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Synthesis and characterization of electroactive polyamide with amine-capped aniline pentamer and ferrocene in the main chain by oxidative coupling polymerization

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Abstract

A novel electroactive polymer, polyamide with well-defined oligoaniline and ferrocene in the main chain, has been successfully synthesized through a novel oxidative coupling polymerization. The polymerization characteristics and structure of the copolymer were systematically studied by gel permeation chromatographic (GPC), Fourier-transform infrared (FTIR) spectra, ^{1}H NMR and X-ray powder diffraction (XRD). And its spectroscopic properties and electrochemical behavior were studied by UV–vis spectra and cyclic voltammetry (CV). It was found that the obtained polyamide bearing amine-capped aniline pentamer and ferrocene segments had a reversible electrochemical property in the cyclic voltammetry, but showed four distinct oxidation states, which is different from polyaniline. Moreover, its electrical conductivity is about 7.6×10^{-7} S cm^{-1} at room temperature upon preliminarily protonic-doped experiment.

Keywords: Electroactive polyamide; Amine-capped aniline pentamer; Ferrocene

1. Introduction

Metal-containing polymers have been shown to possess interesting electrical, magnetical, and optical characteristics as a result of electron delocalization [1]. The favorable properties of the ferrocene nucleus make this molecule a particularly promising candidate for the incorporation into polymer chains for utilizing in a broad range of applications, ranging from batteries [2] to non-linear optical (NLO) material [3]. Up to now, there are several pathways to synthesize poly(ferrocenes), such as: polycondensation reactions using difunctional ferrocenes (e.g. ferrocene-containing polyesters, polyamides, and polyureas) [1], the synthesis of ferrocene derivatives bearing polymerizable substituents (e.g. vinylferrocene) [1], ring-opening polymerization of strained and ring-tilted ferrocenophanes [4–6].

Polyaniline (PANI) is one of the most frequently investigated (semi)conducting polymers potential for advanced applications such as organic lightweight batteries, electrochromic displays, electroluminescent, biosensor and chemical sensors [7–12] due to its excellent environmental stability, easy synthesis, and reversible acid/base doping/dedoping chemistry [13–19]. However, polyaniline, which is synthesized by chemical and electrochemical methods has defected site [20,21] and exhibits an ill-defined structure. It is, therefore, a very important challenge to design and synthesize polyaniline and its derivatives, which have a well-defined structure. One way to get such a structure is the incorporation of oligoanilines into the copolymers [22–24].

In this paper, we reported for the first time the synthesis of a new electroactive polyamide, which had alternating conjugated oligoaniline (amine-capped aniline pentamer) and difunctional ferrocene in the main chain by a novel and simple method, oxidative coupling polymerization. Furthermore, Fourier-transform infrared (FTIR) spectra, ^{1}H NMR, X-ray diffraction (XRD) patterns, UV–vis spectra, cyclic voltammetry (CV) and electrical conductivity measurement were employed to characterize the product.

2. Experimental

2.1. Materials

All chemicals, aluminium chloride (anhydrous) (99%, Beijing Chemical Factory), ferrocene (98%, Shanghai

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Chemical Factory), acetyl chloride (98%, Shanghai Chemical Factory), ethanol (99.7%, Beijing Chemical Factory), sodium hydroxide (96%, Beijing Chemical Factory), sodium hypochlorite solution (5.5%, Tianjin Chemical Factory), sodium hydrogen sulfite (99%, Tianjin Chemical Factory), sodium carbonate (crystal) (99%, Tianjin Chemical Factory), pyridine (99%, Beijing Chemical Factory), petroleum ether (60–90 °C, Tianjin Chemical Factory), *N*-phenyl-*p*-phenylenediamine (98%, Aldrich), *p*-phenylenediamine (99%, Beijing Chemical Factory), triethylamine (99%, Beijing Chemical Factory), ammonium persulfate (APS, 98%, Tianjin Chemical Factory), dichloromethane (99.5%, Tianjin Chemical Factory), diethyl ether (99%, Tianjin Chemical Factory), *N*,*N*′ -dimethylformamide (DMF, 99.5%, Tianjin Chemical Factory), *N*-methyl pyrrolidone (NMP, 98%, Beijing Chemical Factory), tetrahydrofuran (THF, 99%, Tianjin Chemical Factory), hydrochloric acid (37%, Beijing Chemical Factory) and ammonium hydroxide (30%, Changchun Chemical Factory) were used as received without further purification. Furthermore, distilled and deionized water was used.

