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Polymer 48 (2007) 1269–1275
polymer
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A promising copolymer of aniline and *m*-aminophenol: Chemical preparation, novel electric properties and characterization

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Received 29 June 2006; received in revised form 1 October 2006; accepted 15 December 2006
Available online 17 December 2006

Abstract

A copolymer, poly(aniline-*co*-*m*-aminophenol), was synthesized chemically. The monomer concentration ratio strongly affects the copolymerization rate and the properties of the copolymer. A solution consisting 0.34 M aniline, 0.012 M *m*-aminophenol, 0.47 M ammonium peroxydisulfate and 2 M H_2SO_4 was found to be an optimum mixture for the chemical copolymerization. The visible spectra show that a high concentration ratio of *m*-aminophenol/aniline in the mixture inhibits the chain growth of the copolymer. The spectra of IR and ^{1}H NMR demonstrate that *m*-aminophenol units are included in the copolymer chain, which play a key role in extending usable pH region of the copolymer. The result of cyclic voltammograms in a wide potential region of -0.20–0.80 V (vs. SCE) indicates that the copolymer prepared under the optimum condition still held 52.7% of the electrochemical activity when the copolymer electrode was transferred from a solution of pH 4.0 to a solution of pH 11.0, which is much better than that of polyaniline. The X-ray diffraction spectra and images of the copolymers reveal a fact that the changes in the crystal structure and morphology of the copolymers are as a function of the monomer ratio in the mixture. The conductivity of the copolymer prepared under the optimum condition is 2.3 S cm^{-1} and slightly depends on the pH value.

Keywords: Chemical copolymerization; Aniline copolymer; Electric properties

1. Introduction

Polyaniline is one of the most promising conducting polymers due to its high conductivity, good redox reversibility, swift color change with applied potential and good stability in aqueous solutions and air. These properties provide favorable conditions for its potential applications in rechargeable batteries [1,2], electrocatalysis [3], electrochromic devices [4,5], corrosion prevention [6], conversion of light to electricity [7], and super capacitor [8]. In addition, research in the field of polyaniline nanostructures has also received a great deal of attention [9–11]. Especially, the successful preparation of polyaniline nanostructures without using templates [12] is expected to open new applications for polyaniline. However, polyaniline has a low conductivity and a little electrochemical activity at pH > 4, which limit its applications in some fields, such as biochemistry and rechargeable batteries. A possible way for solving this problem is to improve the pH dependence of polyaniline.

In recent years, a great deal of attention has been paid to synthesize aniline-based copolymers. A possible reason is probably attributed to great difficulty to synthesize new conducting polymers with electric properties and stability better than polyaniline and polypyrrole. The copolymerization of aniline and other monomers offers a possibility to prepare a new polyaniline type of copolymer that not only retains the good properties of polyaniline itself but also possesses new properties. The copolymerization of aniline and a monomer was carried out by using chemical [13–18] and electrochemical [19–22] methods. Some of the aniline-based copolymers exhibited a small pH dependence of the electric properties including the conductivity and the electrochemical activity.

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0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.12.021

Especially, poly(aniline-*co*-4,4′-diaminodiphenyl sulfone) showed multicolor electrochromic behavior in a wide potential region [23].

Experimental results already demonstrated that introducing a functional group, such as $-SO_3H$ [24–26] or $-OH$ [27,28] onto polyaniline chain is a strategic way to improve the pH dependence of the conductivity and the electrochemical activity. Poly(aniline-*co*-*m*-aminophenol) prepared electrochemically has a rather high conductivity and a good electrochemical activity up to pH 11.0 [29]. So, this copolymer is a promising material for practical applications. To prepare a large amount of the copolymer to meet needs of the practical applications, we tried to synthesize it chemically. In this work, we reported the effect of the monomer concentration ratio on the properties of the copolymer, an optimum copolymerization condition and characterization of the copolymers.

2. Experimental

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. The pH values for the solution of sodium sulfate were adjusted by using a solution of sulfuric acid or a solution of sodium hydroxide.

