

Electrochemical copolymerization of aniline with *m*-aminophenol and novel electrical properties of the copolymer in the wide pH range

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Abstract

A copolymer, poly(aniline-*co-m*-aminophenol), has been synthesized using repeated potential cycling. The monomer concentration ratio, acid concentration and applied potential strongly affect the copolymerization rate and the properties of the copolymer. The optimum conditions for the copolymerization are that the scan potential range is controlled between -0.10 and 0.95 V (vs.SCE), and a solution consists of 0.34 M aniline, 0.012 M *m*-aminophenol and 2 M H_2SO_4 . The IR spectra of the copolymers demonstrate that the *m*-aminophenol units are included in the copolymer chains. The cyclic voltammograms of the copolymers in 0.3 M Na_2SO_4 solution with various pH values were performed at the potential ranges from -0.20 to 0.80 V and at a scan rate of 60 mV s⁻¹. The results indicate that the copolymer still hold 41.7% of the electrochemical activity when the copolymer electrode was transferred from a solution of pH 5.0 to a solution of pH 11.0 in the potential range of -0.20 to 0.80 V. An impedance plot of the copolymer in a solution with pH 12.0 and at 0.40 V is constructed of a semicircle and a Warburg line with a slope of 1. This means that the electrode reaction of the copolymer at pH 12.0 is also under mass transfer control. The conductivity of the copolymer prepared under the optimum conditions is 1.42 S cm⁻¹, and slightly depends on the pH value. Thus, the pH dependence of the electrical properties of the copolymer is improved compared with poly(aniline-*co-o*-aminophenol), and is much better than that of the parent polyaniline.

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1. Introduction

Among conducting polymers, polyaniline is a most promising material due to its high conductivity, good redox reversibility, swift change of color with applied potential and good stability in aqueous solutions and air. However, its properties including conductivity, electrochemical activity, electrocatalytic ability, electrochromic phenomenon and conversion of light to electricity are strongly affected by the pH value. When $pH > 5$, polyaniline has a low conductivity and a little electrochemical activity. In this case, polyaniline almost loses its practical applications. Therefore, pH dependence is a decisive factor that controls the properties and applications of polyaniline. A successful way for improving pH dependence of polyaniline was performed by using sulfonation [1–3]. After sulfonation, polyaniline becomes sulfonic acid ring-substituted polyaniline (i.e. self-doped polyaniline). The self-doped

polyaniline has a conductivity of ~ 0.1 S cm⁻¹, which is independent of pH in the aqueous acid solutions of $pH \leq 7.5$. Since then, many papers reported the preparation of the self-doped polyaniline by the chemical copolymerization of aniline with *o*-aminobenzenesulfonic acid [4] and *p*-aminodiphenylamine with *o*-aminobenzenesulfonic acid [5]; and the electrochemical copolymerization of aniline with *m*-aminobenzoic acid, anthranilic acid, *m*-aminobenzenesulfonic acid (*m*-ABS) [6–8] and other monomers [9–16]. Among these self-doped polyanilines, poly(aniline-*co-m*-ABS) prepared electrochemically still has a redox activity in the buffer solution of pH 9 and at a scan rate of 25 mV s⁻¹ [7]. Also, polyaniline film can directly react with the concentrated sulfuric acid to form the self-doped polyaniline that possesses a good electrochemical activity in the Na_2SO_4 solution of pH 10.6 and at a scan rate of 60 mV s⁻¹ [17]. It is clear that the pH dependence of the electrochemical activity of the self-doped polyaniline was improved significantly. This is because sulfonic acid is a strong acid. The $-SO_3H$ group on the polyaniline chain plays an important role in the self-protonation of the polymer by the internal acid–base equilibrium [2].

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The copolymer, poly(aniline-*co-o*-aminophenol), has rather high conductivity, good electrochemical activity up to pH 9.6 [18] and higher specific energy [19], compared with the parent polyaniline. This is due to the fact that *o*-aminophenol has a functional group –OH. The –OH group in phenyl ring can be oxidized to quinone, and quinone can be reduced, which are accompanied with proton exchange between the copolymer and the solution. The redox reactions of the –OH group play an important role in adjusting pH around the copolymer electrode, which improve the pH dependence of the copolymer. After sulfonation, a –SO₃H group was introduced on the poly(aniline-*co-o*-aminophenol) chain. Thus, the pH dependence of the conductivity and the electrochemical activity of the sulfonated poly(aniline-*co-o*-aminophenol) was improved further [20].

Above results show that the copolymerization of aniline and a monomer possessing a functional group is a promising way to improve the pH dependence of polyaniline. Wei et al. first reported the electrochemical copolymerization of aniline with *o*- or *m*-toluidine [21]. In comparison with the chemical copolymerization, one of advantages for the electrochemical copolymerization is that the effect of various factors including monomer concentration ratio, pH and the applied potential on the copolymerization rate is readily observable, which is very convenient for determining optimum copolymerization conditions.

