

Electrochemical copolymerization of *o*-toluidine and *o*-phenylenediamine

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Abstract

Electroactive copolymers of *o*-toluidine (OT) and *o*-phenylenediamine (OPD) were electrosynthesized in aqueous sulfuric acid. Cyclic voltammetry was used both for the electrochemical synthesis and characterization of the copolymers deposited on a gold electrode. The voltammograms exhibited different behavior for different concentrations of OPD in the feed. At optimum conditions the rate of copolymerization was found to be between the rates of homopolymerizations. The resulting poly(OPD-co-OT) shows an extended useful potential range of the redox activity as compared to the corresponding homopolymers. The effect of scan rate and pH on the electrochemical activity was studied. The copolymer was electrochemically active even at pH 9.0. In situ conductivity measurements further support the formation of a copolymer because the copolymers have a potential region of maximum conductivity completely different from that of POT. However, conductivities of the copolymers were lower by 2–2.7 orders of magnitude than of POT.

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1. Introduction

The recent use of conducting polymers for numerous technological applications has attracted significant attention of researchers with a growing trend towards interdisciplinarity. Polyaniline (PANI) is presumably the most widely studied member of this very promising class of intrinsically conducting organic polymers. PANI has a rigid and planar backbone providing good conductivity, but the same feature makes it insoluble in common organic solvents and incompatible with common polymers [1]. To overcome the difficulties associated with the limitations in the use of PANI, many researchers have directed their attention to polymers of substituted anilines prepared through different approaches. Electrochemical or chemical polymerization of ring- or *N*-substituted aniline [2–5] have been effectively used for the preparation of substituted

PANIs. However, the conductivity of substituted PANIs is much lower than that of PANI alone.

Next to PANI a great deal of attention has been paid to copolymers based on aniline or substituted aniline. Copolymerization greatly increases the ability of polymer scientists to tailor a material with specific properties as the synthesized copolymers show electrochemical characteristics quite different from those of the homopolymers [6–9]. Consequently copolymerization is also considered to be an important method to improve the properties of homopolymers.

With respect to aniline based copolymers pioneering work was carried out by Wei et al. [10]. They reported that aniline could be polymerized with *o*-toluidine yielding a copolymer film with a conductivity, which could be controlled over a broad range of electrode potentials. Pekmez-Özcicek et al. [11] reported that incorporation of aniline units within polythiophene chains led to copolymers having an increased range of electrochemical stability. Similarly, small quantities of 2-fluoroaniline and 2-chloroaniline have been demonstrated to have a dramatic effect

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on the conductivities of poly(aniline-co-2-flouroaniline) and poly(aniline-co-2-chloroaniline) [12]. Monomers bearing sulfonate, alkylsulfonate and carboxylate groups were copolymerized with aniline, yielding self-doped copolymers [13]. Savita and Sathyanarayana chemically synthesized copolymers of aniline with *o/m*-toluidine and reported that copolymers have better stabilities and comparatively higher conductivities than the homopolymers [14]. They have also synthesized copolymers of *o*-nitroaniline (which does not homopolymerize under conditions employed for the polymerization of aniline and its derivatives) with *o/m*-toluidine and reported better solubilities of the copolymers in dimethylsulfoxide (DMSO), *N*-dimethylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) and higher conductivities, than the homopolymers [15]. Malinauskas et al. [13] electrochemically synthesized copolymers and bilayer structures of polyaniline and poly(*o*-phenylenediamine). Electrochemical copolymerization of aniline with *p*-phenylenediamine was reported to enhance drastically the copolymerization rate [16], whereas its isomer *m*-phenylenediamine caused an opposite effect [17]. Thus, copolymerization could provide a convenient synthetic method and process for preparing new conducting materials with improved properties.