2.2. Instruments

Mass spectra (MS) were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR 22 Spectrometer. ^{1}H NMR spectra were run on a BRUKER-500 spectrometer, referenced to internal tetramethylsilane. Elemental analysis results were obtained on a Flash Ea 1112 elemental analysis instrument. The molecular weight of the copolymer was measured with Shimadzu GPC-802D gel column and SPD-M10AVP detector. X-ray powder diffraction (XRD) patterns of the product were recorded on a Rigaku D/max 2500/PC powder diffractometer with Cu Kα radiation using a tube voltage and current of 40 kV and 200 mA. UV–vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU). The cyclic voltammetry (CV) was performed with a CHI 660A Electrochemical Workstation (CH Instruments, USA) in a conventional three-electrode cell, by using thin film cast onto g–c electrode from NMP solution. The film was cycled at 1 M H_2SO_4 aqueous solution in the range of -0.1 to $+1.0$ V. The electrical conductivity of the obtained copolymer at room temperature (RT) was measured by a four-probe method using a 2182 Nanovoltmeter and 2400 Sourcemeter as the current source.

2.3. Synthesis of 1,1′-ferrocenedicarbonyl chloride

The synthetic route for the preparation of 1,1′-ferrocenedicarbonyl chloride from ferrocene is depicted in Scheme 1. Suitable preparations for 1,1′-diacetylferrocene [25], 1,1′-ferrocenedicarboxylic acid [26] and 1,1′-ferrocenedicarbonyl chloride [27] have been reported in the literature.

2.3.1. Characterization of 1,1′-diacetylferrocene

MALDI-TOF-MS: *m*/*z* calculated for $C_{14}H_{14}FeO_2 = 270.1$. Found 269.8 ($M^+$).

IR (KRr, cm^{-1}): 3087, 1658, 1456, 1375, 1279, 1117, 1051, 843, 621, 542, 501.

^{1}H NMR ($CDCl_3$): $\delta = 4.78$ (s, 2H), $\delta = 4.52$ (s, 2H), $\delta = 2.36$ (s, 3H).

A typical elemental analysis for $C_{14}H_{14}FeO_2$: Calcd. C 62.25, H 5.22, O 11.85; Found C 61.97, H 5.14, O 11.96.

2.3.2. Characterization of 1,1′-ferrocenedicarboxylic acid

MALDI-TOF-MS: *m*/*z* calculated for $C_{12}H_{10}FeO_4 = 274.1$. Found 273.9 ($M^+$).

IR (KBr, cm^{-1}): 3116, 2883, 2634, 2559, 1687, 1490, 1403, 1301, 1169, 1034, 918, 841, 750, 575, 515.

^{1}H NMR (d_6-DMSO): $\delta = 12.33$ (s, 1H), $\delta = 4.69$ (s, 2H), $\delta = 4.45$ (d, 2H).

A typical elemental analysis for $C_{12}H_{10}FeO_4$: Calcd: C 52.59, H 3.68, O 23.35; Found C 52.73, H 3.67, O 23.06.

2.3.3. Characterization of 1,1′-ferrocenedicarbonyl chloride

MALDI-TOF-MS: *m*/*z* calculated for $C_{12}H_8Cl_2FeO_2 = 310.9$. Found 310.8 ($M^+$).

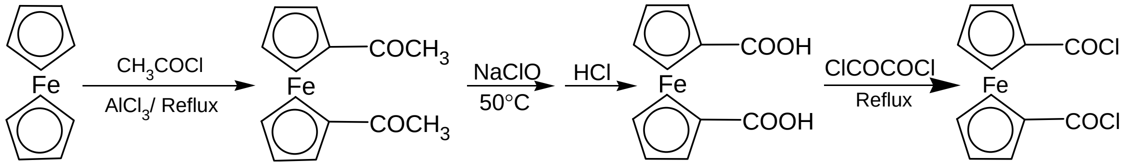
IR(KBr, cm^{-1}): 3114, 1758, 1438, 1369, 1242, 1045, 771, 696, 511, 480.

