



Electrocopolymerization of *meta*-phenylenediamine and *ortho*-phenetidine

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Abstract

Copolymerization of *meta*-phenylenediamine (*m*PD) and *ortho*-phenetidine (PHT) was performed by three facile electropolymerization techniques including cyclic voltammetry, constant potential and constant current on platinum electrodes in H₂SO₄. The electrochemically functional characteristics, including electroactivity and electrochromism, of the polymers formed are significantly dependent on *m*PD/PHT ratios and the electropolymerization technique. It is interesting that the black *m*PD/PHT copolymers obtained by the three electropolymerizations were all soluble in DMSO, i.e., electropolymerized *m*PD/PHT copolymers exhibit higher solubility than corresponding copolymers produced by chemical oxidation. During the cyclic voltammetry electropolymerization, a significant inhibition effect of *m*PD monomer on the PHT electropolymerization was observed.

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1. Introduction

Polyaniline(PAN) and its derivatives have attracted much attention in the field of conductive polymers due to their excellent electrical property and extensive potential applications [1–3]. The oxi-

dative polymerization of phenylenediamines, showing novel macromolecular structure and properties [4–10], has been a very active area of research recently. All three isomers of phenylenediamine may be considered as derivatives of the parent aniline (AN), having an additional amino group in its *ortho*-, *para*- and *meta*-positions. Despite the structural similarity of these isomers, an essentially different electropolymerization behavior has been reported. *Ortho*-phenylenediamine

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(*o*PD) is able to electropolymerize, forming a linear poly(aminoaniline) [7–10] or a ladder-type polymer containing phenazine units [11,12]. Most of the physicochemical properties of resulting *o*PD polymer, such as the electrical conductivity, electrochemical characteristics, spectral, and anion doping behaviors, are very different from those of PAN. Also, some properties of electropolymerized *o*PD/AN copolymer are significantly dependent on the *o*PD/AN ratio and polymerization conditions [13]. It is reported that the *para*-phenylenediamine (*p*PD) can efficiently enhance the electropolymerization rate of AN [14]. The electrochemical properties and morphology of the *p*PD/AN copolymers are apparently different from those of PAN. Similar results have also been obtained for AN copolymerization with a substituted *p*PD, i.e., 2,5-diaminobenzenesulfonic acid [15].

In contrast, the third known isomer, *meta*-phenylenediamine (*m*PD), shows a very strong inhibition of the anodic process rate in the electrochemical copolymerization of *m*PD and AN. The *m*PD/AN copolymers formed thus seem to bear some remaining functionalities and some properties that are quite different from those of pure homopolymers. Furthermore, the conductivity of the *m*PD/AN copolymers could be facily adjusted by controlling the *m*PD/AN ratios [5]. The redox properties of the polymers depend greatly on the monomer concentration [16]. In particular, the many primary amino groups on the *m*PD/AN copolymer chains are very useful for further modification [17]. However, the *m*PD homopolymer and *m*PD/AN copolymer exhibit much lower solubility than the homopolymers of *o*PD and *p*PD as well as their copolymers with AN. In fact, the poor solubility of *m*PD polymers is always an insurmountable obstacle to their characterization, modification and processing.

We have previously investigated the chemical oxidation copolymerization between *m*PD with AN derivatives [9,18,19]. Unfortunately, the solubility of the copolymers with more than 70 mol% *m*PD is still low although *m*PD/*ortho*-phenetidine (PHT) copolymer exhibits much better solubility than *m*PD/*o*-anisidine/2,3-xylylidine copolymer. Until now, it seems that no information is known on the electrocopolymerization of *m*PD with PHT. In

the present work, the PHT which contains an ethoxy group was chosen as a comonomer to improve the solubility of *m*PD polymer from the three electropolymerization techniques. The dependence of electropolymerization characteristics, electroactivity, electrochromism, and solubility of polymer films on the *m*PD/PHT ratio and polymerization technique was systematically studied for the first time.

2. Experimental

Meta-phenylenediamine (*m*PD), *ortho*-phenetidine (PHT) (ACROS), and H₂SO₄ of analytical reagent grade were obtained commercially and used as received. We used a typical three-electrode cell consisting of a 1 cm² platinum(Pt) sheet as working electrode, a 1 cm² Pt sheet as counter electrode, and a saturated calomel reference electrode (SCE). Before carrying out electropolymerization the Pt electrode was cleaned with concentrated sulfuric acid, DMSO, and water. All the electrochemical experiments were performed at room temperature in air atmosphere, using an EG&G Princeton Applied Research (Princeton, NJ, USA) Model 273A potentiostat. *m*PD/PHT polymer films were obtained and deposited on the working electrode in solutions of 0.02 M monomers and 0.5 M H₂SO₄ by applying a sequential linear potential sweep between –0.2 and +1.2 V at 50 mV s^{–1}, a constant potential or a constant current. Cyclic voltammetric (CV) measurement of the electroactivity of the *m*PD/PHT copolymer films was performed in 0.5 M H₂SO₄ at 50 mV s^{–1}. Prior to the CV measurement, the film electrode was rinsed by dipping it into distilled water for about 24 h to remove the excess acid and oligomers produced.

3. Results and discussion

3.1. Cyclic voltammetry of *meta*-phenylenediamine and *ortho*-phenetidine copolymerization

A series of representative cyclic voltammograms (CVs) of *m*PD/PHT copolymerization on a platinum electrode in 0.5 M H₂SO₄ containing

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