The solutions consisting 0.68 M aniline, 2 M H_2SO_4 and different concentrations of *m*-aminophenol (0.020–0.17 M) and the solutions containing 2 M H_2SO_4 and different concentrations of ammonium peroxydisulfate (0.40–1.36 M) were prepared freshly prior to the copolymerization of aniline and *m*-aminophenol. The chemical copolymerization was carried out as follows. For example, 25 ml of an aqueous solution containing 2 M H_2SO_4 and 0.68 M ammonium peroxydisulfate was slowly added in a same volume of a solution consisting 0.68 M aniline, 0.024 M *m*-aminophenol and 2 M H_2SO_4, i.e. the mixture consisted of 0.34 M aniline, 0.012 M *m*-aminophenol, 0.34 M ammonium peroxydisulfate and 2 M H_2SO_4. The mixture was stirred with a stirring magnetic bar for 15 h at room temperature. Meanwhile, a platinum foil (4×4 mm^2) and an indium–tin oxide (ITO) conducting glass were immersed into the mixture. The copolymer was polymerized on a platinum foil and an ITO conducting glass. Both of them were washed thoroughly by using 0.02 M HCl solution followed by distilled water before the determination of cyclic voltammograms and visible spectra. Of course, most of the product was precipitated into a beaker, then filtered and finally washed with 0.02 M HCl solution until the filtrate was colorless. The purpose is to remove unreacted aniline and *m*-aminophenol, and polymers with low molecular weight. The presence of low molecular weight byproducts in the copolymer influences its macroscopic properties as well as polyaniline [30], such as density and solubility etc. The resulting product was dried under dynamic vacuum at 90 °C for 15 h and then was used to determine IR spectra, diffraction spectra, proton NMR, molecular weight and morphology.

An electrolytic cell for cyclic voltammetry consisted of a copolymer working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The cyclic voltammograms were performed on a CHI 407 electroanalysis apparatus. Before recording the cyclic voltammogram, the copolymer film was pre-treated in six cycles in the corresponding solution. This is because before the first five cycles, the area of the cyclic voltammogram decreases slowly with cycling numbers, but the shape of the cyclic voltammogram changes hardly. The former is caused by the pH difference between inside the copolymer film and the bulk solution. As further increasing the number of cycles, the equilibrium of pH between the copolymer film and the tested solution is established. In that case, the electrochemical activity of the copolymer in a solution with a given pH attains the steady state. Thus, the area of the cyclic voltammogram hardly changes with cycling number. The conductivity of the copolymer was measured on a pressed pellet using a four-probe technique. The dried copolymer sample in the oxidation state was divided into two portions. One was directly used for the determination of conductivity, and the other one was immersed into doubly distilled water for 15 h, followed by washing using distilled water and dried prior to the determination of conductivity.

The molecular weight of the copolymer was determined by using osmometry. The copolymer sample used for the determination of the molecular weight was immersed in 0.1 M NH_4OH solution with ultra-sonication for 6 h followed by filteration. The precipitate cake on the filter paper was partially dried under suction and finally was washed several times with distilled water. The purpose is to remove dopant in the copolymer. Here, the dopant is SO_4^{2-} ions that were doped into the copolymer during the copolymerization process. The copolymer used for the determination of the molecular weight was dissolved in 10 ml of *N*-methyl-2-pyrrolidone, which was sonificated for 12 h.

The visible spectra of the copolymers were carried out in a quartz cuvette with a path length of 1 cm, using an MPS-2000 double-bean spectrophotometer. The IR spectra of the copolymer and the parent polyaniline were measured on a pressed pellet with KBr using a Tensor 27 spectrometer. The proton NMR of the copolymer was conducted on a 600 MHz Bruker spectrometer at 303.1 K in dimethyl sulfoxide-d_6 (DMSO-d_6) in a 5 mm diameter NMR tube. The X-ray diffraction data of the copolymer powder were recorded using a Bruker D8 super speed X-ray instrument (Cu Kα radiation, $\lambda = 1.542$ Å). The morphology of the copolymers was observed by using an XL-30 scanning electron microscopy (SEM).

The copolymers, synthesized by using various mixed solutions, were labeled copolymer A (0.34 M aniline, 0.085 M *m*-aminophenol, 0.34 M ammonium peroxydisulfate and 2 M H_2SO_4), copolymer B (0.34 M aniline, 0.023 M *m*-aminophenol, 0.34 M ammonium peroxydisulfate, and 2 M H_2SO_4), copolymer C (0.34 M aniline, 0.012 M *m*-aminophenol, 0.34 M ammonium peroxydisulfate and 2 M H_2SO_4), copolymer D (0.34 M aniline, 0.010 M *m*-aminophenol, 0.34 M ammonium peroxydisulfate and 2 M H_2SO_4), copolymer E (0.34 M aniline, 0.012 M *m*-aminophenol, 0.47 M ammonium peroxydisulfate and 2 M H_2SO_4). Polyaniline used in the following experiments was synthesized in a solution containing 0.34 M aniline, 0.47 M ammonium peroxydisulfate and 2 M H_2SO_4.