^{1}H NMR ($CDCl_3$): $\delta = 5.05$ (s, 2H), $\delta = 4.77$ (s, 2H).

A typical elemental analysis for $C_{12}H_8Cl_2FeO_2$: Calcd: C 46.35, H 2.59, O 10.29; Found C 46.47, H 2.73, O 10.36.

2.4. Synthesis of monomer (1)

A solution of 4.665 g (15 mmol) 1,1′-ferrocenedicarbonyl chloride in 90 mL of dry methylene chloride was added dropwise over a period of 50 min to a stirring mixture of *N*-phenyl-*p*-phenylenediamine (5.526 g, 30 mmol) and triethylamine (10.8 mL) in 90 mL of methylene chloride. The reaction, carried out in an atmosphere of dry nitrogen to avoid oxidation of *N*-phenyl-*p*-phenylenediamine, proceeded readily at room temperature, with the formation of a brown solution. The reaction mixture was stirred for 3 h and then the monomer



Scheme 1. Synthesis of 1,1′-ferrocenedicarbonyl chloride from ferrocene.

precipitated as a fine brown crumb. The product, filtered from the solution, was subsequently washed with methylene chloride, 1.0 M ammonium hydroxide and diethyl ether, filtered and dried under dynamic vacuum at room temperature for 24 h. The powder was got in 90% yield.

MALDI-TOF-MS: *m/z* calculated for $C_{36}H_{30}FeN_4O_2$ = 606.5. Found 606.5 (M^+).

IR(KBr, cm^{-1}): 3400, 3300, 3132, 3091, 3047, 1631, 1597, 1516, 1400, 1308, 1275, 1232, 1174, 1147, 1026, 827, 746, 694, 511.

^1H NMR (d_6-DMSO): $\delta = 9.55$ (s, 2H), $\delta = 8.05$ (s, 2H), $\delta = 7.58$ (d, 4H), $\delta = 7.20$ (t, 4H), $\delta = 7.07 - 7.02$ (m, 8H), $\delta = 6.77$ (t, 2H), $\delta = 4.93$ (s, 4H), $\delta = 4.47$ (s, 4H).

A typical elemental analysis for $C_{36}H_{30}FeN_4O_2$: Calcd: C 71.29, H 4.99, N 9.24, O 5.28; Found C 71.37, H 5.14, N 9.25, O 5.16.

2.5. Synthesis of polyamide

2.426 g (4 mmol) monomer (1) and *p*-phenylenediamine 0.432 g (4 mmol) were dissolved in 50 mL mixture solution (including 40 mL DMF, 5 mL distilled water and 5 mL concentrated hydrochloric acid). The solution of ammonium persulfate ($(NH_4)_2S_2O_8$ 1.824 g in 10 mL 1.0 M HCl aqueous solution) was added dropwise over a period of 40 min to the above solution with stirring at room temperature. After the addition, the resulted solution reacted for another 10 h. And it was poured into 200 mL distilled water to precipitate the product. Then the mixture was filtered using a Buchner funnel and water aspirator, and the filter cake was washed with distilled water for three times, followed by drying under dynamic vacuum at 40 °C for 24 h. Then the crude product was extracted with tetrahydrofuran using a Soxhlet extractor for 40 h until the extracted solution became colorless, and the purified powder was dried under vacuums at 40 °C for 24 h. (1.44 g yield 75%). M_n: 56,200, M_w: 99,700, M_w/M_n: 1.77.

