

In situ UV–vis spectroelectrochemistry of poly(*o*-phenylenediamine-*co*-*m*-toluidine)

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Received 3 December 2006; received in revised form 4 February 2007; accepted 10 February 2007

Available online 17 February 2007

Abstract

Results of *in situ* UV–vis spectroelectrochemical studies of the electropolymerization of *o*-phenylenediamine (OPD), *m*-toluidine (MT) and the copolymerization of OPD with MT are reported. Electropolymerization was performed in aqueous acidic medium at a constant potential of $E_{\text{SCE}} = 1.0$ V at an indium doped tin oxide (ITO) coated glass electrode. The course of homopolymerization was followed for MT and OPD solutions with various monomer concentrations. The spectral characteristics of the mixed solutions were studied at a constant concentration of MT and various concentrations of OPD in the comonomer feed. An absorption band at $\lambda = 497$ nm was assigned to the head-to-tail mixed dimer/oligomer resulting from the cross reaction between OPD and MT cation radicals. UV–vis spectra recorded during copolymerization show dependence of the growth of the band at $\lambda = 497$ nm on OPD concentration in the feed. At lower OPD feed concentration it appears as the major band in the corresponding spectra. The UV–vis spectra recorded for the copolymer films suggest the incorporation of both monomer units in the copolymer. The FT-IR spectra of the copolymers show the presence of phenazine type structures in the copolymer backbone.

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Keywords: Poly(*m*-toluidine); Poly(*o*-phenylenediamine); Copolymers; Spectroelectrochemistry

1. Introduction

Electronically conducting polyaniline (PANI) has attracted significant attention, its application in sensors [1], microelectronic devices [2], corrosion protection [3], electromagnetic shielding [4] and in optical and electronic devices [5] is under investigation.

However, the insolubility of PANI in common organic solvents makes its applications difficult. Therefore, efforts have been made to modify PANI structure and to overcome the difficulties associated with the use of PANI by using different approaches. Preparation of substituted PANI through posttreatment of the base form of the PANI [6] has been reported. Extensive studies of polymers of substituted anilines, prepared through electrochemical or chemical homopolymerization, have been carried out [7–9]. *m*-Toluidine (MT) is a substituted aniline with a $-\text{CH}_3$ group attached to the aromatic ring. A number

of reports is available on studies of poly(*m*-toluidine) (PMT). The redox and electrochromic behavior of PMT is closely similar to PANI but PMT shows better solubility in comparison with PANI [10–14]. *o*-Phenylenediamine (OPD) is another substituted aniline having an extra $-\text{NH}_2$ group in the *ortho* position. Poly(*o*-phenylenediamine) POPD has shown differences in molecular structure and properties when compared with PANI [15]. It has been reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoxaline repeat units and to exhibit unusually high thermal stability [16–18]. POPD has a variety of potential applications in the fields of electrochromism [19], sensors [20–22], rechargeable batteries [23] and corrosion protection [24]. In recent years copolymerization is also considered as an important method to improve the properties of homopolymers. Copolymerization of ANI with substituted anilines, which bear various functional groups, leads to modified copolymers, which show electrochemical characteristics considerably different from those of the homopolymers [25–29]. The primary advantage of copolymerization is that the properties of the resulting material (copolymer) can be regulated by adjusting the ratio of the monomer concentrations [30]. Several reports are available on aniline or substituted aniline-based

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copolymers [31–37]. In many cases the copolymers exhibit better properties than the homopolymers [38–45]. Recently we have reported on the electrochemical copolymerization of OPD with *o*-toluidine OT and MT, respectively, both being substituted anilines, with various concentrations of OPD in the comonomer feed [46–47]. The homo/copolymers were characterized with cyclic voltammetry (CV) and *in situ* conductivity measurements. The copolymers showed an extended electrode potential range of redox activity and good redox response at higher pH-values in comparison with the homopolymers POPD, POT and PMT as well as good electrochemical stability.