3. Results and discussion

3.1. Electrochemical property and conductivity of poly(aniline-co-m-aminophenol)

To explain the cyclic voltammogram of the copolymer and compare the electrochemical property of the copolymer with that of polyaniline, the cyclic voltammogram of polyaniline is also presented in Fig. 1. Curves 1 and 2 in Fig. 1 are the cyclic voltammograms of polyaniline and copolymer E in 0.2 M H_2SO_4 solution, respectively. The scan rate was set at 60 mV s^{-1}. There are three oxidation peaks at 0.17, 0.45 and 0.73 V in curve 1, and their corresponding reduction peaks are at 0.01, 0.40 and 0.65 V. The first redox couple corresponds to the redox reaction between leucoemeraldine and emeraldine, which is accompanied by the exchange of anions between the polyaniline film and the solution based on the experimental result of the electrochemical quartz crystal microbalance (EQCM) [31]. The third redox couple corresponds to the redox reaction between emeraldine and pernigraniline, which is accompanied by the exchange of protons between the polyaniline film and the solution based on the results of EQCM [31] and the shift of the peak potential on the cyclic voltammogram with pH values [32]. The second redox couple belongs most probably to quinone intermediates, because of the progressive degradation of this redox peaks with increasing cycles.

As can be seen from Fig. 1, the cyclic voltammogram (curve 2) of copolymer E in 0.2 M H_2SO_4 solution is analogous in shape to that of polyaniline (curve 1), indicating that the electrochemical property of copolymer E is similar to that of polyaniline in more acid solution. The main difference between curve 1 and curve 2 is that there are four oxidation peaks on curve 2. A new oxidation peak at 0.28 V on curve 2 is attributed to the oxidation of the −OH group in the copolymer chain, and its corresponding reduction peak is merged into the first reduction peak to make a broad peak.

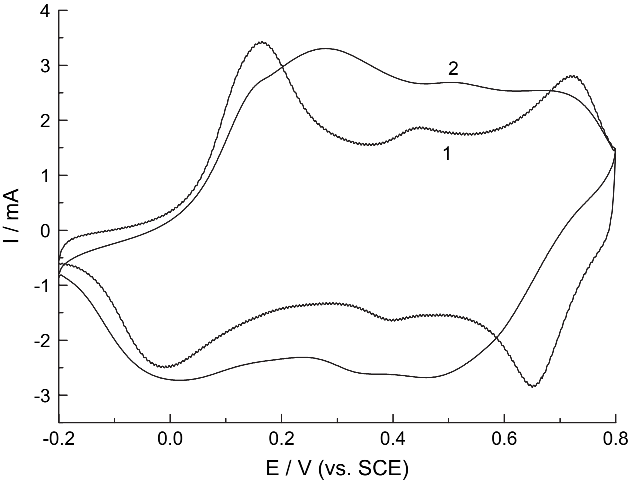


Fig. 1. Cyclic voltammograms of polyaniline (1) and copolymer E (2) in 0.2 M H_2SO_4 solution, at a scan rate of 60 mV s^{-1}.

Fig. 2 shows the cyclic voltammograms of copolymer E in 0.3 M Na_2SO_4 solution with different pH values. The scan rate was also controlled at 60 mV s^{-1}. A broad oxidation peak and a broad reduction peak appear on each curve. The anodic peak and the cathodic peak shift towards more positive and negative potentials, respectively, as the pH increases from 4.0 to 11.0. This is caused by a voltage drop across the copolymer film, owing to the decrease in the conductivity of the copolymer film with increasing pH. Based on the area in curves 1 and 6 in the potential region of −0.20 to 0.80 V in Fig. 2, 47.3% decay of the electrochemical activity was observed when copolymer E electrode was transferred from a solution of pH 5.0 to a solution of pH 11.0. This result is better than that of poly(aniline-*co*-*m*-aminophenol) prepared electrochemically [29], in which 58.3% decay was observed when the copolymer electrode was transferred from pH 5.0 to 11.0 of 0.3 M Na_2SO_4 solution. Our experimental results demonstrate that the pH dependence of the electrochemical activity of copolymer E is little better than that of copolymer C, i.e. copolymer E has the best pH dependence of the electrochemical activity among the copolymers prepared using various monomer concentration ratios at a constant concentration of aniline and sulfuric acid. To our knowledge, the electrochemical property of poly(aniline-*co*-*m*-aminophenol) prepared chemically is better than that of other aniline-based copolymers and much better than that of polyaniline. It is obvious that copolymer E has a good electrochemical activity in a wide pH region with a wide potential region. This is caused by the reversible redox of the −OH group in the copolymer chain, which is accompanied by the proton exchange between the copolymer electrode and the solution. The latter improves the pH dependence of the electrochemical activity of the copolymer.