The wide scope of tuning different properties of conducting polymers triggered us to explore possibilities of copolymerization of toluidines with phenylenediamines, both being substituted anilines. A close analysis of the literature shows a large number of reports on the chemical and electrochemical synthesis of polytoluidine, polyphenylenediamine and their copolymers with aniline and other substituted anilines [10–18]. These homo- and copolymers have also been tested for various applications in sensors [19,20], in corrosion inhibition [21] and in rechargeable batteries [22]. So far there is no report on the chemical or electrochemical copolymerization of phenylenediamine with *o*-toluidine.

The present study describes the preliminary results of electrochemical copolymerization of *o*-toluidine (OT) with *o*-phenylenediamine (OPD). Cyclic voltammetry (CV) was used to synthesize and analyze the electrochemical properties of homopolymer/copolymers in order to obtain evidence for copolymer deposition when a mixture of monomers was used. In addition to this the electrochemical growth characteristics of the corresponding homopolymer films were compared to identify the differences in the behavior of the copolymer films. In situ conductivities were measured in order to identify differences between the conductivities of homopolymers and copolymers supporting the assumption of true copolymers instead of merely mixed homopolymers being electropolymerized.

2. Experimental

Reagent grade *o*-toluidine (Merck) was distilled under vacuum, the resulting colorless liquid was stored under nitrogen. *o*-Phenylenediamine (Merck) was used as

received. Ultrapure water (Seralpur pro 90 C) was used for the preparation of electrolyte solutions containing 1.5 M H₂SO₄ (Merck). A three-electrode cell was used with a saturated calomel reference electrode. Gold sheets served as working and counter electrodes. The surface area of the working electrode was 2.0 cm². Electrochemical synthesis and characterization were carried out under nitrogen atmosphere. Cyclic voltammetry studies were performed with a computer-interfaced custom-build potentiostat with general-purpose electrochemical system software.

Electrochemical polymerization and copolymerization were carried out potentiodynamically by cycling the potential between $-0.2 < E_{SCE} < 0.85$ V for *o*-toluidine (OT) and $-0.3 < E_{SCE} < 0.85$ V for *o*-phenylenediamine (OPD) and copolymers at a scan rate of 50 mV/s. Homopolymers were obtained by electropolymerization of solutions 0.1 M of OT and OPD at five different concentrations between 0.01 and 0.05 M. Copolymerization was done using various concentrations (0.01, 0.02, 0.03, 0.04 and 0.05 M) of OPD with a constant concentration of OT (0.1 M) in the feed. Cyclic voltammograms of the growing films were recorded continuously during electropolymerization. For all copolymers and every concentration of pure OPD CVs were recorded up to 210 cycles, in case of OT only 40 cycles were recorded because of the particularly fast film growth. The deposited films of homopolymers/copolymers were washed with deionized water and subsequently placed in a monomer-free supporting electrolyte solution wherein CVs of the film-coated electrodes were recorded. The CVs of the homopolymer/copolymer films were recorded in their respective potential ranges at various scan rates.

The dependence of electrochemical activity of polymers on pH was studied in 0.2 M Na₂SO₄ adjusted with sulfuric acid to different pH values. The pH of the electrolyte solution was determined with a MV81 Präcitronic pH-meter calibrated with standard buffers. For in situ conductivity measurements the polymer was deposited on a double-band gold electrode in a three-electrode cell with a specially designed electronic circuit described elsewhere [23]. The electrode potential was increased stepwise by 50 mV and after approximately 5 min the electrochemical cell was cut off from the potentiostat and a stable resistance value was recorded.

3. Results and discussion

3.1. Electrochemical polymerization of *o*-toluidine and *o*-phenylenediamine

Fig. 1a shows cyclic voltammograms recorded for the homopolymerization of OT. In the first cycle an irreversible oxidation peak appeared at 0.84 V, which corresponds to the oxidation of the monomer. In the second and subsequent scans a reversible process observed around about 0.45/0.41 V is either due to soluble products that may be identified as the dimer, which were shown to be capable of growing into polymer during electrochemical deposition

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