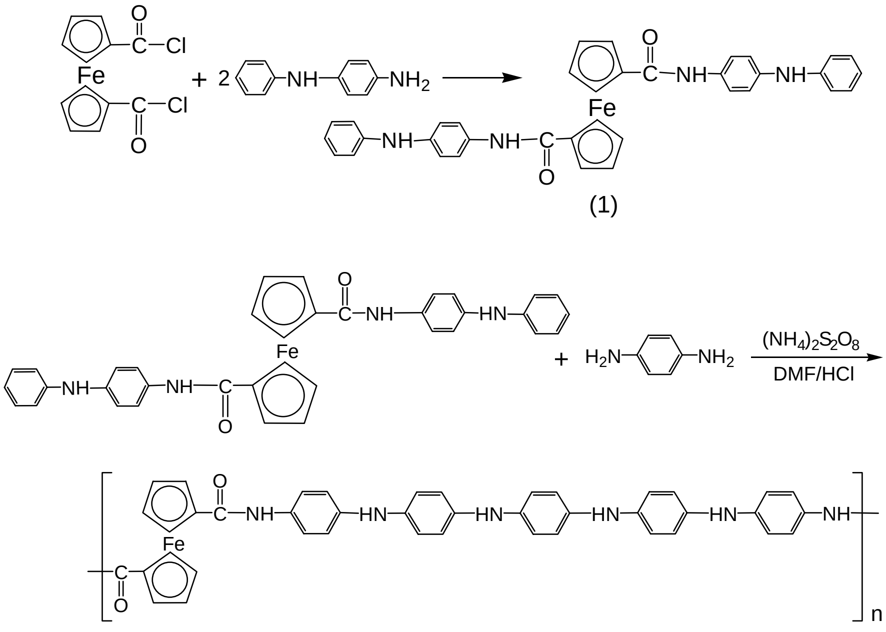
IR (KBr, cm^{-1}): 3402, 3199, 1631, 1598, 1514, 1399, 1308, 1233, 1173, 1130, 827, 745, 692, 511.

^1H NMR (d_6-DMSO): $\delta = 9.54$ (s, 2H), $\delta = 8.05$ (s, 2H), $\delta = 7.59 - 7.52$ (m, 4H), $\delta = 7.21 - 7.10$ (m, Ar–H), $\delta = 7.06 - 6.94$ (m, Ar–H), $\delta = 4.93$ (s, 4H), $\delta = 4.46$ (s, 4H).

3. Results and discussion

3.1. Oxidative coupling polymerization of the polyamide

The synthetic route for the preparation of electroactive polyamide with amine-capped aniline pentamer and ferrocene in the main chain is depicted in Scheme 2. The novel electroactive polyamide was not obtained from polycondensation reaction initiated by amine-capped aniline pentamer and 1,1′-ferrocenedicarbonyl chloride but synthesized from the reaction of the monomer (1) and *p*-phenylenediamine by oxidative coupling polymerization reaction, which developed from our present work [28]. Meanwhile, the new monomer (1) was prepared by polycondensation reaction from *N*-phenyl-*p*-phenylenediamine and 1,1′-ferrocenedicarbonyl chloride. In this method, neither the synthesis of the amine-capped aniline pentamer nor the protection of the secondary amino group of amine-capped aniline pentamer with the *tert*-butoxycarbonyl (BOC) group is needed, therefore, many steps are avoided. Such a synthetic strategy leads to the copolymer not only with a non-defective conjugated structure but also with good mechanical properties and electroactivity [22,24] and it will provide an opportunity for solving the problems that exist in traditional blended conductive polymer composites materials, such as phase separation, migration, extraction, etc.



Scheme 2. Synthesis of the monomer (1) and polyamide.

