

Design, Synthesis and Characterization of Novel Electroactive Polyamide with Amine-Capped Aniline Pentamer in the Main Chain via Oxidative Coupling Polymerization

Danming Chao,¹ Xiaobo Ma,¹ Xiaofeng Lu,¹ Lili Cui,¹ Hui Mao,¹ Wanjin Zhang,¹ Yen Wei²

¹Alan G. MacDiarmid Institute, Jilin University, Changchun, 130012, People's Republic of China

²Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received 26 July 2006; accepted 7 November 2006

DOI 10.1002/app.25749

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: By oxidative coupling polymerization of the macromonomer of oligoaniline and *p*-phenylenediamine we have prepared a novel electroactive polyamide, exhibiting well-defined molecular structure, interesting spectroscopic and electrochemical properties. The well-defined molecular structure of the electroactive polyamide was confirmed by FTIR, NMR spectroscopy, elemental analysis and X-ray powder diffraction (XRD) and the resulting polyamide exhibit an enhanced solubility in most of the organic solvents as compared with polyaniline. The UV-Vis spectra were used to monitor the chemical oxidation process of the reduced polyamide. Electrochemical activity

of the polyamide was tested in 1.0M H₂SO₄ aqueous solution and it shows three redox peaks, which is different from the polyaniline. Moreover, the thermal properties of the polyamide were evaluated by thermogravimetric analysis (TGA) and it shows moderate thermal resistance in the N₂ atmosphere. Its electrical conductivity is about $1.04 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature upon preliminarily protonic-doped experiment. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1603–1608, 2007

Key words: electroactive; oligoaniline; oxidative coupling polymerization

INTRODUCTION

Conducting polymers have been intensively studied over the past decade because they are synthetic materials that can achieve high conductivities upon doping. For example, films of stretch-oriented, doped polyacetylene¹ have conductivities approaching those of conventional metals. Within this class of materials, polyaniline (PANI) has attracted special attention due to its high conductivity, good environmental stability, facility of synthesis (chemical or electrochemical oxidation of aniline), cheapness of the monomer, and large variety of applications such as rechargeable batteries, antistatic coatings, corrosion inhibition, organic field-effect transistors, photovoltaic cells, and electrochromic device.^{2–6} PANI is unique among the family of conducting polymers because its doping level can be readily controlled through an acid-base doping/de-doping process.⁷ Thus, PANI offers the promise of

a relatively low-cost conducting polymer that is both stable and processable. In addition, many efforts have been devoted to investigate PANI structure synthesized by chemical and electrochemical means, and the data reveal that most PANI exhibit an ill-defined structure and has limited solubility in a handful of organic solvents.^{8,9} It is therefore a very important challenge to design the PANI and its derivatives in a form that is easily processable and applicable and at the same time gives the final product a well-defined structure.

One approach is design and synthesis of polymers with the well-defined oligoaniline as the side chains or in the main chains by covalent bond to combine the properties of the oligoaniline and desirable polymers properties such as mechanical strength and film-forming. Recently, Pron and coworkers¹⁰ copolymerized 3-octylthiophene with thiophene containing tetra-aniline in the 3-position of thiophene to prepare a hybrid copolymer. Both of the oligoaniline side chains and the polymer main chains could be doped. Zhu et al.¹¹ prepared a novel polymer with tetra-aniline and phenylene sulfide segments in the main chain as repeat unit, which displayed good solubility in most common organic solvents such as THF, DMSO, and DMF and its electrical conductivity could be up to 100 S cm^{-1} upon preliminarily protonic-doping. Gao et al.¹² reported the introduction of the

Correspondence to: W. Zhang (wjzhang@jlu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: NNSFC-50473007.

Contract grant sponsor: National Major Project for Fundamental Research of China; contract grant numbers: 001CB610505, G2003CB615604.