Copolymer A is almost an insulator for a high concentration ratio of *m*-aminophenol/aniline in the mixture. The conductivity of copolymer C without and with treatment of

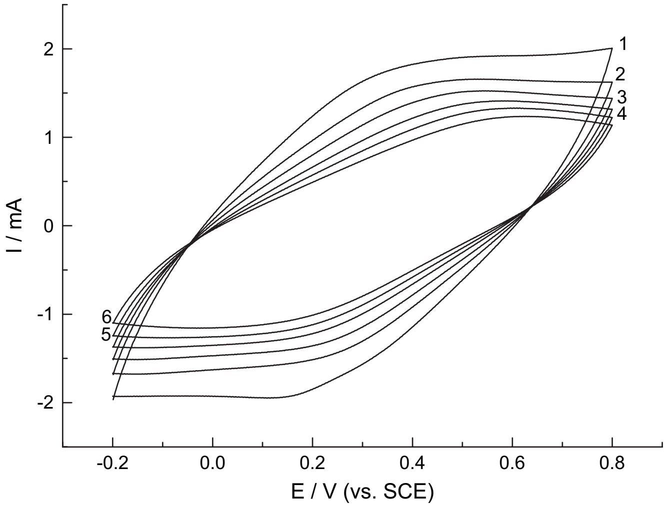


Fig. 2. Cyclic voltammograms of copolymer E in 0.3 M Na_2SO_4 solution with various pH values: (1) 4.0, (2) 6.0, (3) 7.0, (4) 9.0, (5) 10.0, and (6) 11.0 at a scan rate of 60 mV s^{-1}.

distilled water is 2.86 and 0.47 S cm^{-1}; the conductivity of copolymer E without and with treatment of distilled water is 2.34 and 0.57 S cm^{-1}. Therefore, the conductivity of the copolymer prepared chemically is higher than that prepared electrochemically (1.42 S cm^{-1}) [29], but lower than that of the parent polyaniline.

3.2. Molecular weight of poly(aniline-co-m-aminophenol)

The molecular weight of copolymer E was measured by using osmometry. The height of the solvent generated by flowing through the semi-permeable member was 1.2 cm. Based on the liquid column height, the concentration of the copolymer, the density of *N*-methyl-2-pyrrolidone (1.032) and temperature (292.9 K), the relative molecular weight of copolymer E was calculated to be 2.99×10^4. After completing the experiment, it was found that only 14.9 mg of copolymer E was dissolved in 10 ml of *N*-methyl-2-pyrrolidone and the remaining undissolved portion was hardly dissolved in the pure solvent because no change in the color of the solvent was observed.

3.3. Visible spectra of the copolymers

Curves 1 and 2 in Fig. 3 are the visible spectra of copolymer A and copolymer E in air. There is only a very small band around 600 nm on curve 1, indicating that copolymer A has a very short $\pi-\pi^*$ conjugation chain. A possible explanation is that the high concentration of *m*-aminophenol in the mixture inhibited the growth of the copolymer chain. This is why copolymer A has a very low conductivity as presented previously. However, there are two absorption peaks at 430 and 840 nm on curve 2. The latter is attributed to $\pi-\pi^*$ transition of semi-quinoid rings in polyaniline [33], or polarons, since the polaron band of polyaniline is usually observed at around 840 nm [34].

Curve 3 in Fig. 3 is the visible spectrum of copolymer E in water, in which two absorption peaks are at 420 and 850 nm, comparison of curve 2 and curve 3 shows that the position of the peak at 430 nm on curve 2 shifts to 420 nm on curve 3. This is caused by the polarity of water which is larger than that of air. It is clear that the λ_{max} decreases by 10 nm in going from air to water, or a hypsochromic shift is observed. Therefore, it is reasonable to make a conclusion that the absorption peak at 430 nm on curve 2 and the absorption peak at 420 nm on curve 3 are attributed to the $n-\pi^*$ transition, which is caused by nitrogen with lone-pair electrons on the copolymer chain. This result is in agreement with the visible spectrum of polyaniline [35]. The polyaniline synthesized enzymatically in the solutions without sulfonated polystyrene showed an absorption band at approximately 460 nm, indicating the presence of multiple branched structures in the polymer [36]. In comparison with the spectra of copolymer E, there is no an absorption band at approximately 460 nm on curves 2 and 3 in Fig. 3. This means that no branched structures were present in copolymer E, i.e., copolymer E has the linear structure. The visible spectra of copolymers B, C and D are similar to that of copolymer E.