3.2. Structure characterization of the polyamide

The molecular structure of the resulting polyamide was confirmed by Fourier-transform infrared (FTIR) spectroscopy and ^{1}H NMR. FTIR spectrum is shown in Fig. 1 and it is similar to those reported previously for PANI powder. The peak at 3402 cm^{-1} is attributed to N–H stretching vibration and the vibration at 1631 cm^{-1} is a C=O stretch. The main peak at 1598 cm^{-1} and 1514 cm^{-1} can be assigned to the stretching vibration of quinone and benzene rings, respectively. The peak at 1308 cm^{-1} can be assigned to the C–N stretching vibration that arises from secondary aromatic amine groups. The peak at 1147 cm^{-1} is from the N=Q=N (Q is quinoid ring) stretching mode. And out-of-plane bending of C–H in the 1,4-disubstituted benzene ring is reflected in the 827 cm^{-1} peak. The ^{1}H NMR spectrum of the polyamide is shown in Fig. 2. The signals at $\delta = 9.55$, 8.05 ppm are attributed to the amino protons of polyamide and the signals at $\delta = 4.93$, 4.47 ppm are ascribed to the protons of ferrocenyl segments. Furthermore, the other expected splitting of the aromatic proton signal is seen at $\delta = 7.58 - 6.77$ ppm, demonstrating the well-defined structure of the polytamide.

3.3. X-ray diffraction (XRD) patterns of the polyamide

The X-ray diffraction (XRD) patterns of the as-synthesized polyamide (Fig. 3) show a broad peak, which is characteristic of the diffraction by an amorphous polymer. However, it consists mainly of two intense peaks centered at about 19° mainly ascribed to the periodicity parallel to the polymer chain and 26° corresponding to the periodicity perpendicular to the chain direction [29], which is quite different from PANI-β-naphthalene sulfonic acid (NSA) microtubes with high crystallinity. The short conjugated segment and the novel stereochemistry structure section in the polyamide molecular structure main chain increase the interchains separation, which leads to the difference in crystallinity between PANI-NSA nanotubes and our copolymer.

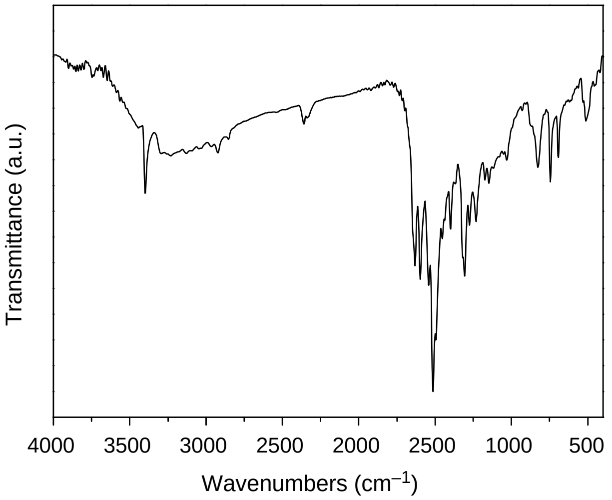


Fig. 1. FTIR spectra of the obtained polyamide.

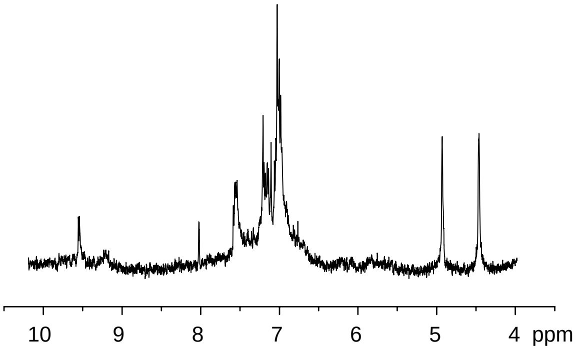


Fig. 2. ^{1}H NMR spectrum of polyamide.

3.4. Chemical oxidation of obtained polyamide

The obtained polyamide was dissolved in DMF solution without deoxidizing, and a UV–vis spectrum obtained was shown in Fig. 4. The first absorption peak at 317 nm was observed which is associated with a π–π* electronic transition of the conjugated system including both amine-capped aniline pentamer and ferrocenyl segments [30,31]. However, it shows