Journal of Applied Polymer Science, Vol. 104, 1603–1608 (2007)
© 2007 Wiley Periodicals, Inc.

oligoaniline units into the main chain of the polyamides. In our present work, a novel approach of oxidative coupling polymerization to synthesize electroactive copolymers is developed,¹³ which started with the macromonomer of oligoaniline and *p*-phenylenediamine. Compared with the previous organic method, oxidative coupling polymerization is very convenient because it can be carried out under mild conditions by only a few steps and the protection of the secondary amino group of oligoaniline is avoided.

In this work, we report the synthesis of a new electroactive polyamide that has alternating conjugated segment (amine-capped aniline pentamer) and nonconjugated segment in the main chain; and the obtained polyamide has an enhanced solubility in most of the organic solvents because of the existence of long and flexible alkyl chain in the main chain. Furthermore, the size, structure, and properties of the resultant product were characterized by Fourier-transform infrared (FTIR) spectra, ¹H-NMR, elemental analysis (EA), X-ray powder diffraction (XRD), UV-Vis spectra, cyclic voltammetry (CV), thermogravimetric analysis (TGA), and electrical conductivity measurement.

EXPERIMENTAL

Materials

All chemicals, *N*-phenyl-*p*-phenylenediamine (98%, Aldrich), *p*-phenylenediamine (99%, Beijing Chemical Factory), adipoyl chloride (98%, Aldrich), triethylamine (99%, Beijing Chemical Factory, Beijing, China), ammonium persulfate (APS, 98%, Tianjin Chemical Factory, Tianjin), dichloromethane (99.5%, Tianjin Chemical Factory), diethyl ether (99%, Tianjin Chemical Factory, Tianjin), *N,N'*-dimethylformamide (DMF, 99.5%, Tianjin Chemical Factory, Tianjin), *N*-methyl pyrrolidone (NMP, 98%, Beijing Chemical Factory, Beijing, China), tetrahydrofuran (THF, 99%, Tianjin Chemical Factory, Tianjin), hydrochloric acid (37%, Beijing Chemical Factory, Beijing, China), hydrazine hydrate (50%, Beijing Chemical Factory, Beijing, China), and ammonium hydroxide (30%, Changchun Chemical Factory, Changchun, China) were used as received without further purification. Distilled and deionized water was used.

Synthesis of the macromonomer of oligoaniline

A solution of 2.745 g (15 mmol) adipoyl chloride in 90 mL of dry methylene chloride was added dropwise over a period of 1 h 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 tempera-

ture, with the formation of a gray solution. The reaction mixture was stirred for 3 h and then the macromonomer of oligoaniline precipitated as a fine gray crumb. The product, filtered from the solution, was subsequently washed with methylene chloride, 1.0M ammonium hydroxide and diethyl ether, filtered and dried under dynamic vacuum at room temperature for 24 h. The gray powder was obtained in 90% yield.

MALDI-TOF-MS: *m/z* calculated for C₃₀H₃₀N₄O₂ = 478.6. Found 478.2 (M⁺).

FTIR (KBr, cm⁻¹): 3388 (s, ν_{NH}), 3294 (s, ν_{NH}), 3050 (w, ν_{CH}), 3028 (w, ν_{CH}), 2949 (w, ν_{CH}), 2868 (w, ν_{CH}), 1653 (versus, ν_{C=O}), 1603 (s, ν_{C=C} of quinoid rings), 1535 (versus, ν_{C=C} of benzenoid rings), 1444 (m, δ_{CH}), 1323 (s, ν_{C-N}), 1265 (m, ν_{C-C}), 1169 (m, δ_{CH}), 962 (w, δ_{CH}), 819 (m, δ_{CH}), 741 (m, δ_{CH}), 692 (m, δ_{CH}).