3.4. IR spectra of the copolymer and polyaniline

The IR spectra of copolymer E (curve 1) and polyaniline (curve 2) are shown in Fig. 4. The main difference between them is that an absorption peak at 3664 cm^{-1} appears on curve 1, and an absorption peak at 3402 cm^{-1} appears on curve 2. The latter is attributed to the stretching vibrations of N–H, since the stretching vibrations of N–H band in aromatic

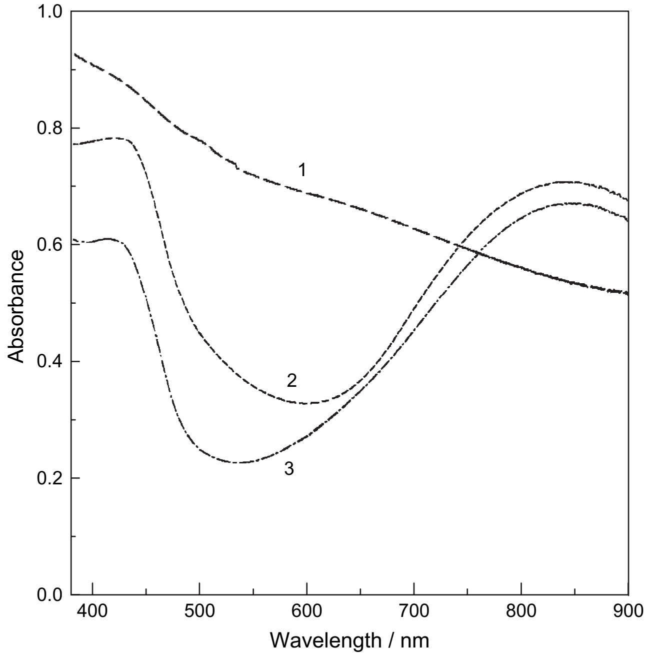


Fig. 3. Visible spectra of (1) copolymer A in air, (2) copolymer E in air, and (3) copolymer E in water.

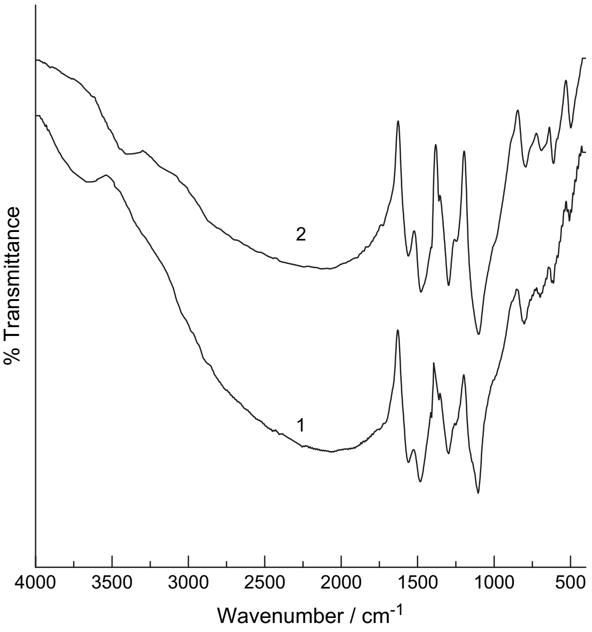


Fig. 4. IR spectra of (1) copolymer E and (2) polyaniline.

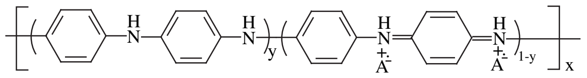
amines are in the region of 3400–3000 cm^{-1}. A broad band at 3664 cm^{-1} appears on curve 1. Its wavenumber is higher than that of N–H in the parent polyaniline. This is attributed to the merger of two individual absorption peaks from the stretching vibrations of –OH group in *m*-aminophenol and $-NH_2$ group in both *m*-aminophenol and aniline. This indicates that the copolymer contains *m*-aminophenol units. Two peaks at 1562 and 1479 cm^{-1} are attributed to the C=C stretching vibrations of benzene and quinone rings, respectively. The peak at 1298 cm^{-1} is assigned to the C–N stretching vibrations, because the C–N stretching vibrations in aromatic amines are in the range of 1280–1180 cm^{-1}. A sharp peak at 1101 cm^{-1} is attributed to the vibrations of SO_4^{2-} ions that were doped into the copolymer during the copolymerization of aniline and *m*-aminophenol in the sulfuric acid solution.