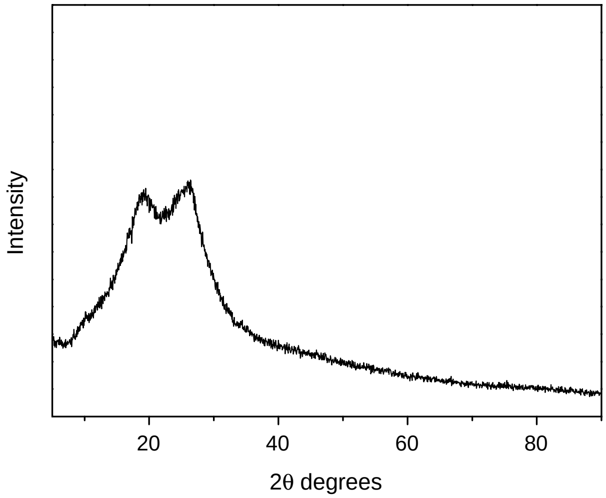


Fig. 3. X-ray diffraction (XRD) patterns of the obtained polyamide.

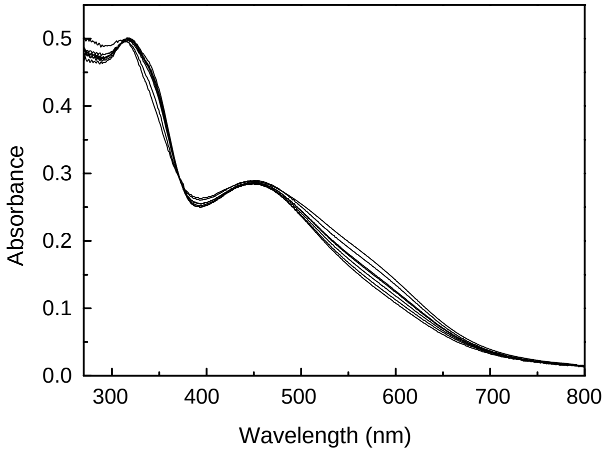
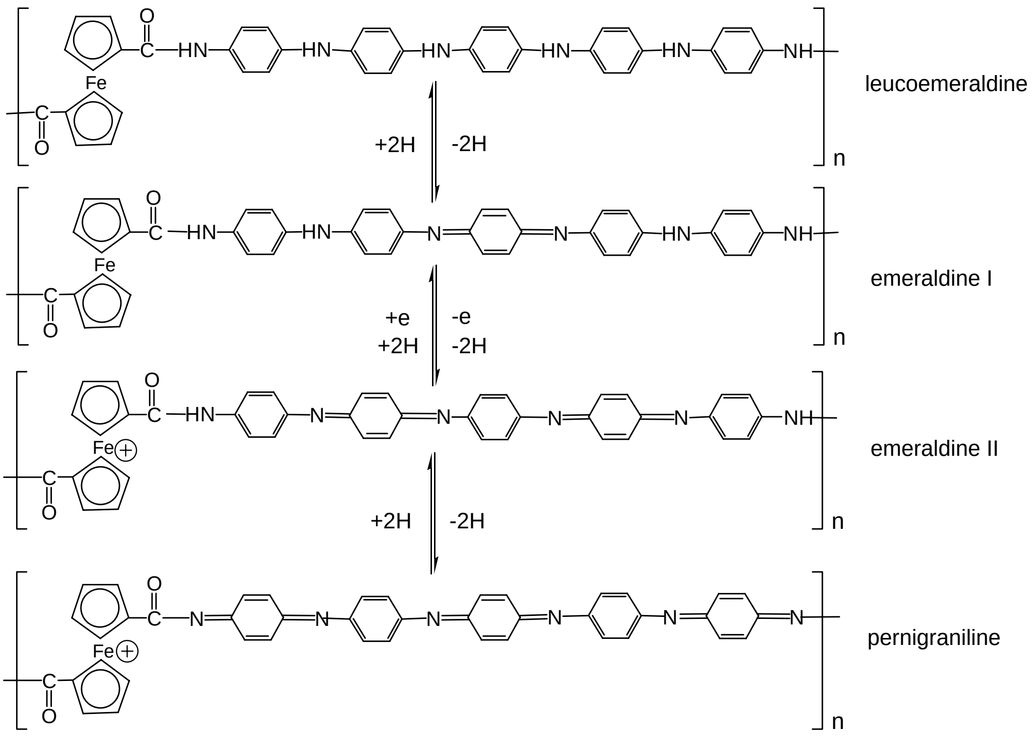


Fig. 4. UV–vis absorption spectra monitoring chemical oxidation of the obtained polyamide.



