گزارش به‌سرعت در وب آکادمی (Graph Attention Networks)
کارگاه آنلاین آموزش استفاده از وب آکادمی
کارگاه آنلاین مقاله روزنامه انگلیسی
Water-soluble Aniline/o-Anisidine Copolymer: Enzymatic Synthesis and Characterization

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Received 5 January 2010; accepted 19 July 2010

The synthesis of aniline/o-anisidine copolymer was described by enzymatically oxidative polymerization of aniline (An) and o-anisidine (As) using poly(sodium 4-styrene sulphonate) (SPS) as a template. The enzyme horseradish peroxidase (HRP) was used as a catalyst with a stoichiometric amount of hydrogen peroxide as an oxidant at pH 4.3 in 0.01 M sodium phosphate buffer solution medium. The UV-vis spectra of An/As copolymer (1:1) exhibited more similarity to the spectral features of o-anisidine. To address the effect of monomer ratio in the synthesized copolymer, the polymerization was carried out in different ratios of o-anisidine to aniline. The resultant An/As copolymer was characterized by FTIR and UV-vis techniques. The results showed that the enzymatic polymerization produced a real copolymer containing aniline and o-anisidine units. The similarity of the UV-vis spectra of the copolymer to enzymatically synthesized poly(o-anisidine) confirmed that the amount of monomeric unit of o-anisidine was higher than aniline. This was due to a much higher reactivity of the former. Thus, as expected, this copolymer spectral characteristics were more similar to the enzymatically synthesized poly(o-anisidine). UV-Vis and FTIR spectra confirmed that the undoped form of An/As copolymer, unlike the chemically synthesized copolymer, has formed a complex with SPS. This biomimetic approach offered an unsurpassed easiness in the synthesis, processability, stability and environmental compatibility.

INTRODUCTION

The field of conducting polymers has attracted considerable attention due to their fascinating electrical and optical properties that are used in many technological applications [1,2]. Polyaniline is one of the most explored conducting polymers because of its applications in a wide range including electrochromic devices [3], light-emitting diodes [4], lightweight batteries [5] and corrosion protection [6]. However, the practical applications of polyaniline have been limited due to harsh chemical conditions in the synthesis and purification procedure that often lead to an inflexible polymer. To address this problem and improve processability, a diverse set of modified polymerizations have been investigated [7-9]. The enzymatic polymerization of anilines has been studied as a...
promising, environmentally benign and more efficient alternative; this is also within the context of "green polymer chemistry". The HRP is a Fe containing porphyrin type structure which is shown in Scheme I. The enzyme horseradish peroxidase (HRP) in the presence of hydrogen peroxide catalyzes the polymerization of phenol and aromatic amines [10]. For the polymerization of aniline a unique enzymatic approach (HRP as a catalyst and \( \text{H}_2\text{O}_2 \) as an oxidizing agent) was recently developed. This polymerization has been carried out in presence of a polyelectrolyte template such as \( \text{poly}(4\text{-styrene sulphonate}) \) (SPS) or \( \text{poly}(\text{vinylphosphonic acid}) \) (PVP) under mild conditions in aqueous pH 4.3 buffer [11,12].

The other approach that may improve the poor processability of polyaniline is to produce its corresponding composites or copolymers. Accordingly, on the polyaniline-type copolymers a pioneering work was done by Wei et al. [13,14]. The copolymerization of aniline and \( o\)-anisidine was performed by chemical oxidation [15]. It was observed that in the chemical polymerization the amount of \( o\)-anisidine incorporated in the copolymer chains are more than aniline monomers due to the higher reactivity of the former.

Recently, we have reported the enzymatic polymerization of aniline derivatives [16]. The aniline and \( o\)-anisidine were chosen for enzymatic copolymerization in this study since they are homopolymerized under the same conditions. The results of enzymatic copolymerization were also compared with the chemical synthesis of these monomers. This comparison demonstrates that the results of these two methods are completely different. In a chemical procedure, the copolymer is produced in a doped form but by enzymatic method, the copolymer is in an undoped form. Due to the higher reactivity of \( o\)-anisidine relative to aniline, it is expected that the results would be similar to the enzymatic-catalyzed polymerization of \( o\)-anisidine.

This paper describes an enzymatic copolymerization of aniline and \( o\)-anisidine in presence of an anionic polyelectrolyte, SPS. The reaction was carried out in mild conditions such as aqueous, pH 4.3 buffer solution. The final product was a water-soluble and electroactive aniline/\( o\)-anisidine (An/As) copolymer/SPS complex. The details of the synthesis and characterization of this simple, cost-effective and environmentally compatible method are presented.

**EXPERIMENTAL**

**Materials**

Poly(sodium 4-styrene sulphonate) (\( M_W \) of 70000), used in this study was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without any further purification. HRP (EC 1.11.1.7) (about 170 units/mg), hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) (30 wt%), aniline and \( o\)-anisidine were obtained from Merck. Before the usage, aniline was purified by vacuum distillation in the presence of Zn powder.

