

Studies on monitoring the composition of the copolymer by cyclic voltammetry and in situ spectroelectrochemical analysis

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Abstract

Electrochemical copolymerization of diphenylamine (DPA) with *ortho*-toluidine (OT) was carried out in 4M sulphuric acid medium by cyclic voltammetry. Cyclic voltammograms (CVs) of the copolymer films were recorded to deduce the electrochemical characteristics. In situ UV–visible spectroelectrochemical studies on copolymerization were carried out using indium tin oxide (ITO) coated glass plate as working electrode for different feed ratios of DPA and OT. UV–visible spectral characteristics show clear dependencies on the molar feed composition of DPA or OT used in electropolymerization. Derivative cyclic voltabsorptogram (DCVA) was deduced at the wavelength corresponding to the absorption by the intermediate species and used to identify the intermediates generated during the electropolymerization. The molar composition of DPA and OT units in the copolymer for the copolymers synthesized with different molar feed ratios of DPA and OT was determined by UV–visible spectroscopy. Reactivity ratios of DPA and OT were deduced by using Fineman–Ross and Kelen–Tudos methods and the observed differences in the composition of DPA/OT in the copolymers were correlated with CV characteristics and results obtained from in situ spectroelectrochemical studies.

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1. Introduction

Electrically conducting polymers have attracted a great deal of attention in the last few decades because

of their unusual intrinsic properties. The possibility of synthesizing materials having combined properties of organic polymers and of semiconductors becomes the main interest for both the academician and industrial researchers [1–4]. Among conducting polymers, polyaniline (PANI) is the most frequently used one for commercial applications, probably due to its thermal and environmental stability [5–7]. The multi various applications for conducting polymer demand different properties and good processability. As far as PANI is

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concerned, its insolubility in common organic solvents and infusibility restricts processability. Nevertheless, enhanced solubility has been noticed for alkyl, alkoxy and sulphonic acid substituted PANIs [8–10]. However, many substituted PANI showed lesser conductivity than PANI [11]. Furthermore, the conductivity of doped emeraldine form of PANI is mainly due to the formation of polarons, which confer metallic properties of the polymer [11,12].

The synthesis of poly(alkyl anilines) has enabled the stabilization of charge carriers, since the electron-donating effect of these substituents increases the basicity of the imine units [13]. Recently, polymerization of poly(2,3-dimethoxy aniline) were carried out and used as humidity sensor [14]. Extensive studies on PANI and some of its substituted derivatives have been carried out in the past few years. Poly(*ortho*-toluidine) (POT) is a derivative of PANI, where $-\text{CH}_3$ is substituted in the aromatic ring. It has been reported that the conductivity of POT at room temperature is one or two order of magnitude lower than PANI [15]. Meixiang Wan et al. [16] studied the structure and electrical properties of POT in aqueous HCl medium. Electrochromic properties of POT have been reported [17].

The N-substituted derivatives exhibit an additional property of having conductivity comparable to that observed for PANI. Poly(diphenylamine) (PDPA), a *N*-aryl substituted PANI derivative, possesses properties intermediates between PANI and poly(*p*-phenylene). In comparison with PANI, the copolymers with phenyl-substituted and N-substituted anilines give better solubility, disordered structure and decreased conductivity with enhanced electrochemical stability [18–21]. Reports are also available on the polymerization of *N*-alkyldiphenylamine, 3-methoxydiphenylamine and 3-chlorodiphenylamine [22,23]. Poly(*N*-methyl aniline), an alkyl N-substituted aniline is one of the materials which has received relative attention and few reports discussing its electrochemical properties [24].

Copolymerization of aniline with some of its derivatives, which bear various functional groups, leads to modified copolymers, having some remaining functionalities and possessing interesting properties. The primary advantage of copolymerization is that it leads to a homogenous material, the properties of which can be regulated by adjusting the ratio of the concentration of monomers in the feed. Karyakin et al. [24,25] obtained self-doped PANI by copolymerization of aniline with some carboxyl and sulfonyl substituted derivatives. Yang and Wen [26,27] reported an acceleration of rate for electropolymerization of PANI with *p*-phenylenediamine or with 2,5-diaminobenzenesulfonic acid. Several reports are available on the copolymerization of aniline and aniline derivatives [24–27]. However, reports involving diphenylamine (DPA) as one of the monomer in copolymerization is scarce. Recently Wu et al. [28] re-

ported the electrochemical copolymerization of DPA with anthranilic acid and the copolymer formation were further confirmed by X-ray photon spectroscopy (XPS). Electrochemical copolymerization of DPA with aniline using pulse potentiostatic method have been reported [29]. Electrochemical copolymerization of DPA with benzidine [30] have been carried out. Electrochemical copolymerization of DPA with 2,5-diaminobenzene sulphonic acid (DABSA) were reported [31]. The intermediates formed during the electrochemical copolymerization between DPA and DABSA were followed through in situ UV-visible studies. XPS was used to characterize the copolymer formed between DPA and DABSA. Copolymerization of 2-methoxyaniline with substituted anilines have been recently reported [32].

The characterization of the conducting forms of polymers have been performed by in situ spectroelectrochemical measurements, including optical absorption, vibration spectroscopy etc. UV-visible spectroscopy appears to be a useful tool for studying the electropolymerization process. Highly reactive intermediates are formed during the electropolymerization, these species react subsequently with solution species, giving oligomers and polymers, which are deposited on the electrode surface as a compact phase. This kind of study has the advantage to follow the doping process step by step. Leger et al. [33] presented a detailed study on the electropolymerization of *o*-toluidine by fast scan UV-visible differential reflectance spectroelectrochemistry. They identified a few possible intermediates as precursors to polymer formation. Genies and Lapkowski [34] used UV-visible spectroscopy to follow the course of polymerization of aniline and reported that the formation of nitrenium cations as intermediates during the polymerization. Malinauskas et al. [35,36] has monitored the early stages of polymerization of aniline and its derivatives through UV-visible spectroscopy.

In this present study, DPA and OT have been selected as monomers for performing electrochemical copolymerization in 4M H_2SO_4 medium. Cyclic voltammetry was used to deposit polymeric films on platinum working electrode and subsequent characterization. UV-visible spectroelectrochemical studies were performed to identify the intermediates formed during copolymerization. Copolymers were synthesized and the composition of the two monomers in the copolymer and reactivity ratios of DPA and OT were determined. A copolymer model which explains the changes in electrochemical and spectroelectrochemical characteristics is deduced.

2. Experimental

Diphenylamine (E-Merck) and *ortho*-toluidine (E-Merck) were used without any further purification. All the reagents used are of analytical grade.

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