¹H-NMR (*d*₆-DMSO): δ = 9.71 (s, 2H, due to H₃), δ = 7.98 (s, 2H, due to H₆), δ = 7.46 (d, 4H, due to H₄), δ = 7.18 (t, 4H, due to H₈), δ = 7.01 (d, 4H, due to H₇), δ = 6.99 (d, 4H, due to H₅), δ = 6.75 (t, 2H, due to H₉), δ = 2.30 (t, 4H, due to H₂), δ = 1.62 (m, 4H, due to H₁).

A typical elemental analysis for C₃₀H₃₀N₄O₂: Calcd. C 75.29, H 6.32, N 11.71, O 6.69; Found C 75.36, H 6.14, N 11.76, O 6.74.

Synthesis of electroactive polyamide

1.914 g (4 mmol) the macromonomer of oligoaniline and 0.432 g (4 mmol) *p*-phenylenediamine were dissolved in 50 mL mixture solution (including 40 mL DMF, 5 mL distilled water, and 5 mL concentrated hydrochloric acid). A solution of ammonium persulfate ((NH₄)₂S₂O₈ 1.824 g in 10 mL 1.0M HCl aqueous solution) was added drop-wise over a period of 30 min to the above solution with stirring at room temperature. After the addition, the resulting solution reacted for another 12 h. Then it was poured into 400 mL distilled water to precipitate the product. The product was washed with distilled water for three times, followed by drying under dynamic vacuum at 40°C for 24 h. Finally, the crude product was extracted with THF using a Soxhlet extractor for 20 h until the extracted solution became colorless, and the purified powder was dried under vacuum at 40°C for 24 h. (1.814 g yield 77%). *M_n*: 29,100, *M_w*: 55,400, *M_w*/*M_n*: 1.90.

FTIR (KBr, cm⁻¹): 3430 (m, ν_{NH}), 3244 (m, ν_{NH}), 2922 (w, ν_{CH}), 2852 (w, ν_{CH}), 1653 (m, ν_{C=O}), 1585 (s, ν_{C=C} of quinoid rings), 1506 (versus, ν_{C=C} of benzenoid rings), 1303 (s, ν_{C-N}), 1146 (s, N=Q=N, where Q represents the quinoid rings), 822 (m, δ_{CH}), 748 (w, δ_{CH}).

¹H-NMR (*d*₆-DMSO): δ = 9.61 (s, 2H, due to —CO—NH—), δ = 7.98 (s, 0.66H, due to —NH—), δ = 7.61–7.36 (m, due to Ar-H), δ = 7.18–7.16 (m, due to Ar-H), δ = 7.01–6.75 (m, due to Ar-H), δ = 2.28 (t, 4H, due to —CH₂—), δ = 1.61 (m, 4H, due to —CH₂—).

A typical elemental analysis for the copolymer: Found C 74.20, H 5.88, N 14.42, O 5.49.

Reduction of the electroactive polyamide

The obtained polyamide (0.4 g) was dispersed into a stirring mixture solution (3 mL hydrazine hydrate in 40 mL 1.0M ammonium hydroxide) and stirred for 12 h. Then it was filtered and washed with distilled water for several times, followed by drying under dynamic vacuum at 40°C for 24 h. Finally, the dedoped polyamide was reduced to the leucoemeraldine oxidation state.¹²

Measurement

Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT).

FTIR measurements were recorded on a BRUKER VECTOR 22 Spectrometer. The samples were mixed with KBr and pressed into a plate for measurement at 25°C.

The ¹H-NMR spectra of the macromonomer of oligoaniline and the polyamide in deuterated dimethyl sulfoxide (DMSO) were run on a BRUKER-500 spectrometer to determine the chemical structure and tetramethylsilane was used as the internal standard.

The composition of the macromonomer of oligoaniline and the polyamide was calculated from the results of elemental analysis. The weight percentages of carbon, hydrogen, nitrogen, and oxygen in the samples were measured by a Flash Ea 1112 elemental analysis instrument.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution of the electroactive polyamide were measured with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector with *N,N'*-dimethylformamide as an eluent at a flow rate of 1 mL min⁻¹. The sample was prepared in DMF (high-performance-liquid-chromatography-grade). Before analysis, the

sample was filtered through a 0.2- μ m poly(tetrafluoroethylene) syringe filter. Calibration was accomplished with monodispersed polystyrene standards.