It is frequently assumed that during electropolymerization of ANI and substituted anilines highly reactive intermediates (radical cations) are produced [48]. These intermediates react subsequently either with neutral solution species or with other intermediates (most likely radicals) being present at the electrode/solution interface in significant concentration giving oligomers/polymers which are finally deposited on the electrode surface. Generally, formation of PANI is believed to proceed via the head to head, tail to tail or head to tail coupling of radical cations. The radical cation intermediates formed during the polymerization of ANI have been examined with a rotating disc electrode [49] and electrochemical thermospray mass spectroscopy [50]. An analysis of the possibility of the participation of radical cations via fast scan cyclic voltammetry has been reported [51]. Several reports are available on the use of *in situ* UV–vis spectroscopy to detect short-lived intermediates formed during the electrooxidation of ANI/substituted ANIs. The presence of a short-lived intermediate (nitrenium cation) during the electrooxidation of ANI has been suggested by Genies and Lapkowski [52]. A transient absorbance band at $\lambda = 430$ nm observed during the polymerization process of ANI has been assigned to an intermediate species [49,53]. Studies of the initial stages of electropolymerization of ANI and *p*-aminodiphenylamine using *in situ* FT-IR and UV–vis spectroscopy also reveal the formation of radical intermediates [54]. It was observed during fast scan UV–vis spectroelectrochemical studies of electrooxidation of *o*-toluidine that the spectrum corresponding to the first scan of the potential was different from those of the polymer itself [55]. Malinauskas and Holze [56–58] have used UV–vis spectroscopy for the investigation of the intermediates generated during the electrooxidation of various ring and *N*-alkyl substituted anilines. In all cases stable intermediates were observed.

There are only few reports on the processes following the early stages of electrochemical copolymerization [59–62]. The present study describes the initial stages of copolymerization of OPD with MT, monitored with *in situ* UV–vis spectroscopy and optically transparent indium–doped tin oxide (ITO) glass electrodes in different solutions having a constant concentration of MT and varying OPD concentrations. For comparison further polymer films were prepared by depositing homo/copolymer films on ITO glass electrodes; their spectra were recorded at selected electrode potentials. Additional evidence needed for suggesting a molecular structure of the electropolymerization was obtained with FT-IR spectroscopy (*ex situ*) of the homo/copolymers.

2. Experimental

Reagent grade *m*-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).

In situ spectroelectrochemical studies were performed using a spectroelectrochemical cell containing an optically transparent ITO coated glass as working electrode, a platinum wire and saturated calomel electrode as counter and reference electrode, respectively. The electropolymerization process was carried out in a quartz cuvette of 1 cm path length assembled as an electrochemical cell with the working electrode (ITO coated glass electrode with a specific surface resistance of 10–20 Ω cm⁻²) mounted perpendicular to the light path. The reference electrode was connected to the cuvette with a salt bridge. In the reference channel of the spectrometer a quartz cuvette containing an ITO coated glass electrode without polymer coating was inserted. Before each experiment, the ITO coated glass sheets were degreased with acetone and rinsed with plenty of ultrapure water. Before each spectroscopic measurement base line correction was made. A constant potential of $E_{\text{SCE}} = 1.0$ V was applied by using a custom-build potentiostat. UV–vis spectra were collected continuously at different polymerization times for the pure and mixed solutions of the monomers and at different applied potentials for the respective polymer films, with a PC-driven Shimadzu UV-2101 PC scanning spectrometer (resolution 0.1 nm). Homopolymerization was performed with OPD containing solutions with five different concentrations ranging from 0.01 to 0.05 M and a 0.2 M MT solution. 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 MT (0.2 M) in the feed. FT-IR spectra of the homo/copolymers were recorded with a Perkin-Elmer FT-IR-1000 spectrophotometer and KBr pellets at 2 cm⁻¹ resolution (eight scans each).

3. Results and discussion

3.1. Spectroelectrochemistry of the homopolymerization of OPD

Representative spectra recorded during the initial stages of electrooxidation of an OPD solution are shown in Fig. 1a. After switching the electrode potential to $E_{\text{SCE}} = 1.0$ V, two bands at $\lambda < 300$ and 492 nm were observed. Soon afterwards a band at $\lambda = 462$ nm appears followed by the appearance of a shoulder at $\lambda = 420$ nm and a band at $\lambda = 600$ nm. The band at $\lambda = 492$ nm diminishes after some time while the band initially observed at $\lambda = 462$ nm becomes the principal band in the corresponding spectra as the electrolysis proceeds.

There are two different types of structures suggested for POPD. Work based on infrared, Raman and UV–vis spectroscopies, quartz crystal microbalance, radiotracer and electrochemical techniques have led to the hypothesis of a phenazine-type structure of POPD [23,32,63–68]. A PANI-like

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