Based on the previous work, we try to study the copolymerization of aniline and *m*-aminophenol. This is because the different positions of the –OH group on phenyl ring may affect the copolymerization behavior, which would affect the properties of the copolymers.

2. Experimental

The chemicals used were of reagent grade. Aniline was distilled before use. Doubly distilled water was used to prepare solutions. The pH values of the solutions were determined by using a PXD-12 pH meter. An electrolytic cell for the synthesis of the copolymer consisted of two platinum foils and a saturated calomel reference electrode (SCE). The area of a working electrode was 4 mm × 4 mm. All potentials given here are referred to a saturated calomel electrode (SCE).

After synthesis, poly(*m*-aminophenol) and poly(aniline-*co-m*-aminophenol) were washed with 0.05 M H₂SO₄ solution to remove unreacted *m*-aminophenol and aniline. The cyclic voltammograms of the copolymers were performed in 0.2 M H₂SO₄ solution first, and then in 0.3 M Na₂SO₄ solution with various pH values. The scan rate was set at 60 mV s⁻¹ in all experiments of cyclic voltammetry. Before recording the cyclic voltammograms and impedance plots in the following tested solutions, poly(aniline-*co-m*-aminophenol) films were pre-treated for six cycles in the corresponding tested solution. The aim is to establish pre-equilibrium of pH between the polymer films and the tested solution. The experiments of cyclic voltammetry and impedance measurements were performed on a CHI 407 electroanalysis apparatus and an Autolab instrument, respectively. Frequency sweeps extended from 10⁴ to 0.01 Hz using a sinusoidal perturbation signal of 10 mV, peak-to-peak.

The molecular weight of the copolymer was determined by using osmometry. The copolymer sample for the determination of the molecular weight was immersed in 0.1 M NH₄OH solution for 24 h followed by filtering. The precipitate cake on the filter paper was partially dried under suction and finally was washed for several times with distilled water. The purpose is to remove the dopant in the copolymer. Here, the dopant is SO₄²⁻ ions that were doped into the copolymer film during the copolymerization process. 30.0 mg of the copolymer were added in 10 ml of *N*-methyl-2-pyrrolidone, which was sonicated for 6 h. In fact, only 14.8 mg of the copolymer were dissolved. The temperature for the determination of the molecular weight was controlled at 20.3 °C.

The copolymer samples used for the determination of IR spectra were in the oxidized forms. They were first washed by using 0.05 M H₂SO₄ solution as mentioned above, and then washed by using 0.01 M HCl solution followed by drying under dynamic vacuum at 105 °C for 24 h. The IR spectra of the copolymer samples were measured on a pressed pellet with KBr employing a Tensor 27 spectrometer. The conductivity of the copolymer was determined on a pressed pellet using a four-probe technique. All experiments were carried out at 25 ± 2 °C, except the determination of the molecular weight of the copolymer.

3. Results and discussion

3.1. Electrochemical polymerization of *m*-aminophenol

A solution consisting of 0.012 M *m*-aminophenol and 0.3 M Na₂SO₄ with pH 4.0 was used for the synthesis of poly(*m*-aminophenol). The electrochemical polymerization of *m*-aminophenol was carried out by using repeated potential cycling between –0.10 and 1.00 V (Fig. 1). An anodic peak appears at 0.66 V on the cyclic voltammogram for the first cycle and then its peak current decreases quickly with time. The electrochemical polymerization behavior of *m*-aminophenol is quite different from that of *o*-aminophenol, in which there are two anodic peaks on the cyclic voltammogram for the first cycle [18]. After electrolysis, a thin yellow film was found on the working electrode, which was poly(*m*-aminophenol). The cyclic

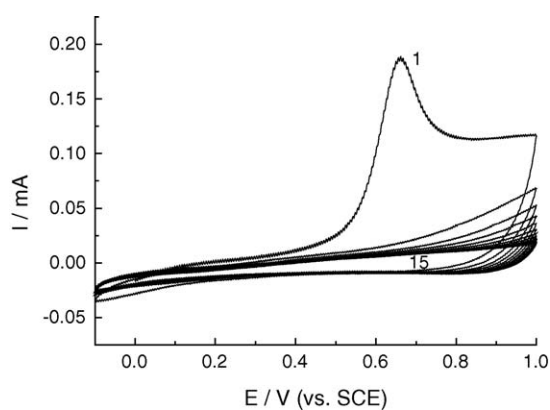


Fig. 1. Growth of poly(*m*-aminophenol) film during electrolysis of a solution containing 0.012 M *m*-aminophenol and 0.3 M Na₂SO₄ with pH 4.0: (1) first cycle; (15) 15th cycle, at a scan rate of 60 mV s⁻¹.

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