X-ray powder diffraction (XRD) patterns of the product were recorded on a Siemens D5005 diffractometer using Cu K α radiation.

UV-Vis spectra were obtained using a UV-2501 PC Spectrometer (SHIMADZU) in DMF. Initial solution of the copolymer in the leucoemeraldine oxidation state was quite dilute (around 0.05 mg mL⁻¹).

Cyclic voltammetry (CV) was performed with a CHI 660A Electrochemical Workstation (CH Instruments, USA) in a conventional 3-electrode cell, by using thin films cast from NMP solutions onto a g-c electrode. The film was cycled at 1.0M H₂SO₄ aqueous solution in the range from 0 V to +1.0 V.

A Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of the electroactive polyamide powder in the temperature range from 40 to 780°C at a rate of 10.0°C min⁻¹ under nitrogen protection.

The electrical conductivity of the obtained copolymer at room temperature (RT) was measured by a 4-probe method using a 2182 Nanovoltmeter and 2400 Sourcemeter as the current source. Three samples of the obtained copolymer were tested and the conductivity of each sample was measured four times at different current values. The average of 12 measurements was taken as the conductivity of the copolymer. The formula used for calculating conductivity is as follows: $\sigma = I24.4/Udh$, where σ , I , U , d , and h are conductivity (S cm⁻¹), current (A) set, voltage (V) measured, width (mm), and thickness (mm) of the sample.

RESULTS AND DISCUSSION

Synthesis and characterization of electroactive polyamide

The macromonomer of oligoaniline was obtained from the reaction of *N*-phenyl-*p*-phenylenediamine with adipoyl

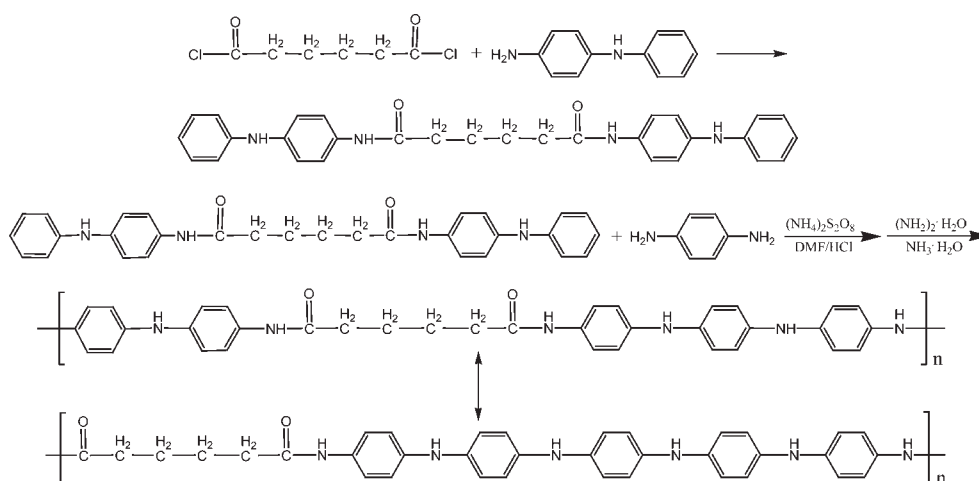


Figure 1 Synthesis of the macromonomer of oligoaniline and polyamide.