3.5. *Diffraction spectra of the copolymers*

The crystal structure of the parent polyaniline has received substantial attention because of the change in its structure with doping level [37]. Curve 1 in Fig. 5 is the diffraction spectrum of polyaniline prepared chemically, which was in the oxidation state, i.e. emeraldine salt. The diffraction peaks at $2\theta = 19.8°$ and 25.1° arise from momentum transfer perpendicular to the chain direction [38]. A small shoulder at $2\theta \approx 16°$ appears on curve 1; however, this small shoulder becomes an evident broad band on curve 2 (copolymer C) and a sharp peak on curve 3 (copolymer B). Also the peak at $2\theta \approx 19.8°$ on curve 1 shifts towards 20.0° on curve 2 and 20.6° on curve 3. It is clear that these regular changes are caused by increasing concentration ratio of *m*-aminophenol/aniline in the mixture. Therefore, the X-ray diffraction data provide strong evidence that the crystal structure of the copolymer changes with monomer concentration ratio in the mixture. This gives us a hint that the higher the concentration ratio of *m*-aminophenol/aniline in the mixture, the richer is the content of *m*-aminophenol units in the copolymer. This result is similar to that of the change in the crystal structure of the parent polyaniline with doping level [37].

3.6. *Proton NMR of the copolymer*

Fig. 6(a) shows the ^1H NMR spectrum of copolymer E. Two signals at δ 2.43 and δ 3.48 arise from protons of DMSO and residual water in the sample. The ^1H NMR of aniline trimer shows that the NH proton appeared at 5.3 ppm [39]. Thus, the peak at δ 5.79 in Fig. 6(a) would be caused by the NH resonance. The three lines having almost equal intensities at around δ 7.16 are indicative of the free radical NH proton due to the presence of ^{14}N with unit spin, which splits the proton attached to it into three lines. However, the splitting like this was not detected in the NH proton of polyaniline, in which only a single broad peak at 7.39 attributed to the NMR signal of NH was observed [40]. The above results indicate that protons on nitrogen in copolymer E have two different chemical environments. This is because the molecular structure of copolymer E is similar to that of emeraldine salt of polyaniline, except the presence of *m*-aminophenol units in copolymer E chain. The result from ^{13}C high-resolution solid state NMR shows evidence for the occurrence of quinoid structures and carbon–nitrogen double bonds in the oxidized state of polyaniline [41].



where A^- is an anion.

The splitting peaks at δ 7.16–7.44 in Fig. 6(a) are assigned to the aromatic proton resonance of copolymer E, since the chemical shift for the aromatic protons of the aniline monomer is in the region of 6.9–7.4 ppm [42]. A peak of the OH proton in phenol in DMSO occurs at δ 9.3 [43]. Therefore, the peak at

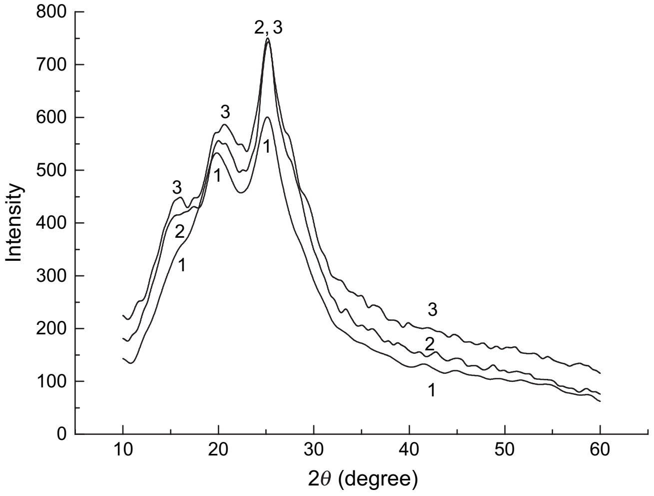


Fig. 5. X-ray diffraction spectra of (1) polyaniline, (2) copolymer C, and (3) copolymer B.

