) was synthesized via Ullmann condensation reaction [16,17]. By varying reaction parameters, either fused or unfused materials were synthesized. The thermal stabilities of the materials were excellent and the solubility in DMF was moderate. Recently, Zamora et al. synthesized TBA from aniline and thiophene via Suzuki reaction using Pd/C which is an efficient but very expensive catalyzer [6]. A copolymer was chemically synthesized in organic solution and its application as sensitizer dye was tested in fabrication of dye sensitized solar cells (DSSCs) [6]. From above mentioned studies it reveals that the presence of thiophene in polyaniline backbone improves the thermal and electrochemical stability of the polymer albeit the conductivity decreases. Literature survey reveals that there are a few researches devoted to the polymerization of TBA in organic solutions [6,14,15] and investigation of electrochemical polymerization of the TBA in aqueous solution has not been performed at all. In this work the desired monomer (TBA) is prepared through a simple method including two simple reactions using an inexpensive catalyzer. We start with the *para*-nitroaniline and thiophene as reactants. Thiophene is substituted on benzene ring through the elimination of amine group and at the second step nitro moiety is reduced to the amine group. The structure of the synthesized monomer is characterized by several techniques. The monomer is utilized to prepare the polymer in acidic aqueous solution by cyclic potential sweep method for the first time. The oxidation potential was swept to 1.1 V, very less than the oxidation potential of thiophene. By this way less degradation of the polymer will occur due to the applying high overoxidation potential. Finally, possibility of the application of the PTBA in corrosion protection is evaluated. Testing results show that the corrosion inhibition of the polymer is noteworthy.

2. Experimental

2.1. Materials

Isopentyl nitrite and thiophene (reagent grade) were prepared from Merck and used without further purification. Aniline (reagent grade) was purchased from Merck and distilled under reduced pressure and kept far from light in refrigerator for subsequent uses.

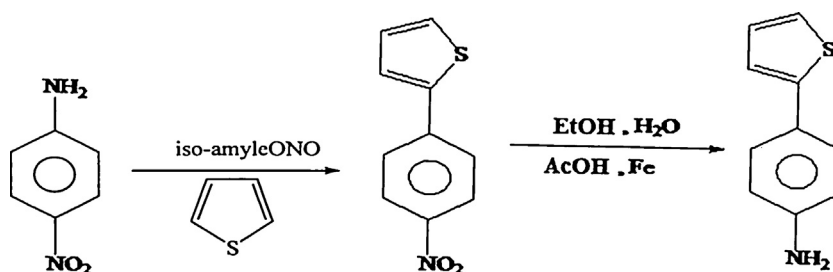
Other reagent grade chemicals were also purchased from Merck. Conductive glass (FTO glass, sheet resistance $8\ \Omega\ \text{sq}^{-1}$, purchased from South Korea) was used as working electrode for precipitating polymer film. A steel electrode with the surface dimensions of $1 \times 1\ \text{cm}^2$ was employed for the electrochemical tests. The chemical composition of the steel used was as follows: 0.05 wt% C, 0.4 wt% Si, 0.4 wt% Mn, 14.5 wt% Cr and the rest was iron.

2.2. Methods

The electrochemical experiments were carried out in a single compartment cell housing three-electrode at room temperature. Glassy carbon (GC) or FTO were used as working and a Pt rod as counter electrodes respectively. The potentials were measured relative to an $\text{Ag}/\text{AgCl}/\text{Cl}^-$ (sat.) reference electrode. Electrochemical and impedance measurements were made using an Autolab general purpose electrochemical potentiostat/galvanostat system PG302N and Autolab frequency response analyzer system (AUT20. FRA2- AUTOLAB, Eco Chemie, B.V., Netherlands) respectively. For the electrochemical impedance spectroscopy (EIS) measurement the frequency was scanned from 10 mHz to 1 MHz with an alternating current amplitude of 10 mV. The impedance parameters were determined by fitting of impedance spectrum using Nova software version 1.8. Electronic absorption spectrum was obtained on an Agilent UV-visible spectrometer (model 8453, USA). IR spectra were recorded using a Shimadzu model 470 grating IR measurement instrument by the KBr pellet technique. NMR spectra were recorded on a Bruker DRX-500 MHz spectrophotometer. Elemental analysis was performed on a COSTECH analyzer model ECS-4010. GC-MS spectrum of monomer was obtained using Agilent Technologies 6890N gas chromatograph and a split/splitless injector coupled with a 5973 Agilent mass selective detector. The mass spectral scan rate was 2.86 scan/s. The GC was operated in split mode at split ratio 20:1 with a helium (grade 5) flow rate of 1 mL/min. The MS was operated in the electron impact (EI) mode using an ionization voltage of 70 eV and a source temperature of $230\ ^\circ\text{C}$ and quadrupole temperature of $150\ ^\circ\text{C}$. The GC injector was maintained at $270\ ^\circ\text{C}$ and the transfer line at $280\ ^\circ\text{C}$. GC-MS chromatographic separations were carried out on a HP-5 column ($30\ \text{m} \times 0.25\ \text{mm i.d.}$) coated with $0.25\ \mu\text{m}$ film. The separation was performed using a temperature program consisting of an initial hold at $90\ ^\circ\text{C}$ for 2 min, ramped to $260\ ^\circ\text{C}$ at a rate of $20\ ^\circ\text{C}/\text{min}$ and held at $260\ ^\circ\text{C}$ for 10 min. Scanning electron microscopy (SEM) images was taken by scanning electron microscope VEGA3, Tescan, Czech.

2.3. Synthesis of monomer

4-(2-Thienyl) benzenamine was synthesized via a two-step procedure reported previously for synthesis of 4-(2-furyl) benzenamine by our group (Scheme 1) [18].



Scheme 1. The synthetic route of the monomer.

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