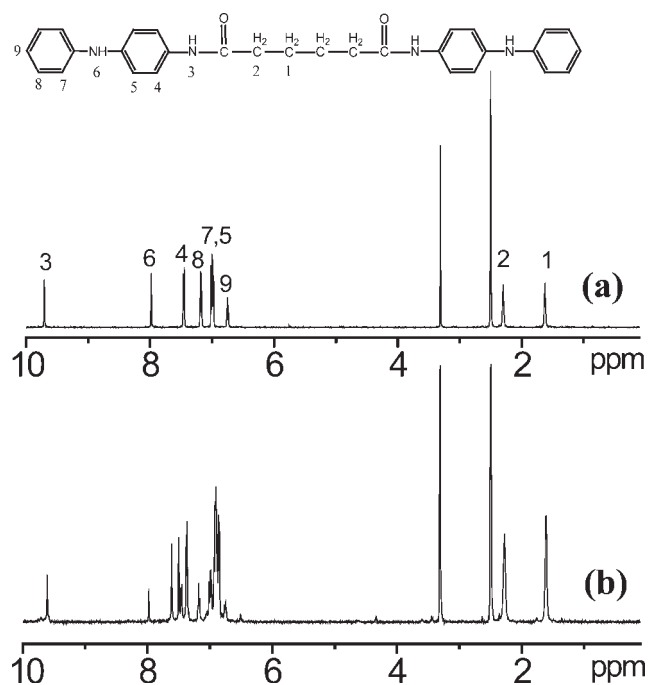


Figure 2 ¹H-NMR spectrum of the macromonomer of oligoaniline (a) and the polyamide (b).

chloride, as shown in Figure 1. The structure of the macromonomer of oligoaniline was confirmed by means of MS, FTIR, NMR spectroscopy and elemental analysis (Fig. 2).

The synthetic route for the synthesis of electroactive polyamide with amine-capped aniline pentamer in the main chain is depicted in Figure 1. The polyamide was not obtained from polycondensation initiated by amine-capped aniline pentamer and adipoyl chlorides but synthesized from the reaction of the macromonomer of oligoaniline and *p*-phenylenediamine by oxidative coupling polymerization, which was developed in our present work.¹³ The structure of the electroactive polyamide was confirmed by FTIR, ¹H-NMR spectroscopy and elemental analysis. The solubility of the electroactive polyamide in some solvents was studied in our work. A majority of the obtained polyamide is soluble at the room temperature in polar solvents such as NMP, DMAc, DMF, and DMSO. The good solubility of the polyamide can be attributed to the introduction of the long and flexible alkyl chain that decrease the hydrogen bonding and π - π interactions interchain, which disturb the close packing of the polymer chains and lead the increase of the free volume. Therefore, it will become easier for solvents to solubilize the polyamide.

X-ray diffraction patterns of the polyamide

The X-ray diffraction (XRD) patterns of the as-synthesized polyamide (Fig. 3) show a broad peak,

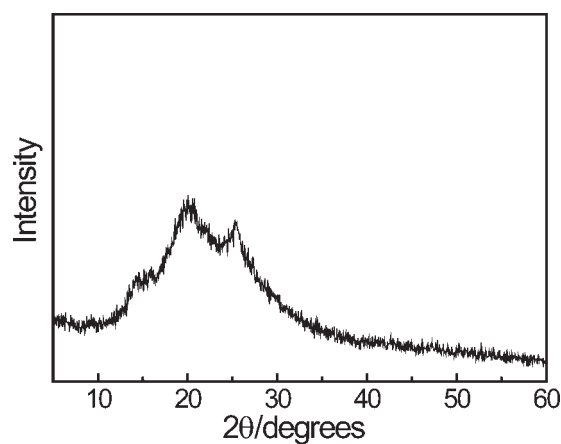


Figure 3 X-ray diffraction (XRD) patterns of the obtained polyamide.

which is characteristic of the diffraction by an amorphous polymer. However, it consists mainly of two intense peaks centered at about 20° mainly ascribed to the periodicity parallel to the polymer chain and 25° corresponding to the periodicity perpendicular to the chain direction.¹⁴