**Polymer Synthesis**

A procedure for the preparation of the An/As copolymer is as follows:

Typically, in 1:1 molar ratio of aniline and \( o\)-anisidine, 2 \( \mu \text{L} \) aniline (0.023 mmol), 2.5 \( \mu \text{L} \) \( o\)-anisidine (0.023 mmol) and 0.0093 g SPS (0.045 mmol) (based on monomer repeat unit) were added to 7.5 mL 0.01 M sodium phosphate buffer solution (pH 4.3) at room temperature under constant stirring. The mixing was followed by the addition of a catalytic amount of the enzyme (1 mg HRP). To initiate the reaction, 2.3 mL of diluted hydrogen peroxide (0.02 M) was added dropwise under vigorous stirring over a period of 1 h and immediately after the first few drops, the reaction solution
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turned bluish-violet. The reaction was then left to stir 24 h at the ambient temperature. The resulting dark violet solution was transferred to a cellulose tube and dialyzed (cut off molecular 3000) overnight to remove any unreacted monomers and oligomers. The An/As copolymer in complex with SPS exhibits nominal structure that is shown in Scheme II.

For comparison, this copolymer was also synthesized by chemical oxidation using ammonium persulphate in 1 M HCl aqueous solution [15]. In a 100 mL flask, equimolar amounts of each monomer and SPS were dissolved in 50 mL 1 M HCl and the solution was cooled below 5°C by using an ice bath. A pre-chilled solution of 6.5 mmol of ammonium persulphate in 15 mL 1 M HCl was added drop by drop under vigorous stirring. The resulting solution was left in an ice bath for 1 h. The final solution was dark green. Further consideration demonstrated that the copolymers obtained by chemical method are different from those derived from enzymatic method (the chemically synthesized copolymer is green whereas the enzymatically produced copolymer is violet).

Characterization
The FTIR measurements were carried out with the help of a Bomem MB-Series FTIR spectrometer in the form of KBr pellets. UV-Vis spectra were obtained using a Shimadzu UV-2100 spectrophotometer. The cyclic voltammetry (CV) measurements were performed with a Metrohm polarograph model 746 VA Trace Analyzer. The cyclic voltammograms were recorded at room temperature using a three electrode cell: platinum as an auxiliary electrode, Ag/AgCl as the reference electrode and Pt foil (0.2 cm² surface area) as the working electrode. The cyclic voltammograms were obtained in a 1.0 M HCl electrolyte and scanned from -0.1 to 1.0 V at various scan rates in the range of 50-500 mV/s.

RESULTS AND DISCUSSION

The copolymerization of aniline with o-anisidine has been carried out by enzymatic polymerization under the condition similar to the enzymatic synthesis of alkoxyanilines [16]. After the addition of the first drop of hydrogen peroxide, the reaction media of 1:1 molar ratio of aniline to o-anisidine developed a bluish-violet colour within several seconds indicating a very fast aniline and o-anisidine oxidation without induction period. The colour of the reaction mixture was violet throughout the reaction which demonstrates the copolymer is in an undoped form.

In contrast, a chemically synthesized copolymer was dark green, an indication of being in a doped...
Figure 1 displays the UV-vis spectra of enzymatically synthesized (a) polyaniline, (b) poly(o-anisidine) and (c) An/As copolymer with 1:1 molar ratio of two monomers.

The UV-vis spectra of An/As copolymer (1:1) exhibit more resemblance to the spectral features of o-anisidine. The spectrum of copolymer is dominated by two bands; a strong absorption band at 300-
Figure 2. UV-Vis absorption spectra of the copolymer with different molar ratios of aniline:o-anisidine (1:1, 1:6, 1:9, 4:1 and 9:1).

360 nm (peak 1) and a broad band at 500-600 nm (peak 2). According to the general practice of peak assignment, first peak is attributed to the $\pi$-$\pi^*$ transition of the benzenoid moieties in the An/As copolymer linear structure or simply to the band gap of the copolymer [15]. The second peak closely resembles the benzenoid-quinoid transition in the copolymer [17-19].

The influence of polymerization conditions such as monomer feed ratios and pH has been also investigated. To address the effect of monomer ratio in the synthesized copolymer, the polymerization was carried out in different ratios of o-anisidine to aniline. The results are shown in Figure 2. In this figure, the UV-vis spectra of five copolymer solutions with An/As ratios of 9:1, 4:1, 1:1, 1:6 and 1:9 are shown.

The comparison of the UV-vis spectra of the copolymers obtained by various ratios of monomers demonstrates that while the ratio of aniline to o-anisidine increases there is an aniline doped peak gradually emerging at 760 nm. Moreover, as the ratio of o-anisidine to aniline increases, the UV-vis spectrum resembles the spectra reported in the previous work [16]. This result is also confirmed by FTIR data.