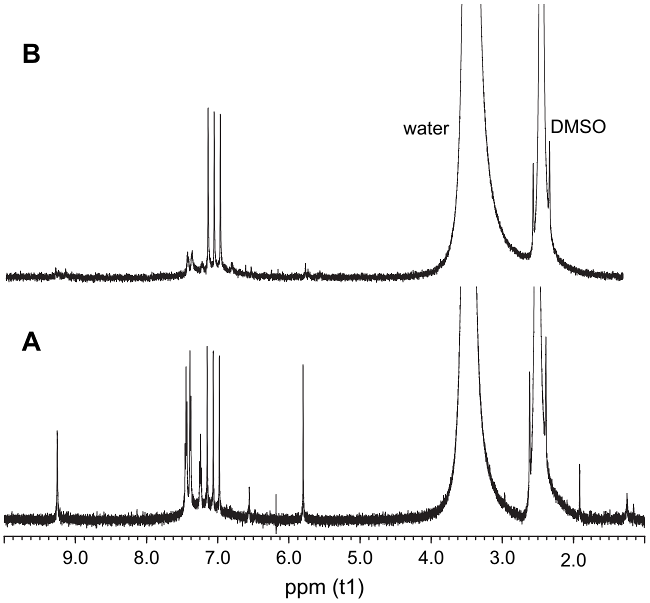


Fig. 6. (A) ^1H NMR of copolymer E and (B) ^1H NMR of polyaniline.

δ 9.26 in Fig. 6(a) characterizes the OH proton in *m*-aminophenol, which is good evidence for the presence of *m*-aminophenol unit in the copolymer chain.

To gain a better understanding of the formation of the copolymer, the ^{1}H NMR spectrum of polyaniline was also shown in Fig. 6(b). There is no a peak at δ 9.26 in Fig. 6(b), because of no −OH group in aniline. Thus, the ^{1}H NMR spectrum of the copolymer is different from that of polyaniline. This difference shows evidence that no polyaniline was contained in poly(aniline-*co*-*m*-aminophenol). This result is in agreement with that of IR spectra of copolymer E and polyaniline.

3.7. Morphology of the copolymers

The images of copolymers A–E (plots A–E) and polyaniline (plot F) are shown in Fig. 7. The morphology of copolymer A is spherical with diameters between 0.5 and 1 μm. The diameters of the particles decrease progressively from plot A to D as the concentration ratio of *m*-aminophenol/aniline in the mixture decreases. The morphology of the parent polyaniline in plot F shows a structure of the fibers with diameters between 110 and 150 nm instead of spherical particles. The change of the morphology in Fig. 7 was caused by the polymerization rate. The beginning polymerization rate is related to the change in the color of the mixture that can be observed obviously. The formation rate of copolymer A is the slowest and the formation rate of the parent polyaniline is the fastest among the copolymers presented here. As the concentration ratio of *m*-aminophenol/aniline in the mixture decreases, the formation rate of the copolymer increases. For a slow polymerization rate, only small amounts of the copolymer nuclei formed, followed by the copolymerization on the copolymer