Chemical oxidation of polyamide in the leucoemeraldine oxidation state

The obtained polyamide in the leucoemeraldine oxidation state was dissolved in NMP solution. Trace amount of (NH₄)₂S₂O₈ was added to it. The solution gradually turned dark blue and finally purple upon being oxidized. This process was monitored by UV-Vis spectra continuously; UV-Vis spectra obtained are shown in Figure 4. First only one absorption at 320 nm was observed, which is associated with a

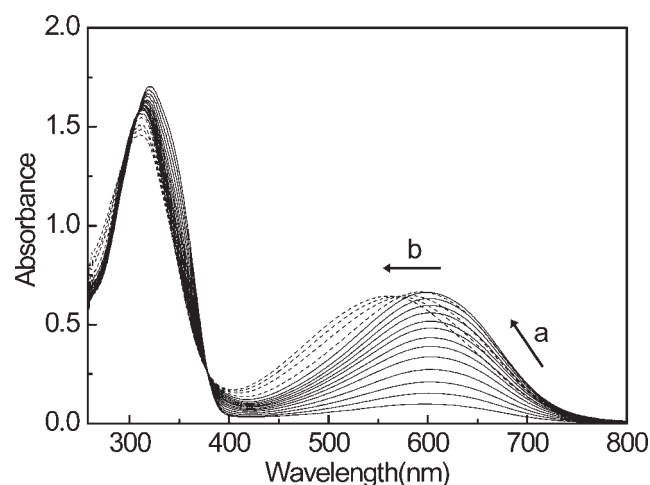


Figure 4 UV-Vis spectra monitoring chemical oxidation of the polyamide in the leucoemeraldine oxidation state (a): the intensity of absorbance increased while being oxidized. (b): the λ_{\max} of absorbance undergo a blue shift.

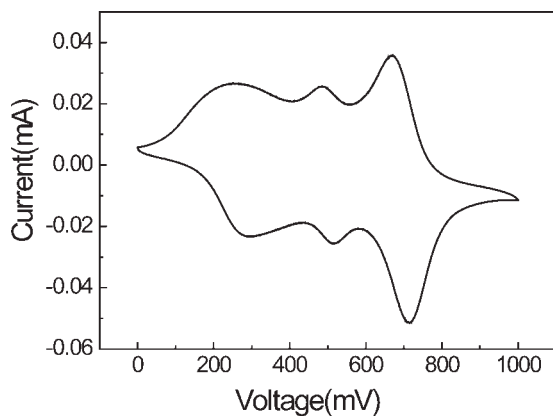


Figure 5 Cyclic voltammety of the polyamide.

π - π^* transition of the conjugated ring system.¹⁵⁻¹⁷ When slow oxidation took place, the absorption started to undergo a blue shift (from 320 to 310 nm) with decreasing in intensity, and the UV-Vis spectra showed a new absorption at about 600 nm, which is assigned to exciton-type transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring¹⁸ and continually increased in intensity. After its intensity reached the maximum, the λ_{\max} of the second absorption began to undergo a blue shift (from 600 to 560 nm). A possible explanation (Fig. 6) of this phenomenon is as following: in the continuous oxidation of the copolymer in leucoemeraldine oxidation state, it reached the first emeraldine oxidation state with each amine-capped aniline pentamer segment containing only one quinoid ring first, which showed the second absorption at longer wavelength. Subsequently, it was oxidized to second emeraldine oxidation state with amine-capped aniline pentamer segment containing two quinoid rings, which showed increase in intensity of the second absorption. After the second absorption reaching the maximum in intensity, it exhibited a blue shift. This showed that the em-

eraldine oxidation state has been reached and just exceeded to form a pernigraniline oxidation state. The chemical oxidation process is similar to that of oligo-aniline.^{15,19}