Scheme 3. Molecular structures of electroactive polyamide at various oxidation states.

strong blue-shift absorption in comparison with its two moieties, possibly because of the interaction effect of the two moieties. And the second absorption peak at 451 nm is assigned to the absorption of the ferrocenyl segments. In order to study the process of chemical oxidation of the obtained polyamide, the trace amount of $(NH_4)_2S_2O_8$ was added to the solution. When it was slowly oxidation, the absorption at about 570 nm which is assigned to the benzenoid to quiniod excitonic transition of the amine-capped aniline pentamer segments [32] continually increased in intensity and started to undergo a blue shift. After the absorption in intensity reached the maximum, the solution gradually turned to purple from dark blue, due to the commencement of formation of pernigraniline as shown in Scheme 3. This indicates that the emeraldine oxidation state has reached and just exceeded to form the pernigraniline oxidation state. The chemical oxidation process is the same as PANI.

3.5. Cyclic voltammetry of obtained polyamider

Fig. 5 shows the cyclic voltammetry of the as-synthesized polyamide obtained in 1.0 M H_2SO_4 aqueous solution using Ag/Ag^+ as the reference electrode with a scan rate of 50 mV s^{-1}. The NMP solution of the polyamide was cast on the g–c working electrode and was evaporated to form thin solid film. Under these conditions, the cyclic voltammetry (Fig. 5) of the polyamide showed three oxidation peaks at 330 (a), 500 (b), and 700 (c) mV, which is different from that for polyaniline. We consider that the first redox wave corresponds to the transition of the oligoaniline segment from the leucoemeraldine form to the emeraldine I, and the second redox wave appears at 500 mV v. Ag/Ag^+ which is assigned to a single-electron reversible redox process of the ferrocenyl moiety and the transition of the oligoaniline segment from the emeraldine I to the emeraldine II. And the last redox wave is due to the transition of the oligoaniline segment from the emeraldine II to the pernigraniline form. Such a possible redox process is illustrated in Scheme 3.

3.6. Electrical properties of the polyamide

Electrical conductivity of the doped copolymer at room temperature is about 7.6×10^{-7} S cm^{-1}. However, the conductivity of the obtained copolymer is much lower than that for the HCl-doped polyaniline [33] because of the distortion of the π-conjugated polymer main chain by

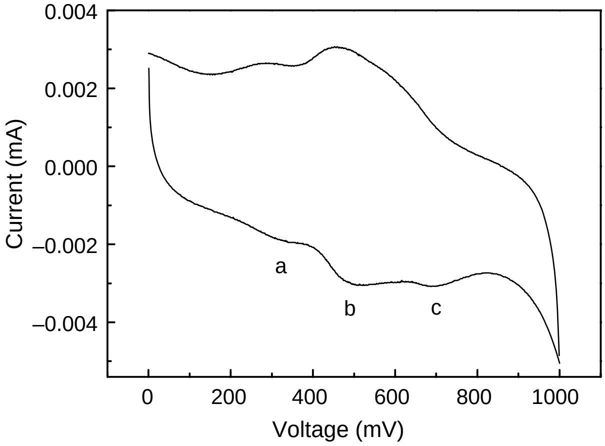


Fig. 5. Cyclic voltammetry of the as-synthesized polyamide.

introduction of non-conjugated segments into the copolymer backbone.

4. Conclusion

We present here the successful synthesis of a novel electroactive polyamide with amine-capped aniline pentamer and ferrocene in the main chain through a simple oxidative coupling polymerization. The structure of resulting polyamide was characterized by IR, ^{1}H NMR, GPC and XRD. And the general properties are studied by UV–vis spectra and cyclic voltammetry (CV). A possible redox process is proposed. With a well-defined and novel molecular structure and reversible electrochemical properties, this type of polyamide not only provides an opportunity for a better understanding of the conducting mechanism of conjugated polymers but also opens a platform to better comprehend the structure–property relationships. Further studies in the regard are currently underway.

Acknowledgements

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