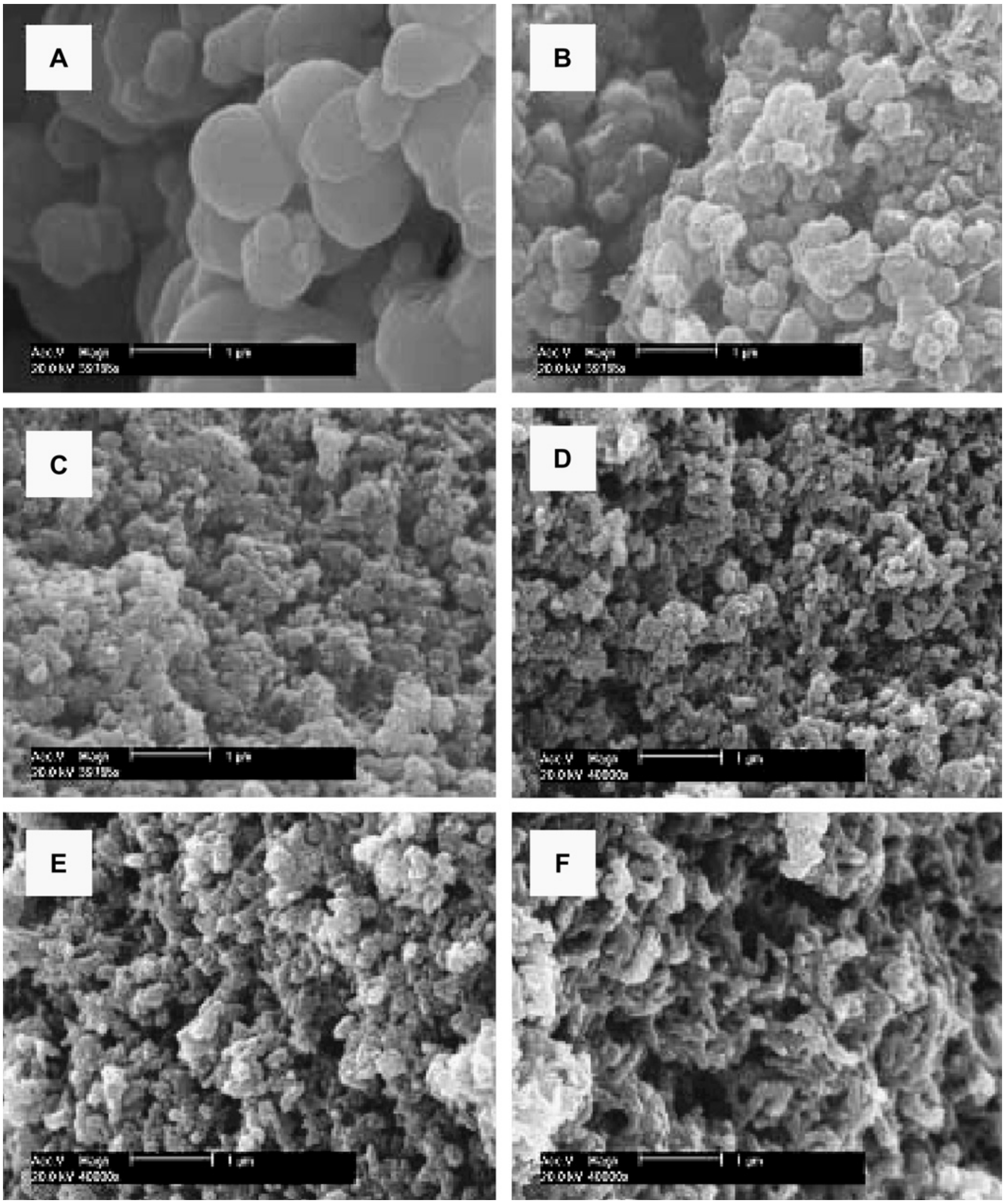


Fig. 7. Morphology of (A) copolymer A, (B) copolymer B, (C) copolymer C, (D) copolymer D, (E) copolymer E, and (F) polyaniline. Scale bar is 1 μm.

nuclei, which results in the continuous growth of the copolymer particles. Thus, the diameters of particles of copolymer A are the largest among the copolymers. The morphology of copolymer E is analogous to that of copolymer D. This is because only the concentration of ammonium peroxydisulfate is a little different in both mixture solutions.

4. Conclusion

The concentration ratio of *m*-aminophenol/aniline in the mixture strongly affects the chemical copolymerization rate of aniline and *m*-aminophenol, and properties of poly(aniline-*co*-*m*-aminophenol). The copolymer synthesized in the optimum condition has a rather high conductivity and a good electrochemical activity in a wide pH region up to pH 11.0 and in a wide potential region of −0.20−0.80 V. These are attributed to the −OH group in the copolymer chain. The reversible redox of the −OH group in the copolymer chain not only contributes some quantity of electricity to the copolymer itself, but also plays a key role in adjusting the pH value around the copolymer electrode, resulting in pronouncedly extending usable pH region. So it is to be expected that poly(aniline-*co*-*m*-aminophenol) prepared chemically has a wider applications compared with the parent polyaniline. A new oxidation peak and a wide reduction peak, appearing on the cyclic voltammogram of copolymer E in 0.2 M H_2SO_4 solution, are indicative of the redox of the −OH group in the copolymer chain. The relative molecular weight of poly(aniline-*co*-*m*-aminophenol) was shown here. However, its absolute molecular weight was not determined, which may be measured by using static light scattering (SLS) [44]. But this work is difficult for us at present. The spectra of IR and ^{1}H NMR of the copolymer offer good evidence for the presence of *m*-aminophenol units in the copolymer chain. The visible spectra indicate that a high concentration ratio of *m*-aminophenol/aniline inhibited the chain growth of the copolymer. The X-ray diffraction spectra and images show that the crystal structure and the morphology of the copolymers depend on the concentration ratio of *m*-aminophenol/aniline in the mixture. However, a reliable ratio of aniline unit to *m*-aminophenol unit in the copolymer chain has not been determined yet by using ^{1}H NMR spectroscopy. A detailed study on the ^{1}H NMR experiment of the copolymer is under way.

Acknowledgement

This work was supported by the National Nature Science Foundation of China (20074027).

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