Electrochemical activity of the polyamide

Figure 5 shows the cyclic voltammety of the synthesized polyamide obtained in 1.0M H₂SO₄ aqueous solution using Ag/Ag⁺ as the reference electrode with a scan rate of 20 mV s⁻¹. The NMP solution of the polyamide was cast on the g-c working electrode and was evaporated to form a thin solid film. Under these conditions, the cyclic voltammety (Fig. 5) of the polyamide showed three pairs of redox peaks, different from polyaniline who has a typical two pairs of redox peaks (350 mV and 800 mV).¹² We consider that the first oxidation wave at around 300 mV corresponds to the transition from the leucoemeraldine oxidation state to the first emeraldine oxidation state, and the second oxidation wave at around 500 mV is assigned to the transition from the first emeraldine oxidation state to the second emeraldine oxidation state and the last oxidation wave at around 700 mV is due to the transition from the second emeraldine oxidation state to the pernigraniline oxidation state (Fig. 6). We believe that the difference in the electrochemical characteristics between the copolymer and PANI are due mainly to differences in their chemical structures.

Thermal properties of the polyamide

The result from TGA curve of the polyamide is shown in Figure 7. The initial weight loss of the copolymer starts at around 150°C with a mass loss of 7%, which could be attributed to the loss of bounded dopant²⁰; the subsequent decomposition occurs in the temperature range 300-800°C with a mass loss of

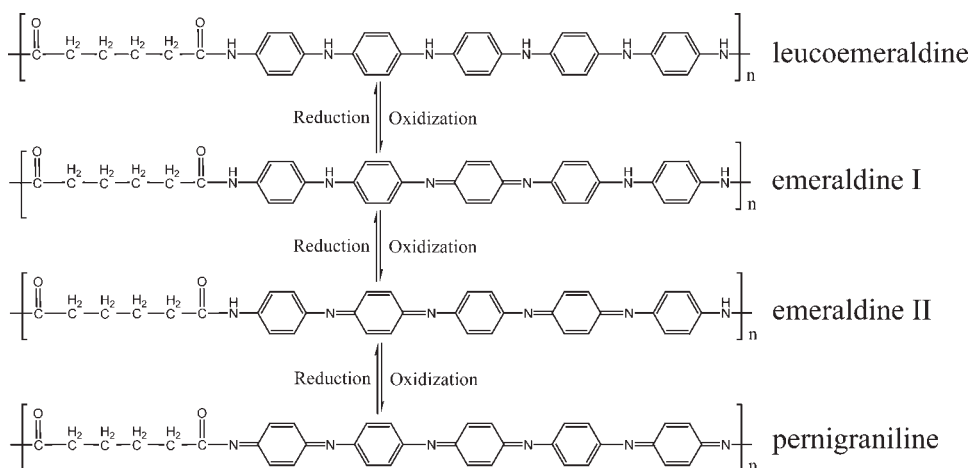


Figure 6 Molecular structures of electroactive polyamide at various oxidation states.

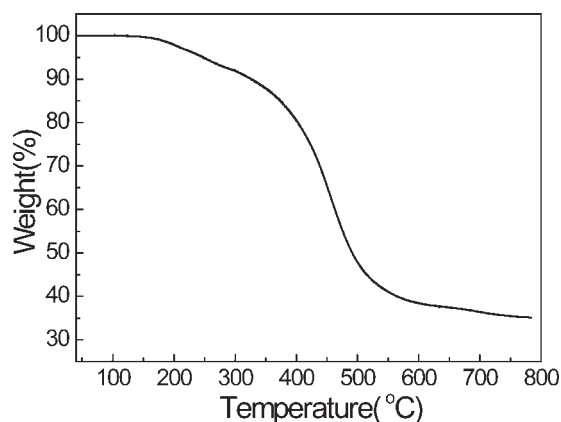


Figure 7 TGA thermograms of the electroactive polyamide in N_2 .

58%, which could be associated to generalize elimination of the decomposition of main copolymer chain.^{21–23} And it indicates that the as-synthesized polymer has a moderate thermal resistance with a weight loss of 5.0% at around 250°C.