The homopolymers of aniline and o-anisidine were synthesized under the same reaction conditions as the copolymer of the two, and then the homopolymers were mixed to confirm the formation of copolymer. In Figure 3, the spectra of enzymatically synthesized (a) polyaniline, (b) poly(o-anisidine) and (c) a mixture of equal parts of two homopolymers are shown. As it is evident in this figure, with addition of poly(o-anisidine) to oxidized polyaniline the absorbance of 760 and 420 nm peaks diminishes. To confirm the formation of a copolymer, UV-vis spectra of enzymatically synthesized (a) An/As copolymer and (b) mixture of two homopolymers were compared with each other, as it is shown in Figure 4.
Figure 4. In other words, the product that is formed by enzymatic polymerization of aniline with o-anisidine is a copolymer rather than a mixture of two homopolymers.

Effect of pH
The copolymerization was investigated in various pH ranges. It was found that the template provides a necessary type of local environment where the pH and charge density near the template molecule are different from that of the bulk solution [20]. Therefore, the pH of the reaction medium dictates the extent of dissociation of the template polyelectrolyte and influences the solubility as well as the nature of An/As copolymer formed in the reaction. To study the effect of pH, the polymerization was carried out under different pH conditions ranging from pH 4 to 6 (pH in 4.3, 5, 5.5 and 6). The absorption spectra of An/As copolymer/SPS complex synthesized using HRP in the above range of pH are given in Figure 5.

The peak at 550 nm suggests that the highest degree of polymerization takes place at pH 4.3 (maximum intensity). These results demonstrate that the SPS-template polymerization of aniline and o-anisidine is strongly pH-dependent.

FTIR Spectroscopy
Figure 6 shows FTIR spectra of An/As (1:1) copolymer/SPS complex by (a) enzymatically and (b) chemical synthesis, in the region from 400 to 4000 cm$^{-1}$. A broad band centered at 3435 cm$^{-1}$ due to the characteristic N-H stretching vibration suggests the presence of -NH- group in the copolymer [21]. Two weak peaks at 3050 and 2922 cm$^{-1}$ are due to the aromatic and aliphatic C-H stretching vibrations, respectively [22]. The absorption peak at 1628 cm$^{-1}$ is characteristic of the electronic-like absorption of the N=Q=N vibration that Q denotes the quinoid ring [23]. The peak at 1590 cm$^{-1}$ is assigned to the ring stretching of the quinoid and the other peak at 1515 cm$^{-1}$ is assigned to the benzenoid ring [24,25]. As it is observed in this figure, the band ratio of benzenoid to quinoid is significantly higher in the chemically synthesized copolymer compared to the enzymatically synthesized copolymer. This demonstrates that the enzymatically synthesized copolymer consists of great amounts of oxidative form of emeraldine base, but the chemically synthesized copolymer is in the form of emeraldine salt. These results are also in agreement with the UV-vis spectra. The band at 835 cm$^{-1}$ corresponds to the C-H bending vibrations of the $p$-substituted benzene ring. This latter observation confirms the expected head-to-tail coupling copolymerization of aniline and o-anisidine at the C-4 and N positions [26]. In the FTIR spectra of the copolymer, the absorption bands appear at 1220 and 1175 cm$^{-1}$, indicating the presence of a methoxy group on a benzene ring [15]. This fact demonstrates unequivocally the presence of o-anisidine units in the polymer. Two bands at 1006 and 1037 cm$^{-1}$ are observed for this copolymer and are attributed to S=O stretching; indicating the
presence of SPS in the enzymatically synthesized copolymer [27].

Cyclic Voltammetry

Figure 7 shows the cyclic voltammograms for An/As copolymer (1:1) in the complex with SPS in 1.0 M HCl at different scan rates. Two oxidation peaks were observed in the anodic sweep at 0.3 and 0.4 V versus Ag/AgCl sweep between -0.1 and 1.0 V. The first peak is not well resolved but it is reversible. The second one is very well defined and reversible over several cycles. The enzymatic polymerization of poly(o-anisidine) exhibits one oxidation peak [16]. Therefore, the enzymatically synthesized An/As copolymer/SPS complex could increase the electrochemical characteristics of conducting polymers. On recording the cyclic voltammograms at different scan rates between 50 and 500 mV/s, appreciable changes in the anodic and cathodic peaks current values were observed. In addition, the cyclic voltammetry confirms the electroactive nature of the An/As copolymer/SPS complex.

CONCLUSION

The An/As copolymers have been synthesized under ambient condition at pH 4.3 by enzymatic polymerization in presence of a template. Due to the much higher reactivity of o-anisidine, the structure and properties of copolymer were found to be dominated by the o-anisidine units. The copolymer functioning as an oxidant, led to an increase in the oxidant concentration of the reaction media. Therefore, the synthetic copolymer of an undoped form is confirmed by UV-vis and FTIR spectra. Also, the FTIR and UV-vis spectra suggest that the resulting polymer is a real copolymer consisting of two monomer units. The cyclic voltammograms of the synthesized An/As copolymer readily exhibit the electroactivity of the copolymer obtained.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support from the Research Council of Shahid Beheshti University, Tehran.

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