Electrical properties of the polyamide

Electrical conductivity of the doped copolymer with HCl at room temperature is about $1.04 \times 10^{-4} \text{ S cm}^{-1}$. However, the conductivity of the obtained polyamide is much lower than that for the HCl-doped polyaniline²⁴ because of the short PANI blocks in main chain by introduction of nonconjugated segments into the polyamide backbone.

CONCLUSIONS

A novel electroactive polymer, polyamide with a well-defined oligoaniline unit in the backbone, has been successfully synthesized and characterized. The conductivity of the polyamide can be achieved up to $10^{-4} \text{ S cm}^{-1}$ when doped with proton acid. The resultant polymer can be represented as a genuine molecular composite material and it has excellent solubility in some solvents. And the general properties of the poly-

amide are studied by UV-Vis spectra and cyclic voltammetry (CV). A possible redox process is proposed.

References

1. MacDiarmid, A. G. *Synth Met* 2002, 125, 11.
2. Heeger, A. J. *Synth Met* 1993, 55, 3471.
3. MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss Chem Soc* 1989, 88, 317.
4. MacDiarmid, A. G. *Synth Met* 1997, 84, 27.
5. Zhang, L. J.; Wan, M. X. *J Phys Chem B* 2003, 107, 6748.
6. Chao, D. M.; Chen, J. Y.; Lu, X. F.; Chen, L.; Zhang, W. J.; Wei, Y. *Synth Met* 2005, 150, 47.
7. Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J Chem Soc Faraday Trans* 1986, 82, 2385.
8. Wang, L. X.; Soczka-Guth, T.; Havinga, E.; Mullen, K. *Angew Chem Int Ed Engl* 1996, 35, 1495.
9. Adams, P. N.; Apperley, D. C.; Monkman, A. P. *Polymer* 1993, 34, 328.
10. Dufour, B.; Rannou, P.; Travers, J. P.; Pron, A. *Macromolecules* 2002, 35, 6112.
11. Zhu, K. Z.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Macromolecules* 2001, 34, 8453.
12. Gao, J. B.; Liu, D. G.; Sansinena, J. M.; Wang, H. L. *Adv Func Mater* 2004, 14, 537.
13. Chao, D. M.; Lu, X. F.; Chen, J. Y.; Zhao, X. G.; Wang, L. F.; Zhang, W. J.; Wei, Y. *J Polym Sci Polym Chem* 2006, 44, 477.
14. Pouget, J. P.; Józefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* 1991, 24, 779.
15. Chen, L.; Yu, Y. H.; Mao, H. P.; Lu, X. F.; Yao, L.; Zhang, W. J.; Wei, Y. *Polymer* 2005, 46, 2825.
16. Conwell, E.; Duke, C. B.; Paton, A.; Leyadev, S. *J Chem Phys* 1988, 88, 3955.
17. Honzl, J.; Tlustakova, M. *Tetrahedron* 1969, 25, 3641.
18. Furudawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I. *Macromolecules* 1988, 21, 1297.
19. Chen, L.; Yu, Y. H.; Mao, H. P.; Lu, X. F.; Zhang, W. J.; Wei, Y. *Synth Met* 2005, 149, 129.
20. Jeevananda, T.; Siddaramaiah; Seetharamu, S.; Saravanan, S.; D'Souza, L. *Synth Met* 2004, 140, 247.
21. Ding, L. L.; Wang, X. W.; Gregory, R. V. *Synth Met* 1999, 104, 73.
22. Lu, X. H.; Tan, C. Y.; Xu, J. W.; He, C. B. *Synth Met* 2003, 138, 429.
23. Sayyah, S. M.; Abd El-Rehim, S. S.; El-Deeb, M. M. *J Appl Polym Sci* 2004, 94, 941.
24. MacDiarmid, A. G.; Chang, J. C.; Halpern, M.; Mu, W. S.; Somasiri, N. L.; Wu, W.; Yaniger, S. I. *Mol Cryst Liq Cryst* 1985, 121, 187.